LEAD-ZINC MINERALIZATION IN DINANTIAN ROCKS OF BOREHOLES THERMAE 2000 AND THERMAE 2002 (VALKENBURG A/D GEUL, THE NETHERLANDS)

by

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(2 figures, 4 tables, 7 plates)

1. DISTRIBUTION AND GENESIS OF SULFIDE MINERALIZATION

Dinantian rocks of boreholes Thermae 2000 and Thermae 2002 (Valkenburg a/d Geul, South-Limburg, the Netherlands) are characterized by several occurrences of more or less pronounced mineralization of sphalerite, wurtzite, pyrite and galena (figure 1). Comparison between lithology and mineralization shows that two different mineralized zones (I and II) may be distinguished.

In both boreholes the upper zone I is marked by the most important mineralization, including well-developed «Schalenblende» (pl. 1, see also color photographs on cover of this volume), sphalerite, iron sulfides, galena and quartz. In Thermae 2000 zone I extends between 242 and 248 m containing up to 12 % sulfide minerals. In Thermae 2002 zone I is located between 238 and 248 m, wherein two main horizons can be distinguished at 242.5 m with 83 % sulfide minerals and at 248 m with 36 %, separated by a minimum of only 8 % at 244 m. These percentages of sulfide minerals have been calculated by counting their proportion within the sieve fraction 1.0-2.4 m of the cuttings.

The lower zone II contains much less important mineralization. «Schalenblende», galena and quartz are rare or absent, sphalerite and iron sulfides being the most obvious minerals under the binocular. The sulfide mineral percentages are much lower than in zone I. In Thermae 2000 zone II is situated between 309 and 321 m with a maximum of about 3 % sulfide minerals (compared to 12 % between 242 and 248 m). In Thermae 2002 zone II consists of two intervals, one between 333 and 343 m with a maximum of 15 % sulfide minerals (compared to up to 83 % between 238 and 248 m) and a second one between 374 and 376 m with up to 2 %.

The downward decrease of Pb-Zn mineralization is common for virtually all Pb-Zn deposits in the Dinantian rocks of the Aachen and Vesdre areas (Gussone 1964, 1967 ; Swennen 1984). Many of these deposits have features in common with the Thermae mineralization like black (siliceous) shale or intensely silicified carbonate host rock.

The frequently sucrosic texture of silicified carbonates suggests that silicification was preceded by leaching. The intensity of both leaching phenomena and silicification seems to decrease downwards. Where leaching has been less pronounced silicified carbonates have a glassy or chert-like appearance. Similar observations have been made for silicified Dinantian rocks in Heugem-1 and Kastanjelaan-2 (Gökdag 1982).

Comparison with other boreholes penetrating the Dinantian subsurface in South-Limburg (figure 2) reveals that leaching and subsequent silicification took place at those locations where the overlying Namurian and Westphalian strata had been eroded completely before deposition of Upper Cretaceous sediments. And it is also obvious that these processes affected the carbonates irrespective of their age (V2 in Heugem, V1-2 and Tn2 in Kastanjelaan, V3 in Houthem and Thermae). This suggests that leaching and silicification have been surface-controlled processes where descendent meteoric water played an important role. The weathered and eroded shales and sandstones of the overlying Namurian may have been the main source for silica (Gökdag 1982).

Lateritic weathering has also affected the top of the silicified Dinantian rocks. The paleosol is marked by white, kaolinitic clay, authigenic quartz and bleached silicified Dinantian rock fragments. Since these have been reworked in the overlying Upper Cretaceous Aachen and Vaals deposits it is concluded that leaching, silicification and lateritic weathering were pre-Santonian.

Kaolinic-smectitic, silica-rich clays also occur on top of the Dinantian carbonate rocks of Cork in Southern Ireland (Colbond Clays). These have yielded (Middle?) Jurassic microfloras (Higg & Beese 1986). Therefore, it seems likely that all these soil-forming processes were already active in Jurassic times.

PLATE 1

Almost completely silicified grainstone. Clasts include skeletal debris (a.o. foraminifera, echinoderm fragments, ostracodes, brachiopods and bryozoans) and coated grains.

