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The Muschelkalk and its lead-zinc mineralization in the eastern Netherlands

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Abstract

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The Muschelkalk of the eastern Netherlands, as exposed in quarries east of Winterswijk, is made up of sequences of dolomitic lime-mudstones. These are interpreted as stromatolites, particularly because of their characteristic algal growth patterns around mudcracks which show evidence of intermittent cracking and sealing. Rare, intercalated skeletal packstone layers with cyclic grain-size grading are thought to represent storm layers deposited within the high intertidal to supratidal algal mat environment. Pyrite, marcasite, sphalerite and galena occur widely dispersed in the limestone but have been concentrated more conspicuously in the storm layers and mudcrack fillings. A widespread occurrence of algal mats could account for initial concentration of considerable amounts of base metals. These probably did not derive from the deeper portions of the main Triassic basin to the north but are more likely of southern provenance, transported in meteoric water draining the emerged Variscan massifs. Secondary concentration of metals during dolomitization and compaction has demonstrably occurred, preferably in coarser-grained fabrics. Supergene enrichment is inferred from high strontium, lead and zinc values below a red bed interpreted to be a paleosol. A further analysis of the metal distribution is required. The area investigated is considered immature as regards economic mineral concentration. However, a place for base metal exploration is advocated in the course of the systematic investigation of the Netherlands subsurface.

Introduction

The post-Variscan Northwest European Basin is estimated to contain considerable amounts of base metals. These are concentrated in copper slates and copper marls at the base of the Zechstein, in lead sandstones of the Bunter and lead sandstones and lead marls of the Muschelkalk formations, respectively. Research on small deposits of copper, lead and zinc minerals in central and western Europe, in part sponsored by the European Community, was intensified in the seventies, with a view to future self-sufficiency in base metal provision. A number of detailed investigations were conducted (e.g. Hofmeister et al. 1972; Macquar & Lagny 1981) and several review papers have resulted (e.g. Dimanche et al. 1979; Schmid 1980; Balcon 1981; Gruszscyk 1982; Walther 1981). Mining companies have shown interest, conducting investigations particularly in the Federal Republic of Germany.

Although exploration efforts in Germany do not seem to have produced economical results, the occurrence in the Muschelkalk of Upper Silezia of major lead – zinc deposits (Zwierzycki 1948; Ekiert 1959; Gruszscyk 1982) has led us to initiate a study of outcrops with very disperse mineralization of iron – lead – zinc sulphides in the apparently not very dissimilar Muschelkalk environment found in the eastern Netherlands (Harsveldt 1963, 1973, 1977; Ruegg 1981). In the subsurface of the Netherlands lead – zinc mineralization is known to occur in carbonate veins, principally in the Westphalian coal measures of Southern Limburg (De Iongh 1918; De Wijkerslooth 1949; Kimpe et al. 1978; Kuyl 1980). Since this mineralization has also been found in the Upper Cretaceous De Wijkerslooth (1949) suggested emplacement to have taken place during the Cenomanian - Senonian. Investigations by Priem et al. (1962) of lead isotope ratios in galena samples from various parts of the South Limburg coal fields point to Caledonian and Early Hercynian ages of the generation of lead. Kimpe et al. (1978) tentatively suggest that origin and mobilization of mineral components are related to leaching of Palaeozoic carbonate/evaporite sequences in the Waubach Anticline by circulating groundwater. Dijkstra & Bot (1968) investigated stream sediments and soils from this area. They found indications of additional sources of metal dispersion. Analyses by Zuurdeeg (1981) of formation water obtained in boreholes indicated elevated zinc contents in levels at the top of the Carboniferous Limestone. The base of the Zechstein is known from bore holes and seismic profiles (Stheeman 1963; Coelewij et al. 1978; Van Wijhe et al. 1980). Wedepohl (1971) referred to an indication of notable lead and zinc contents at that level. No indication has been reported of sulphide deposits in rocks of the Buntsandstein.

The Muschelkalk is exposed in three quarries near Ratum, about four kilometres east of Winterswijk (Fig. 1). Dolomitic limestone and marl are here exploited for the beneficiation of road metal and agricultural fertilizer (Harsveldt 1963, 1973). For several decades minor amounts of pyrite, galena, sphalerite, celestite and fluorspar have been known to occur. The sparse mineralization is particularly found in several thin layers which are relatively coarse-grained and contain fragments of bivalves and gastropodes. Harsveldt (1963, 1973) refers to this level as the 'ore layer'. Harsveldt (1977) reported lead mineralization at the same stratigraphic level in the Enschede area further to the north. In 1982, 1983 and 1984 short field studies were conducted in the quarries near Ratum, followed by petrographical studies employing Alizarine Red – S staining of carbonates and by preliminary XRF analysis of the base metal content of six samples.

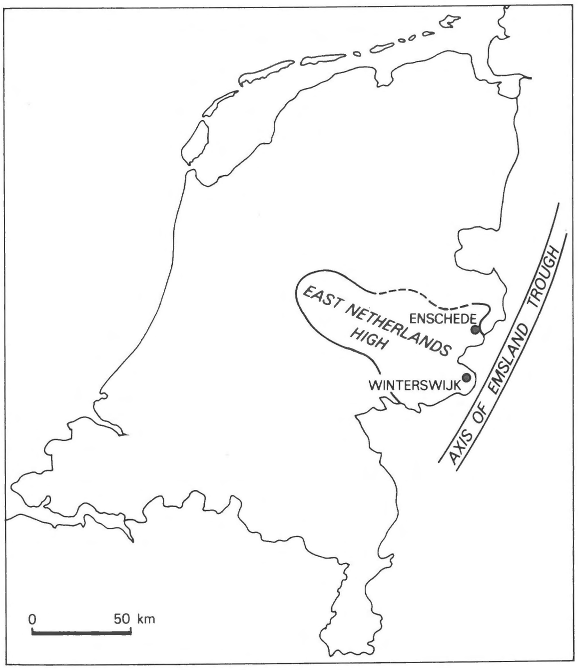


Fig. 1. Locality diagram.