Selective leaching of clasts (fig. 2) produced a moldic porosity with ghost structures of original fossils. Strong leaching affecting both clasts and cement (fig. 3-4) produced a pumiceous texture. Residuary micrite rims vugs, limeclasts and skeletal debris. Often quartz has infilled the cavities. Bar = 0.1 mm.

1   Dense, completely silicified bioclastic grainstone not affected by leaching. Large foraminifer in center is *Latiendothyranopsis* (det. : R. Conil). Thermae 2002-1, 240.0-241.0 m.

2   Completely silicified bioclastic grainstone with limeclasts and skeletal debris showing selective leaching of clasts. Thermae 2002-1, 240.0-241.0 m.

3-4   Completely silicified bioclastic grainstone with limeclasts and bioclasts. Severe leaching of clasts and cement produced a pumiceous texture. Residuary micrite lining the cavities has been overgrown by quartz crystals. Ghost structures of foraminifera, crinoid ossicles and brachiopod fragments can be distinguished. Thermae 2002-2, 241.0-242.5 m.

Most likely, the sulfide minerals were precipitated in karst cavities subsequently. Presumably, Zn and Pb were derived from deeper-seated sources and transported by warm, ascendent saline water. Precipitation of the sulfide minerals occurred where this water mixed with relatively cold, descending meteoric water due to a drop in temperature and salinity in this mixing zone.

Likewise in the boreholes Heugem and Kastanjelaan the principal Zn concentration occurs in silicified carbonates and to a lesser extend in collapse (karst) breccias, in both cases showing a downward decrease of Zn values (figure 2 ; Bless et al. 1981, Bless 1982). The same is true for the Pb values (Bless et al. 1981).

Although silicification of the carbonates preceded precipitation of Pb-Zn sulfide minerals, this does not necessarily imply that this silicification has to be considered as a hydrothermal pre-phase of the main Pb-Zn mineralization (cf. Swennen 1984). Gussone (1964) already indicated that dolomitisation and silicification are independant processes although these precede precipitation of sulfide minerals. On the other hand, a silica-rich host rock seems to facilitate the mineralizing process. Zn-Pb mineralization in the Westphalian rocks of South-Limburg is also preferably linked to sandstones and quartzites rather than to shales (Kimpe et al. 1978).

The age of the sulfide mineralization is as yet unknown. However it should be noticed that the principal Zn-Pb mineralization in the former mining area of South-Limburg are located along the NW-SE running border faults of the Rur Valley Graben (Kimpe et al. 1978). These faults have been reactivated since the early Tertiary and are still active. Descending meteoric water along these «open» faults and ascending,

strongly mineralized water (sometimes warm to hot) in the intersecting area of the Waubach Anticline have frequently created problems for the miners. It has also been noted that mineral water from the porous, silicified Dinantian carbonates of Heugem contains high amounts of zinc (1.384 mg/l Zn ; Bless et al. 1981). This sulfide mineralization may be relatively young. On the other hand, Zn-Pb sulfides do not occur in the Upper Cretaceous or Tertiary deposits of this area.

Two possible answers are forwarded here :
(1) The mixing zone between descendent meteoric water and ascendent mineral water could well be below the Dinantian subsurface. In that case precipitation of sulfide minerals would be below that surface.
(2) The kaolinized (weathered) top of the Dinantian strata and the overlying, clay-rich Aachen and Vaals deposits may form an impermeable layer for the metal-bearing solutions.

For a more detailed study of these mineralization zones six cutting samples from Thermae 2002 have been selected (table I). These samples have been divided into several sub-samples as indicated further on in the text, in tables and in the captions of plates.

PETROGRAPHY AND CHEMICAL ANALYSIS OF HOST ROCK

For the study of the host rock a number of chips has been selected from the cutting samples. The selection was based on macroscopical characteristics (e.g. lithology, porosity, colour). Chemical analysis have been made of all samples (table II), whereas petrogra-
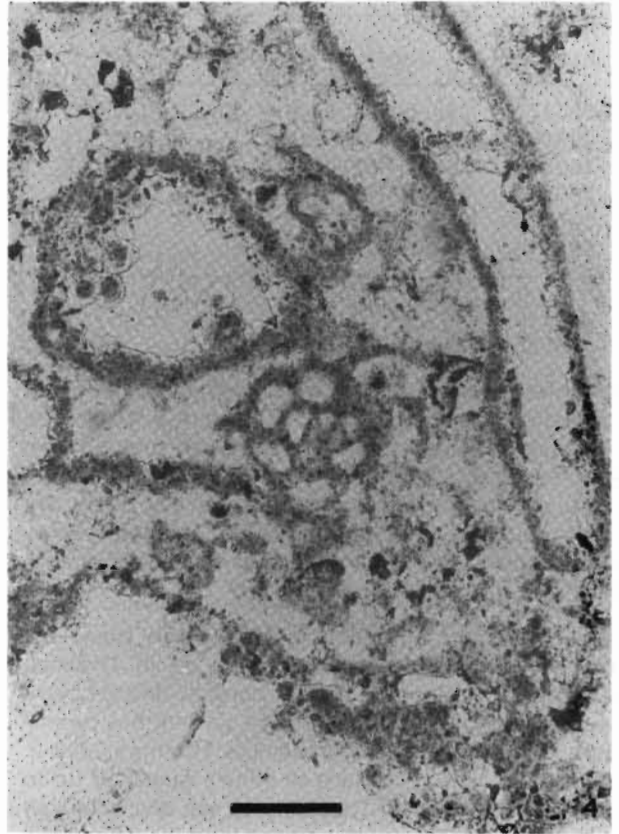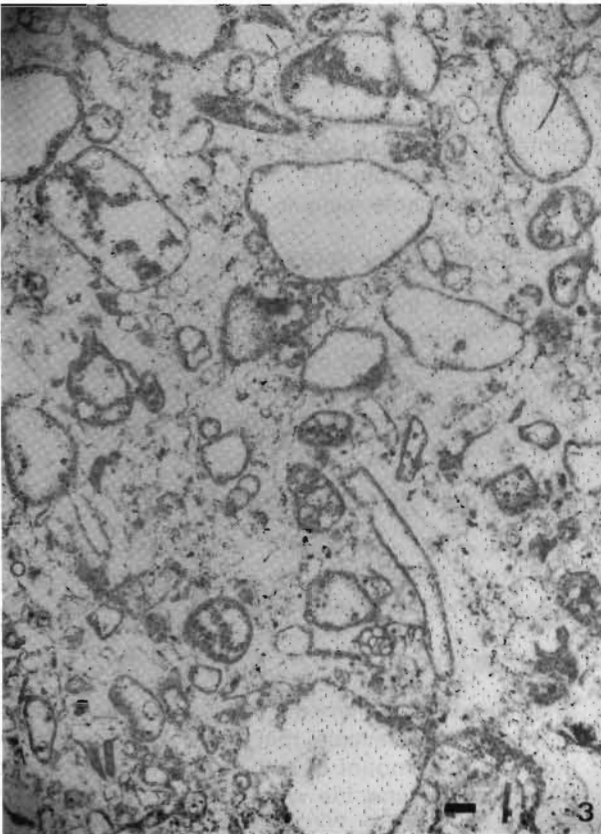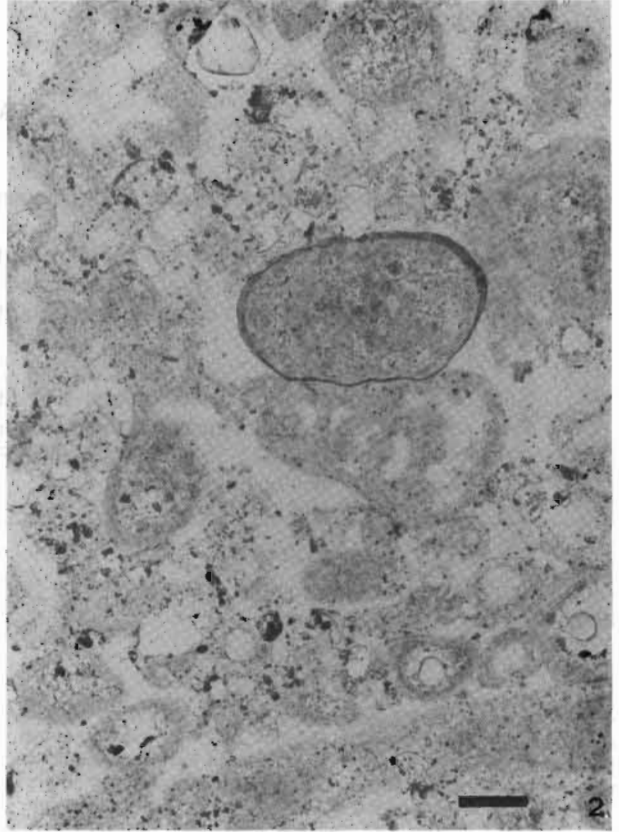
PLATE 2