Lithology and sedimentary environment of the Muschelkalk at Winterswijk

Dolomitic lime-mudstone facies

In the Netherlands the Muschelkalk, according to Nederlandse Aardolie Maatschappij & Rijks Geologische Dienst (1980), is developed as a sequence of marls, dolomitic marls and dolomites, limited at the base by the lowest marl or carbonate bed on top of the clastic sediments of the Bunter

Group. Towards the basin margin the usual subdivision of the Muschelkalk in four members is not possible. Incomplete sequences occur locally due to gentle disconformities across regional swells. Along the basin margin the Muschelkalk as a whole is rather incomplete, due to the impact of regional unconformities. Harsveldt (1973), on the basis of shallow boreholes, presented a section comprising, from top to bottom, 'Calcareous Marl' with limestone and marl, 'Clayey Marl' with marly slates, marls and thin clay layers, and 'Wellenkalk' (Eng.: 'Wavy limestone') consisting of finely laminated calcareous marl to clayey marl with undulating stratification. In this section six dolomitic limestone layers occur, each between 40 and 120 cm thick. These layers are known, in reverse stratigraphic order by the Roman numerals I to VI. Their MgO content varies between about 11% and 19% and decreases in boreholes away from the quarries to the north (Harsveldt 1982 pers. comm.). According to Ruegg (1981) the dolomitic layers represent the upper portions of sequences beginning with basal marl sediment in 'Wellenkalk' facies grading into the dolomitic limestone. Part of Harsveldt's (1973) section is shown in Fig. 2 as a reference for the section presently elaborated. In many places the dolomitic limestones are distinctly laminated at millimetre scale (Fig. 3), due to the alternation of micritic laminae (maximum grain size 0.01 mm, 40 to 60% micrite and finely dispersed sulphide minerals) and somewhat coarser-grained microsparitic ones (maximum grain size 0.08 mm, less than 40% micrite and occasional sulphide aggregates). Both types of laminae are extensively dolomitized mosaics of tiny dolomite rhombs occupying up to 50% of the volume. Vaguely defined relic structures of algal filament network have been observed in some of the samples (Fig. 7A). The overall flat lamination is crinkly in detail and very characteristic of the cryptalgal laminite type of stromatolites (Monty 1976). Occasionally laminae with dolosparfilled birdseye structures, up to 5 mm long, are intercalated. The lamination is interrupted by dewatering structures of which large mudcracks are the most prominent. Their polygonal patterns, some decimetres wide, are found in extensive exposures of bed surfaces in the quarries.

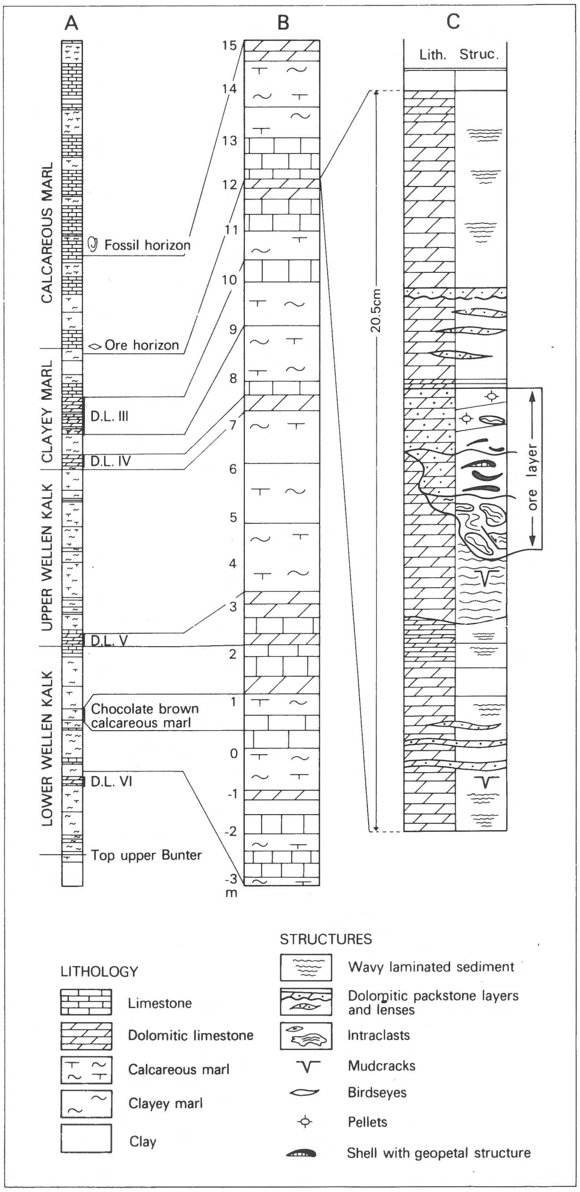


Fig. 2. A. Part of the Muschelkalk section at Winterswijk, after Harsveldt (1973)
B. Presently investigated portion of Muschelkalk section.
C. Lithology and sedimentary structure of 'ore layer' and its foot and hanging walls.

In cross section (Fig. 3 B,C) they provide the best diagnostic features for the stromatolitic character of the laminated mudstones. Continued growth over the rims of the cracks resulted in draping structures. Elsewhere the cracks have been completely bridged by algal growth in a dome – like fashion (Fig. 3B). Both fill and wall of the cracks

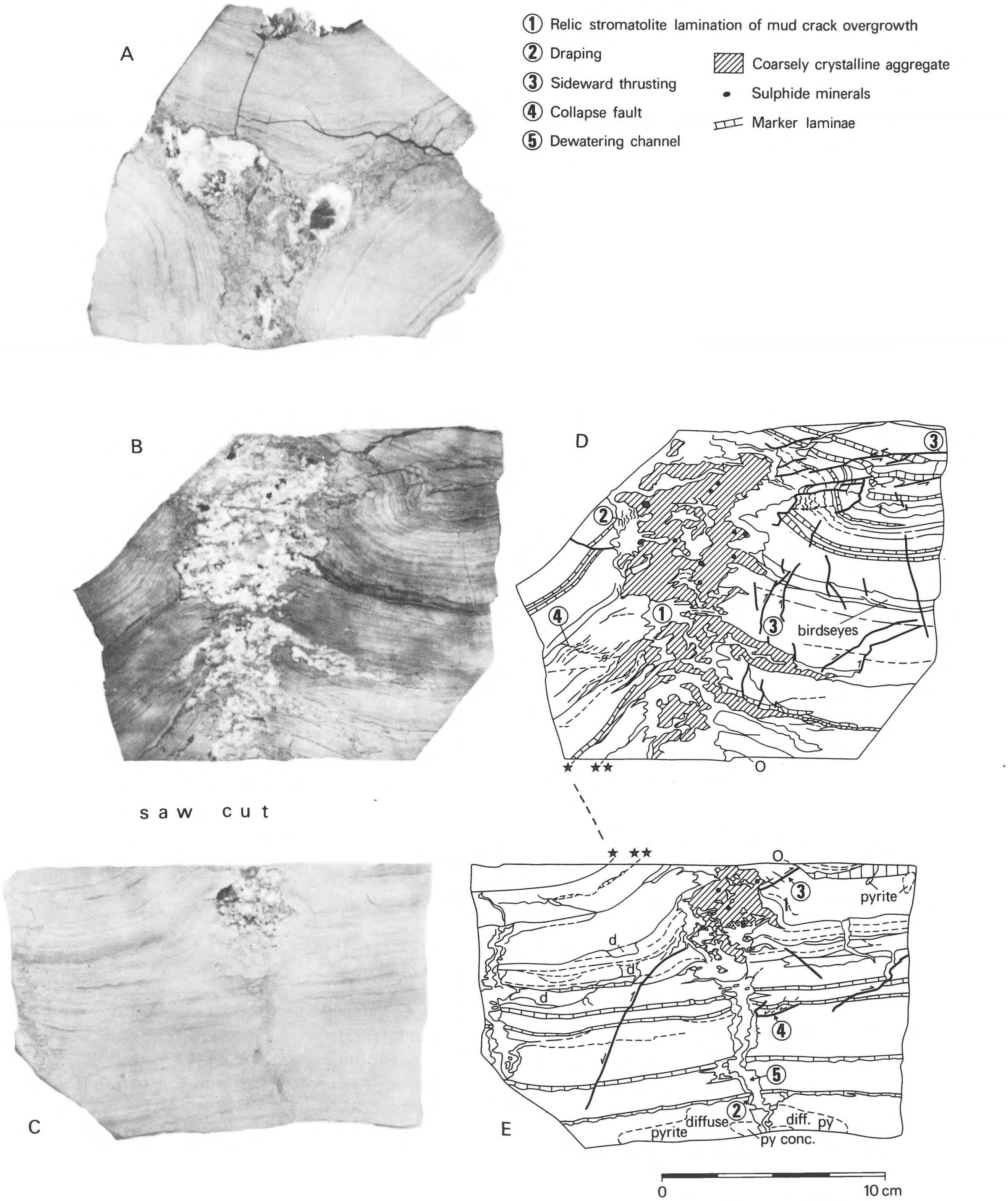


Fig. 3. Polished horizontal (A) and vertical sections (B, C, D and E; two millimetres missing due to saw cut) of cryptalgal-laminated facies. The mudcrack structure has a coarse-grained crystalline fabric in the upper part containing relic structures of stromatolite lamination. Repeated opening, algal overgrowth and early diagenesis resulted in a dome shape of the mudcrack triple junction and in micro-faulting in the stromatolite host rock. Sulphide minerals are dispersed in the coarse crystalline fabric as well as in dusty concentrations within the stromatolite (centre below, and upper right hand corner). Further explanation in text.

have been strongly dolomitized. In horizontal section (Fig. 3A) the triple junction of the cracks has been rounded off by stromatolite growth. The final central infilling consists of aggregates of calcisparite, coarse-grained dolomite, locally celestite and fluorite and sulphide minerals. It also contains platy to angular fragments of the hostrock. These aggregates also replace earlier fabrics (Fig. 3B), leaving behind a spongy network of relic stromatolitic lamination. Lateral protrusions of the sparite into the hostrock along sheet cracks between the stromatolite layers give the entire structure the appearance of a pile of inverted saucers stacked on the vertical stem of the mudcrack intersection. This coarsely crystalline fabric occupies the upper part of the crack, where the host rock is shaped into a dome (Fig.3B). In vertical section many normal and reverse microfaults are seen to accompany the doming. Unconformities in the lamination testify to the syndepositional character of the deformation. The lateral thrusting is best explained as the result of crystal growth and recrystallization in the crack fill. These in turn are probably related to upward moving fluids during dewatering, which because of induced volume changes generated layer-parallel stresses. The entire process is reminiscent of the formation of tepee structures (Assereto & Kendall 1977). The term tepee, however, should be restricted to linear overthrusts and chevron structures, often arranged in megapolygons accompanied by brecciation as a result of sheetlike expansion of superficially cemented carbonate beds.

Type of lamination, relics of algal structure, mudcracking with continued algal growth, birdseyes, the scarcity of terrigenous clastic material, the concurrence of dolomite, sulphate and sulphide and finally the position of the dolomitic limestone facies in shallowing-upward cycles, all point to a high intertidal to supratidal coastal sabkha environment of deposition. This environment is characterized by extensive growth of algal mats alternating with desiccation and with saline fluid transport through the desiccation structures inducing early diagenetic crystallization processes which further modify the algal structures. In such an environment, according to Ruegg's (1981) view, small fluctuations in sea level may have shifted the coastline considerably and dolomite would be expected to occur in a zone parallel to it.

Skeletal packstone layers

About 1.75 m above dolomitic limestone layer III the monotony of another algal-laminated dolomitic mudstone is interrupted by a 20 cm thick interval in which packstone layers and lenses are intercalated (Figs. 2 and 4). A two to ten centimetres thick skeletal packstone, accompanied on both sides by up to 8 m long thin lenses of similar composition can be traced over the entire quarry area and its surroundings. The interval has been known for

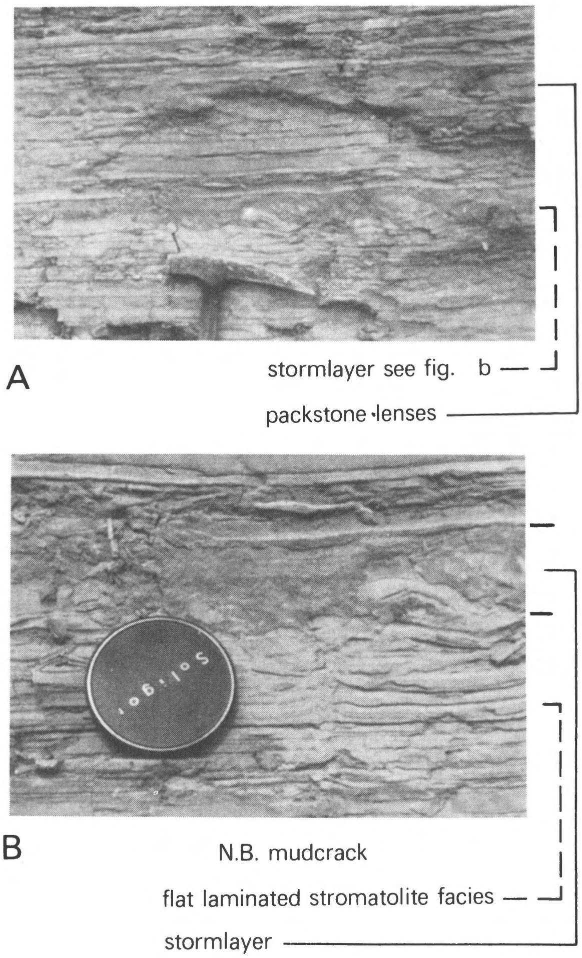


Fig. 4. A. Outcrop in north face of centre quarry with thin packstone storm layers.
B. Packstone storm layer, detail of Fig. 4A.