Partly silicified bioclastic wackestone with finely disseminated opaque (organic?) material. Bar = 0.1 mm.

1-2   Slide showing ghost structures of bioclasts infilled with either sparite or microcrystalline quartz. Fine-grained, corroded (detrital) quartz grains and some mica flakes occur. The matrix of microcrystalline quartz contains a few relics of carbonate (sparite and micrite). Thermae 2002-3a, 333.5-335.5 m. Figure 2 with crossed nicols.

3-4   Slide showing euhedral calcite crystal and fibrous, chalcedonic silica grown in a dissolution cavity. Rare detrital quartz grains and mica flakes occur. Matrix of microcrystalline quartz contains few relics of carbonate. Thermae 2002-3b, 333.5-335.5 m. Figure 4 with crossed nicols.

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phic descriptions are only provided for the upper four samples (table I, pl. 1-3).

Table I - Sample numbers and depth of six selected cutting samples (sieve fraction > 2.4 mm) from Thermae 2002. For each sample is indicated the analysis of sulfide minerals and host rock insofar as these are mentioned in the text, figures or tables. A = ore microscopy/microprobe analysis; B = AAS analysis; C = petrography; D = XRF chemical analysis.

Sample number	depth	A	B	C	D
2002-1	240.0-241.0 m	X	X	X	X
2002-2	241.0-242.5 m		X	X	X
2002-3	333.5-335.5 m		X	X	X
2002-4	335.5-337.5 m	X	X	X	X
2002-5	337.5-339.5 m		X		X
2002-6	374.0-375.0 m				X

2.1. 240.0-242.5 m INTERVAL

This interval consists of (almost) completely silicified bioclastic grainstones (pl. 1). The matrix as well as the clasts (bioclasts, limeclasts, coated grains) have been replaced by microcrystalline to fine-grained, blocky quartz, coarsening towards centers. Residuary micrite outlines skeletal debris and coated grains. Opaque (possibly organic) material occurs disseminated in the matrix and in the clasts.

Various degrees of leaching have been observed. Selective leaching of clasts is noticed in Thermae 2002-1 and produced a moldic porosity. More severe leaching affecting both clasts and cement has produced a pumiceous texture in sample Thermae 2002-2. In hand specimens crystals of smoky quartz of up to 1 mm were observed. The samples are characterized by very high SiO2 contents (more than 98 weight-%).

2.2. 333.5-337.5 m INTERVAL

This interval consists of partly silicified wackestone to packstone and some intercalated bituminous mudstone (pl. 2-3). Opaque (bituminous) material is finely disseminated in the matrix of the wackestone/packstone. The matrix usually consists of microcrystalline quartz and some micrite. Angular, detrital quartz grains and micra flakes have been observed everywhere. Remarkable is the presence of sponge spicules and radiolarians at 335.5-337.5 m depth. Selective leaching of clasts was observed in Thermae 2002-4a.

The samples are characterized by strongly varying SiO2 and CaO contents indicating various degrees of silicification (but never as severe as in the 240.0-242.5 m interval). The significantly higher Al2O3 content of Thermae 2002-4b (compared to that in the other samples from this interval) corresponds to the (clayey) mudstone sample.