decades and was labelled 'ore layer' by Harsveldt (1963), because of its content of sulphide minerals. Details of the main packstone layer are illustrated in Figs. 5 and 6. It is essentially composed of a coarsening-up/fining-up cycle of siliciclastic skeletal packstone. Grading is more evident in the carbonate than in the siliciclastic fraction. The latter consists mainly of fine – grained angular quartz with minor feldspar. The cyclic sequence may be amalgamated as shown in Fig. 5 where the upper finer-grained set overlies with erosive contact the fining-up top of the coarser basal bioclastic set. The dark colours in the finer-grained parts of the layer are due to a higher content of organic material and opaque minerals. From the bottom of the layer upwards the size of the bioclasts increases to about two centimetres for the bivalves in the centre, then drops abruptly. The skeletal fraction is dominated by bivalves both in convex-up and convex-down position (Fig. 6B). Stromatolite flakes are rare, except for local concentrations at the base of the layer. The shells frequently shelter against fine sediment filtered in from above. The original texture, however, is strongly altered by solution and recrystallization, dolomite growth and compaction, leaving only thin moulds of the original shells, several of them being partially filled by sediment. The upper part of the cycle (Fig. 6, layer 'C') contains more siliciclastics, pellets and rounded stromatolite chips (see also Fig. 7C). An early phase of coating cement is obvious in thin section. Fining-up laminae are vaguely visible, oriented at low angles with respect to the set boundaries. This may represent an oblique section through small-scale cross-lamination, which has been observed occasionally in the outcrop. Generally, however, horizontal lamination dominates this fining-up part of the layer. The top is sharply defined against the overlying laminated mudstone by an abrupt decrease of the siliciclastics and opaque components. The packstone layer fills an irregular erosive topography of torn-up stromatolite. In Fig. 5 the contact is very disrupted and clasts of the substrate have been taken up in the base of the shell bed. In the sample of Fig. 6 the bottom is rather flat and depositional over a two cm thick uppermost layer of the underlying stromatolite, evidently disturbed by soft sediment deformation as documented by micro-faults, convoluted clasts and stromatolite chips floating in a micro-slump folded matrix (Fig. 6, layer 'A'). Thin strings of the packstone cover participate in this deformation (righthand side in the figure) while the otherwise sharp contact becomes indistinct in that particular place. Stromatolite deformation, therefore, seems to be closely related to the deposition of the packstone layer.

Apart from minor differences the packstone layer closely resembles those described from the German Muschelkalk. Aigner (1982) interpreted these as tempestites. The coarsening-fining cycle can indeed be satisfactorily explained as the result

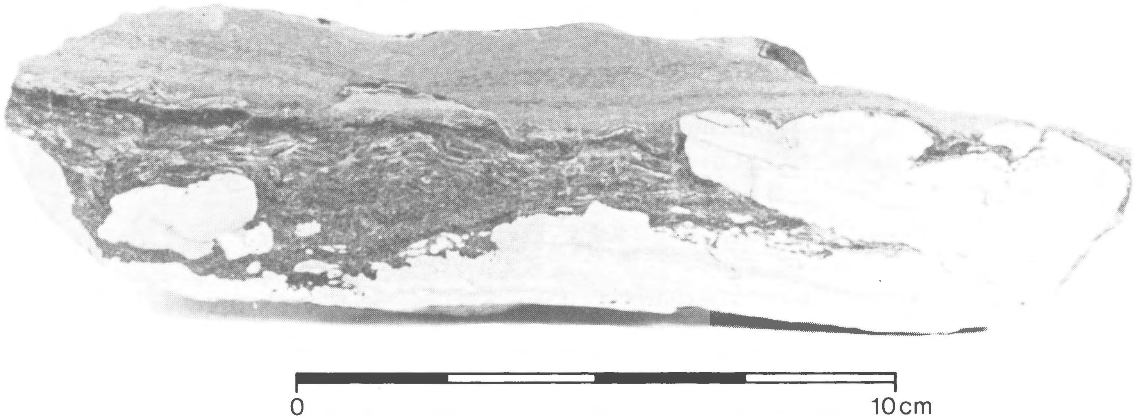


Fig. 5. Skeletal packstone tempestite, infilling a strongly disrupted surface of the underlying stromatolite facies. In the middle of the packstone layer an erosive contact at the base of the overlying, fining-upward set indicates amalgamation during generation of the storm layer (polished slab, detail of Fig. 4).

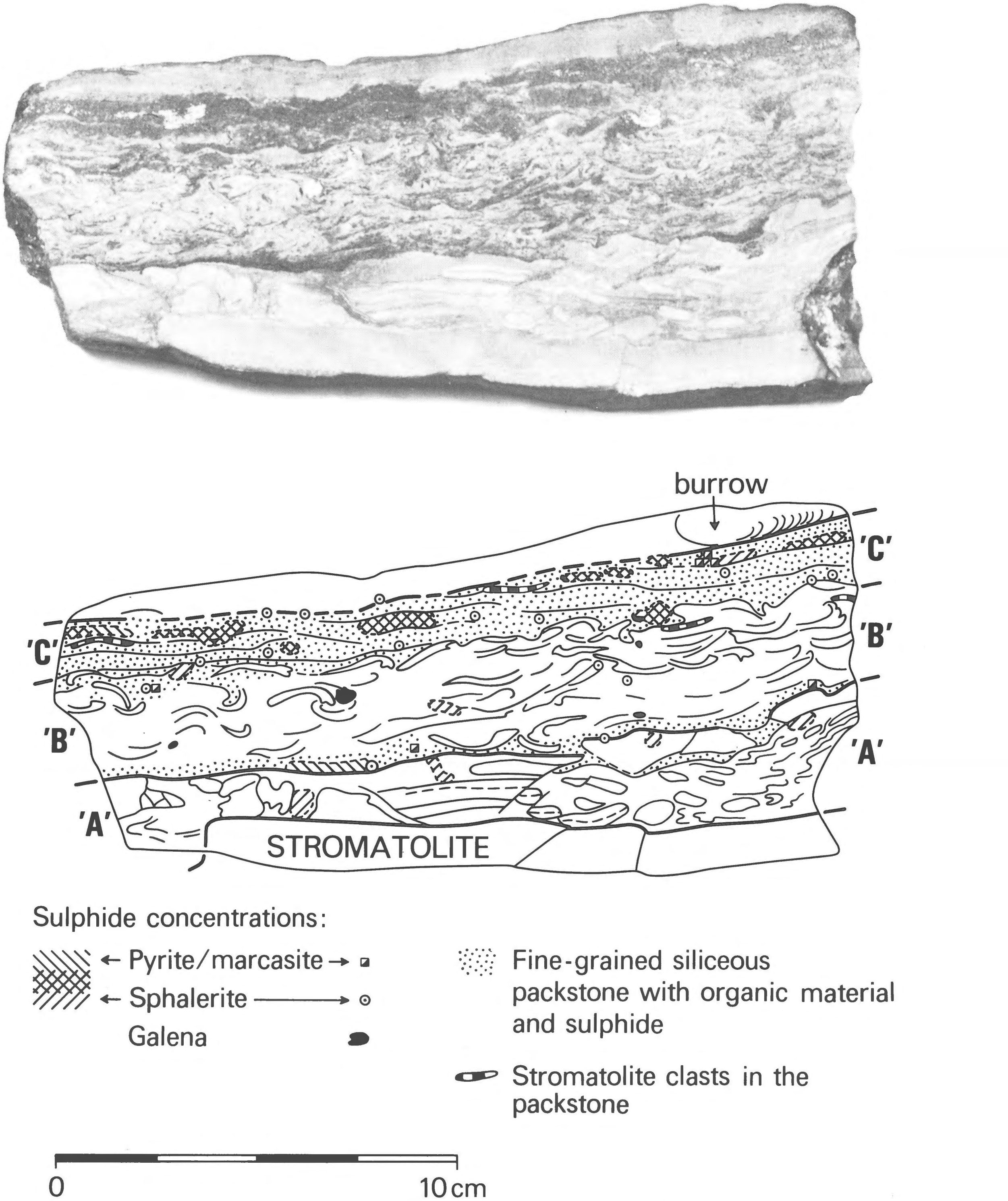


Fig. 6 A. Tempestite deposited on the syn-sedimentary deformed top of the stromatolite substrate ('A'). The storm layer has a cyclic structure, the coarsening-upward lower set ('B') being succeeded by a fining-upward top set ('C'). Note the low angle orientation of the laminae in the top set. For 'A', 'B', and 'C', see Fig. 6B.
B. Distribution of sulphide minerals in the sample of Fig. 6A. For explanation see text.

of a single, or in the case of amalgamation, a doubly pulsed storm event. The extent of the layer and its isolated occurrence in the supra/intertidal stromatolite environment support this interpretation. Although no coarsening-up is mentioned by Aigner, it can be expected to have been formed when deposition of the bulk of the storm layer was tied to backflow over a storm-eroded surface, the coarsening then representing the onset, the fining the waning stage. The observed soft sediment deformation in the stromatolite surface resulted either from drag during the storm surge or from loading by the storm layer. In the latter case, however, the packstone layer itself would have been more affected by the deformation than is actually the case. The thin accompanying layers are considered to represent the shoreward fringes of similar tempestites.

Brown-red marl horizon

At several localities in the quarries, about 180 cm below dolomitic limestone layer V, the marl is coloured brownish red over an interval varying in thickness between 10 and 40 cm. The brown-red colour is probably due to finely dispersed iron(-? manganese) compounds. Preliminary XRF analysis of metal contents of samples from this horizon and from sediments below this horizon in the eastern quarry indicate that the brown-red material is virtually devoid of zinc and lead. Two samples of apparently normal sediments below this horizon show somewhat elevated zinc and lead contents up to about 0.6 and 0.1%, respectively (Table 1). In particular in the western quarry pockets of celestite occur immediately below the brown-red horizon. Sulphides, carbonates and sulphates of zinc and lead have not been observed in these rocks. Pending further investigations this level is tentatively interpreted as a paleosol on the grounds of subaerial oxidation, apparent leaching and supergene concentration of metals.

Table 1. Trace element contents in calcareous marl below brown-red horizon, in ppm.

Sample no.	M1a	M1b	M3	M4	M5	M6
Level relative to chocolate brown calcareous marl*, in metres	− 2.5	− 2.3	− 1.8	− 1.6	− 0.5	0
Pb	624	9	1255	17	9	8
Zn	3886	28	6402	42	62	39
Cu	15	11	19	22	22	12
Sr	251	625	196	695	1626	746
Ba	D.L.	37	42	67	152	103
Mn	253	311	326	385	554	597

*For position see Figure 2

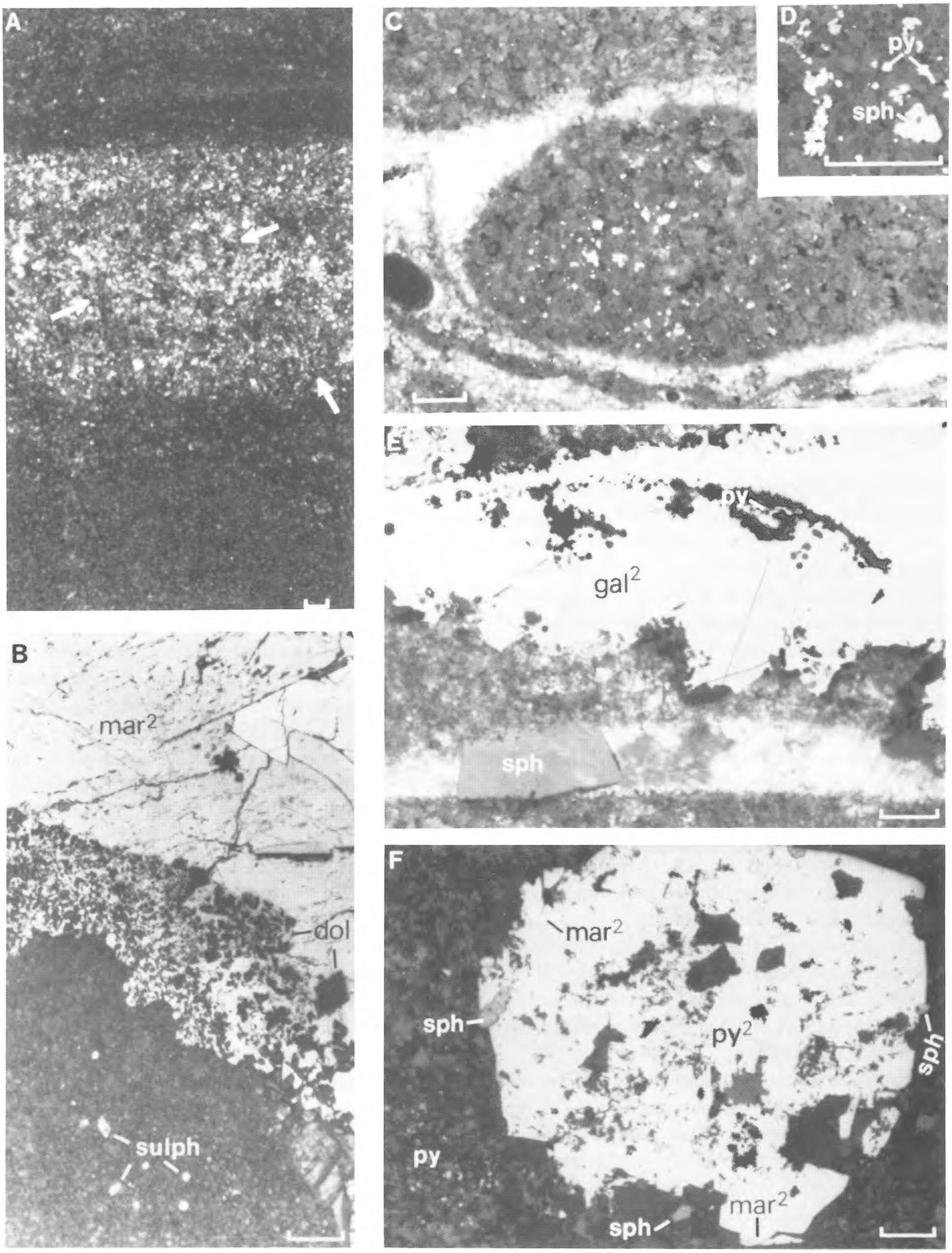
Base metal mineralization

Sulphides in the stromatolite facies

Pyrite, sphalerite and very subordinate galena are sparsely dispersed as minute crystals or crystal aggregates. The grain sizes vary according to those of the dolomite crystals in the micritic and microsparitic laminae of the stromatolite and generally do not surpass them. In particular pyrite and galena may develop euhedral crystals. The sphalerite grains are anhedral or form pseudomorphs after dolomite rhombs, either because they crystallized between the dolomite or replaced it (Fig. 7D).