2.3. 337.5-339.5 m INTERVAL

Samples for this interval have only been analyzed geochemically (table II). The important variations in SiO2, CaO and Al2O3 match the observations for the 333.5-335.5 m interval. These indicate the presence of slightly to intensely silicified carbonates with low clay contents.

2.4. 374.0-375.0 m INTERVAL

The chemical composition of this interval suggests that this consists of partly silicified carbonates with varying amounts of clay minerals.

2.5. REMARKS

Analysis of trace elements in these few spot samples of host rocks reveals that there is no correlation between the amount of sulfide ore recognized under the binocular and the amount of Pb and Zn in the host rock. Sample 2002-2 (241.0-242.5 m) contains up to 83 % sulfide minerals (sieve fraction 1-2.4 mm) whereas the host rock yielded 36 ppm Pb and 245 ppm Zn. Sample 2002-5a (337.5-339.5 m) contains only some 15 % sulfide minerals under the bino-
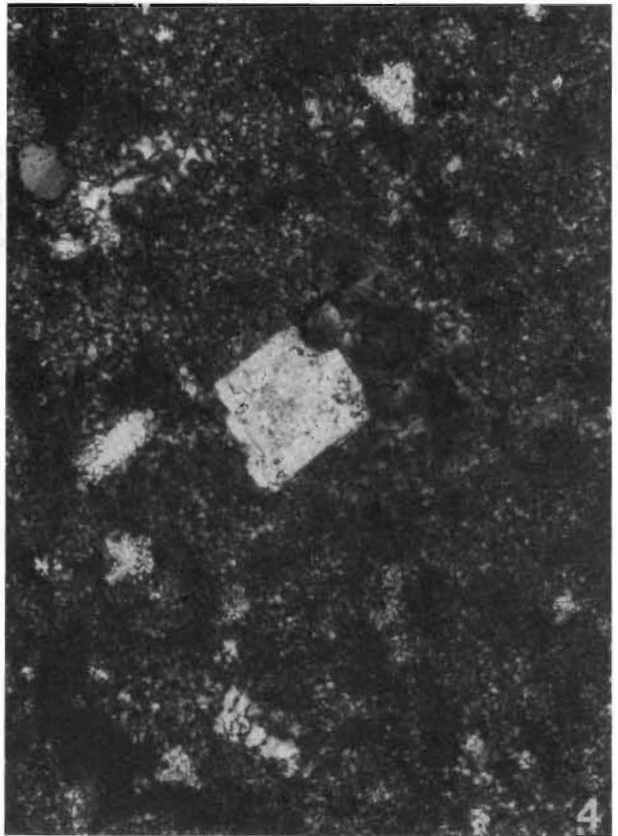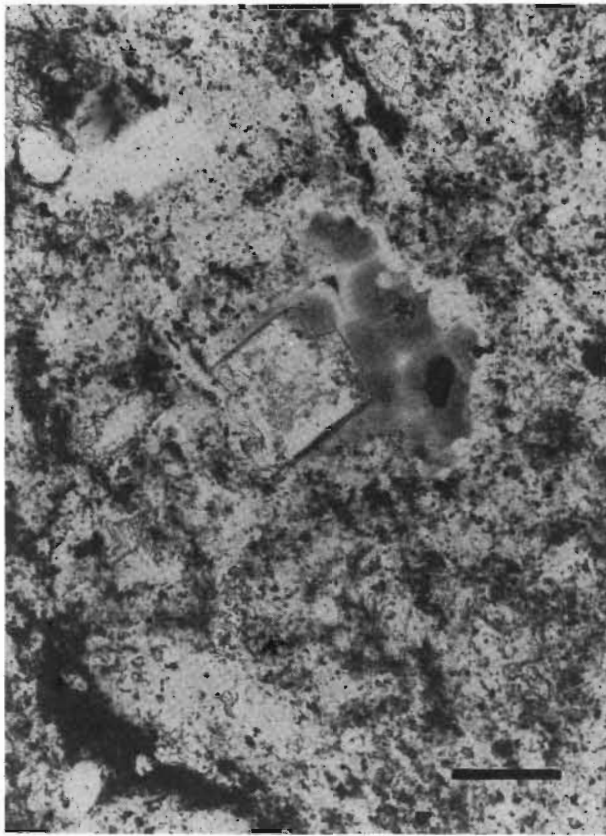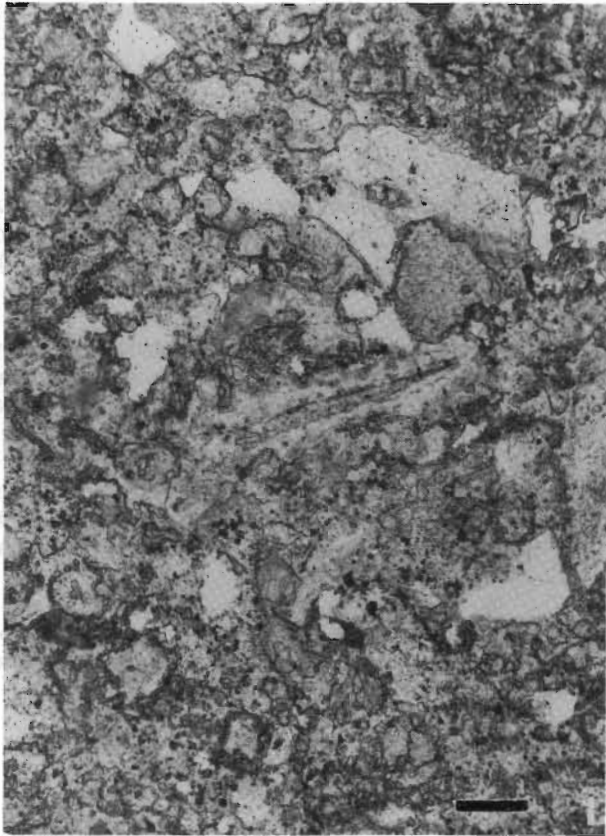
PLATE 3