Fig. 7 (facing page)
A. Cryptalgal laminite with relic structure of upwards branching algal filaments (arrows); stromatolite facies.
B. Coarse-grained marcasite replacing dolomitized host rock with finely dispersed sulphide grainds, leaving the dolomite rhombs unaffected; mudcrack fill in stromatolite facies.
C. Fine-grained pyrite and sphalerite crystals and intergrowth crystal aggregates confined to rounded algoclast in fining-up topset of storm layer packstone facies.
D. Detail of sulphide occurrence in algoclast of Fig. 7C. Note pyrite-sphalerite intergrowth on left-hand side.
E. Galena enclosing pyrite and replacing the skeletal-intraclast fabric of the carbonate host; sphalerite in shell solution cavity with geopetal micrite fill; storm layer facies.
F. Pyrite-marcasite aggregates enclosing sphalerite grains in the periphery. The latter occur with tiny pyrite crystals in the host rock, mainly confined to pellets (lower left); storm layer facies.

All figures with partly crossed nicols; Fig. A: transmitted light, Figs. D and F: reflected light, Figs. B,C, and E: transmitted and reflected light. In Figs. A,C and E the stratigraphic top is oriented upwards. Scale bar: 0.1 mm. The numeral '2' refers to second generation sulphide mineralization.


A
B
mar2
dol
sulph
C
D
py
sph
E
py
gal2
sph
F
mar2
sph
py2
sph
py
sph
mar2

Relatively high concentrations of minute pyrite crystals are found in clouds of crystal dust locally surrounding the mudcracks or tiny fractures (Fig. 3C). Higher concentrations of much larger subhedral to euhedral crystals and crystal aggregates of marcasite, pyrite and galena occur in the coarse, sparitic parts of the mudcrack fills. The crystals, up to one centimetre in diameter, are intergrown with megacrystals of dolomite (cf. Morrow 1982) and celestite. Fluorspar is sometimes associated. Ghost structures consisting of clouds of dolomite rhombs testify of replacement of dolomitized hostrock fragments (Fig. 7B). Sphalerite occurs as tiny flakes either in the hostrock, or concentrated along the grain boundaries of the megacrystals.

Sulphides in the storm layers

Another notable concentration of pyrite, marcasite, sphalerite and galena is found in the packstone layers. An example of their distribution is illustrated in Fig. 6B. Sphalerite occurs scattered throughout the packstone, but it is clearly concentrated along the bottom, especially in the deformed top of the stromatolite substrate ('A' in Fig. 6B) and in the topset ('C') of the packstone layer, where it is intergrown with pyrite and marcasite. Iron and zinc sulphides abound in tiny crystals in the pellets and stromatolite flakes (Figs. 7C and 7D). Large sphalerite crystals, sometimes violet in transmitted light, occupy shell moulds (Fig. 7E). Larger pyrite crystals overgrow earlier marcasite framboids and sphalerite crystals (Fig. 7F). Pyrite is furthermore enriched along the base of the packstone layer. Although galena is not absent elsewhere, large crystals up to several millimetres in diameter occur preferentially in the coarse skeletal fabric ('B' in Fig. 6B). Ghost structures of the shells remain visible in the galena crystals. Pyrite inclusions are also present (Fig. 7E).

In conclusion iron, lead and zinc sulphides are found concentrated in the coarser fabrics of the Winterswijk Muschelkalk. The observations warrant the conclusion that an early generation of mainly pyrite and sphalerite is coeval with or postdates the fine-grained dolomite texture of the stromatolite and is succeeded by a coarser-grained generation of galena and marcasite, with subordinate pyrite and sphalerite. Galena and marcasite are intergrown with the last phase of coarse-grained dolomite and celestite. These relations may suggest a rather early diagenetic crystallization of most of the lead and zinc sulphide.

Palaeogeographic setting

During the Carboniferous, the Permian, and the Trias considerable portions of the Brabant and Ardenno-Rhenish Massifs were probably almost continuously subject to erosion (Van Staalduinen et al. 1979; Van Wijhe et al. 1980; Ziegler 1981, 1982). Already in the Permian the present Winterswijk region or Achterhoek was part of a large platform along the Southern Permian Basin. Rotliegendes sedimentation probably took place only in isolated areas (Van Wijhe et al. 1980). Also during the Lower and Middle Trias considerable areas were characterized by non-deposition according to maps by Wolburg (1969). In the course of the Permo-Triassic the Ems Low developed into the Emsland or Winterswijk Trough to the east of the Netherlands Swell (c.f. Fig. 1; Stheeman 1963; Haanstra 1963; Harsveldt 1963; Nederlandse Aardolie Maatschappij & Rijks Geologische Dienst 1980). Further south the Central Netherlands Graben developed along the northern edges of the Brabant Massif (Heybroek 1974; Brennand 1975; Van Staalduinen et al. 1979).

Along the edges of the Variscan Massifs, the Buntsandstein Formation consists of sandstone and conglomerate, gradually giving way northward to shale and evaporite. Higher areas directed the transport of clastic sediment to the north, both along and away from the ancient massifs (Wolburg 1969; Schröder 1982). In the course of the Triassic the Tethys gained access to the Southern Permian Basin of western and central Europe through two major channel ways: the Burgundy-Thuringian-West Brandenburg depression and further east the Polish Trough (Ziegler 1982). Although a massive incursion through the Trier Embayment does not seem likely, intra-basinal clastic transport between the Brabant and Rhenish Massifs was to the north, through the Emsland Trough, at least during the Scythian (Wolburg 1969; Ziegler 1982). The Muschelkalk developed across a vast platform with limestone, evaporite, marl, and shale deposition. Again the areas north of the Brabant and Rhenish Massifs were on the edges of the marine influence. The partly dolomitic sequences of the Muschelkalk are generally held to represent shallow, hypersaline conditions of playa lakes and inland sabkhas (e.g. Ruegg 1981, Gdula 1983). Along the northern edges of the Variscan massifs the carbonate successions may contain sandstone and shale as for instance in the Oberpfalz, northern Bavaria (Schmid 1981; Krege & Schröder 1981). Haanstra (1963) reported almost pure dolomite in the Peel area north of the Brabant Massif. Local occurrences of rock salt mark the marine passages to the Tethys west of the Bohemian Massif (Schröder 1982). The East Netherlands High has dominated the palaeogeography of the Achterhoek from the Middle Trias. It started to evolve with the Early Kimmerian phase of mild uplift when a series of basins and ridges developed along generally NW-SE strike. These are illustrated by the distribution pattern of the Lower and Middle Jurassic (Heybroek 1974; Van Staalduinen et al. 1979; Ziegler 1978) in the Central and Western Netherlands basins, the Central Netherlands Graben and the Lower Saxony Basin. In the latter the configuration of the Emsland Trough can still be recognized.

Heybroek (1974) emphasized that the Lower Jurassic transgression did not take place everywhere at the same time. This brought about onlap of increasingly younger formations on more deeply eroded portions of the Early Kimmerian land surface. Uplift became general again after the Middle Oxfordian and erosion cut again into the Triassic column during the Late Kimmerian phase, in particular on the higher ridges. After the intervening Aptian-Albian transgression and deposition of a thick sequence of homogeneous chalk of Upper Cretaceous age a widespread inversion of the Jurassic basins and highs took place in the Middle Upper Cretaceous. Locally Triassic formations again became subject to erosion till the widespread Lower Tertiary transgression that accentuated the configuration of the North Sea Basin. From maps by Stheeman (1963), Haanstra (1963), Harsveldt (1963, 1977), Wolburg (1969), Heybroek (1974), Van Staalduinen et al. (1979), Ziegler (1981), Schröder (1982) and Nederlandse Aardolie Maatschappij & Rijks Geologische Dienst (1980) a generalized distribution pattern emerges which shows large areas of the Netherlands with Buntsandstein and Muschelkalk formations variably preserved below the Late Kimmerian unconformity. In particular in the Lower Saxony Basin these subsided into and through oil window conditions as may be inferred from the distribution of oil kitchens illustrated by Ziegler (1978).

Mineralization in surrounding areas with reference to the Germanic Trias and the pre-Triassic subcrop.

Hofmeister & Simon (1971) and Hofmeister et al. (1972) conducted a study of lead-zinc mineralization in the Trochitenkalk of the Upper Muschelkalk in northwestern Germany. In finely bedded intercalations of dolomitic limestone they found stratiform mineralization of predominantly pyrite with minor sphalerite and galena. These concentrations appear independent of more substantially mineralized carbonate veins with occasionally considerable galena content. The lead is not of magmatic origin but was probably provided, together with barium and strontium, by connate brines from adjacent shales, clays and marls. The high zinc values are possibly due to submarine exhalations or to metal-bearing solutions from the adjacent continent. Sulphide-sulphur could have derived from sulphate-sulphur by bacterial reduction of sulphate of Middle Muschelkalk gypsum deposits.

In the area around Freihung, Oberpfalz, Northern Bavaria, cerussite – galena mineralization occurs in several levels of the Muschelkalk and in the Lower Keuper (Schmid 1981; Krege & Schröder 1981). The mineralization is found in fine- to medium-grained sandstones whereas clay intercalations are occasionally also slightly mineralized. Lead would derive, in association with kaolinization, from the crystalline basement and, subsequently, from the potassium-rich feldspar of Triassic arkoses. Leaching and transport by meteoric water is suggested (Schmid 1981).

Gruszczyk (1982) summarized present views on the genesis of the lead-zinc deposits in the Muschelkalk of Upper Silezia, with reference to work by Smolarska (1974), and Smolarska et al. (1972). According to Gustafson and Williams (1981), who emphasized a polygenetic origin, these deposits rank among the three largest sediment-hosted stratiform lead-zinc districts in the world. The ores have no connection with magmatic rocks or regional lineaments. Mineralization occurs in the Muschelkalk and the Rhaet. Recently, apparently similar mineralization has been reported in the Buntsandstein (Gruszczyk 1982). The mineral deposits are as a rule associated with dolomite. They are found in the peripheral parts of the Triassic sedimentary basin and do not occur in zones at distance from the former sea shore. The ore bodies have the form of flat beds and nests, usually discordant with the bedding of the enclosing dolomite. Gruszczyk suggested that in a first stage disseminated sulphides formed synchronously with dolomite. Later epigenetic concentration took place at different stages in relation to karst processes.

To the north and northeast of Winterswijk Stadler (1971) described mineralization of siderite, lead- and zinc sulphides and barite in a large area around Bramsche, in the Lower Saxony tectogene. The mineralization occurs predominantly in Zechstein limestones but has also been observed in levels as high as the Cretaceous. Stadler distinguished three broad zones related to temperature of deposition. In the central part of the area siderite veins with fluorspar and locally pyrophyllite are indicative of relatively high temperatures. Further away from the centre substantial siderite replacement bodies are followed by a later phase of galena-sphalerite-barite deposition. In an outer zone only vein-like occurrences are found with sphalerite, galena and pyrite. The metals would derive from hydrothermal solutions related to a mafic magma of Upper Cretaceous age. The deposits would have been formed towards the end of a main phase of block tectonics between the Neocomian and the Upper Campanian.

Dejonghe & Jans (1983) have proposed a model for the lead-zinc deposits in the Herve synclinorium of eastern Belgium generally following ideas of De Magnée (1967) and Balcon (1981). The authors tended to consider the various ancient massifs as the pre-Devonian sources of these metals. Generally increased geochemical background levels and local concentrations of metals during the Middle Devonian, the Frasnian and the Dinantian, are viewed as precursors of the majority of presently known deposits. Presumably they were further enriched during the Permo-Triassic development of post – Variscan transverse faults related to block fault tectonics of the Rhine graben. Leaching of country rocks and of evaporites by formation water is evoked as the principal mechanism. The authors emphasized the significance of surficial reworking of earlier concentrations during periods of emersion of the older land masses and of further concentration by karst processes. They draw particular attention to the Palaeozoic-Mesozoic Unconformity. Following the ideas of Routhier, Walther (1981) presented an overview of base metal deposits of the Federal Republic of Germany, grouping deposits in WSW-ENE striking belts, with indication of tonnages of metal produced.

Bjørlykke & Sangster (1981) drew attention to a generalized sequence in Europe of relations between particular stratigraphic levels and specific types of mineralization. The Rotliegendes provided the copper-dominated mineralization of the 'Kupferschiefer' (Coppershale) at the base of the Zechstein. Copper marl and lead marl occur at somewhat higher levels (Deans 1948). The Lower Trias gray bed continental to shallow marine sandstones are characterized by galena mineralization. The Middle and Upper Trias shallow marine carbonate formations contain zinc-lead deposits. Schmid (1980), following Bernard & Samama (1970) and Samama (1976), has undertaken to explain these associations by a systematic sequential generation of terrigenous solutions from weathering and decomposition of the Variscide hinterland: leaching of uranium and copper in the Permian, decomposition of silicates, in particular of potassium-rich feldspar and biotite liberating lead, barium, strontium and zinc during the Muschelkalk and Keuper, followed by acid leaching in the Jurassic which set manganese and iron free.

Discussion

A variety of models have been proposed for the genesis of stratabound and stratiform lead and zinc concentrations in carbonate rocks; these relate to the derivation of components, their transportation and mode of deposition. These models fall into two broad categories according to the mode of derivation of the metal components:
- dissolved as chloride- or bisulphide-complexes in connate brines which migrated along aquifers from the deeper portions of a sedimentary basin towards the margins,
- dissolved in surface water or adsorbed on clastic particles from a weathering and decomposing mainland to the edges of the transitional supra- to intertidal environment.

This two-fold division was elaborated by Callahan (1977). Further elements relating to deposition of mineralization are the interaction of connate and meteoric water (anomalous temperature distribution), the role of syn- and diagenetic dolomitization, the activity of micro-organisms, and the presence of discontinuities such as facies changes, fault zones and unconformities (e.g. Schmid 1980; Gustafson & Williams 1981; Bjørlykke & Sangster 1981; Badham 1981; Macquar & Lagny 1981; Cathles & Smith 1983). Derivation of metals from deeper portions of a sedimentary basin is normally indicated, on the evidence of fluid inclusions, by mineralization temperatures between 100° and 150°C. These are anomalous for the environment in which the country rocks were originally deposited (Cathles & Smith 1983; Rickard et al. 1979). For the Winterswijk area data on temperatures of sulphide mineralization and on sulphur isotope ratios are not available, however. Cathles & Smith (1983) listed five characteristics favourable to the formation of lead-zinc deposits in sedimentary basins from episodically expulsed pore fluids. Two of these, stable and relatively steep basin margins, do not appear fulfilled in the eastern Netherlands. On the other hand shales with particularly low permeability, a third requirement, are abundantly found to the north. Evaporites will have contributed to the formation of brines in view of reports on leached Muschelkalk salt (Nederlandse Aardolie Maatschappij & Rijks Geologische Dienst 1980). In the course of the Upper Trias, before the initiation of the NW striking basins and narrow ridges, brines from the deeper parts of the main basin may have been funnelled into NNE striking depressions like the Emsland Trough. However, in the Winterswijk area at the head of the Emsland Trough, derivation of the metals from deep brines appears unlikely in view of the incomplete Muschelkalk and Bunter sequences and the block movements in the area proper. This mode of origin should on the other hand not be ruled out entirely in the subsurface further north where Jurassic sediments in the Lower Saxony Basin reached the oil window. Mineral deposits, if at all developed in this way, are probably small in view of relatively restricted lateral migration due to post-Early Kimmerian differential subsidence and halokinesis.

An alternative mode of metal provenance from the Variscan massifs towards the Emsland Trough presently seems to merit a somewhat higher rating with general transportation of clastic material to the north during the Lower Trias. Renfro (1974) has elaborated on a model on the basis of the processes in Persian Gulf sabkhas, comprising reaction between land-derived interstitial water of low pH and high Eh enriched in metals, and sea-derived interstitial water of high pH and low Eh enriched in calcium, magnesium, sodium, sulphate and chlorine, about the sea water – terrestrial water interface. With the abundance of H_2S, CH_4 and CO_2 resulting from bacterial decay of algal mats, metal sulphides may precipitate interstitially between the algal-bound detritus. The stromatolitic origin of the Muschelkalk rocks, inferred from the distinctly laminar stratification and from the remnants of algal structures, could account for capture and concentration of metals in algal mats (Mendelsohn 1976; Trudinger & Mendelsohn 1976). The notable lead and zinc contents just below the brown-red oxidized horizon (Table 1) would indicate that these metals not only occur in the dolomitic limestone but also in the calcareous marl where their sulphides have not been observed. Clearly further geochemical investigations are required.

Harsveldt (1963, 1973) distinguished six dolomitic limestone levels with relatively high MgO content. It would appear that this division stems primarily from economical reasons of dolomitic limestone exploitation. The level of storm layers for instance is found within a more massive, laminated, partly dolomitic lime-mudstone (7.8% MgO, Harsveldt 1963) which is not classified as one of Harsveldt's six magnesium-rich layers. Judging from Harsveldt's composite section there are more of these economically inconspicuous but sedimentologically probably significant levels. Ruegg (1981), in suggesting that the Muschelkalk Formation is characterized by sequences beginning with basal marl in 'Wellenkalk' facies grading into dolomitic limestone, opened the way to a sedimentologically more coherent model. In the context of shallowing-upward sequences we tend to interpret secondary sulphide concentration in relation to dolomitization during early diagenesis. Primary differences in grain size distributions between laminae would become somewhat enhanced during dolomitization, in association with a generally increasing porosity and permeability. At this stage migration and consequent (short range) redistribution are envisaged of metals towards coarser laminae and mudcracks. The thin storm layers are distinguished by their initially already higher porosity and probably also a higher permeability. They may have acted as micro-aquifers owing to the differences in porosity and permeability relative to their foot and hanging walls.

The inferred stromatolitic origin may well imply that the sequences distinguished by Ruegg (1981) all held metal contents of a similar order of magnitude. Only higher porosity of the thin storm layers has brought about a visible concentration of metal sulphides. Intervening oxidation caused leaching and some supergene enrichment of strontium, lead and zinc. This concept concurs with the findings of Hofmeister et al. (1972) concerning the lead and zinc mineralization in the Upper Muschelkalk of northwestern Germany. The surface derivation of lead and zinc in the Winterswijk area would also fit in the model proposed by Schmid (1980) for subsequent liberation of different metals from the Variscan massifs.

It appears that the area investigated is to be considered immature from the point of view of economical mineral concentration. Possibly only prolonged or repeated karst weathering could have led to anything like economical concentrations by analogy to the findings in Upper Silezia. However, since little relevant detail is available from published accounts on the areas and levels concerned in the Netherlands, the presence of considerably elevated metal contents in particular horizons and in areas as far apart as Winterswijk and Enschede (Harsveldt 1977) would, in our opinion, justify a place for base metal exploration in the systematic investigation of the subsurface.

Strata with increased relative porosity and permeability, such as storm layers, but also sandstones, oölitic beds, claystones and calcareous dolomite with either primary or secondary porosity as described by Gdula (1983) from the De Wijk field, and indications of intervening oxidation and leaching, merit special attention. A more common occurrence of storm layers should not be precluded in view also of their recorded abundance in the Muschelkalk of Western Germany. Potential structural traps such as reverse faults are not uncommon either, as is manifest in the complicated Plantengaarde-Oeding zone in the Winterswijk area and the Gronau zone to the north of Enschede.

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