Alternating bituminous mudstone and bioclastic wackestone to packstone. Clasts include rare detrital quartz grains, coated grains and skeletal debris (a.o. foraminifera, echinoderm fragments, sponge spicules and radiolarians). Occasionally, selective leaching of limeclasts and bioclasts has produced a moldic porosity (fig. 2). Bar = 0.1 mm.

1　　Alternate bedding of bituminous mudstone and bioclastic packstone. Mudstone consists of finely laminated matrix of dark, bituminous material with lenses of micrite or microcrystalline quartz and rare grains of detrital quartz. Matrix of packstone is partly silicified. Fossils include crinoid ossicles and a radiolarian (central portion of slide). Thermae 2002-4b, 335.5-337.5 m.

2　　Wackestone to packstone with bioclasts (a.o. foraminifera, crinoid ossicles) and coated grains. Rare, small grains of detrital quartz. Matrix consists of blocky sparite. Intergranular pores partly filled with micrite cement. Selective leaching of clasts has produced moldic porosity. Thermae 2002-4a, 335.5-337.5 m.

3-4　　Silicified bituminous mudstone with finely laminated matrix containing lenses of micrite and micro-crystalline quartz and few grains of detrital quartz. Skeletal debris mainly sponge spicules (fig. 3) and radiolarians (fig. 4). Thermae 2002-4b, 335.5-337.5 m.

Table II - Chemical analysis of host rock samples from Dinantian of Thermae 2002. Analysis carried out by XRF (PHILIPS PW 1400).
Main element determination was done on dried (110°C/24 h) ignited samples (1000°C/2 h) fused with a Li-borate flux (sample to flux ratio 1:10).
Instrument was calibrated with 20 International Rock Samples using De Jongh's alpha coefficients for matrix correction.
The values (recalcutated with the measured LOI) are based on the dried sample. Trace elements were determined on pressed powder pellets using Rh-Compton Scatter for matrix correction.

Main elements

Sample	SiO_2	Al_2O_3	CaO	K_2O	Fe_2O_3	MnO	TiO_2	P_2O_5	MgO	SO_3	Cr_2O_3	V_2O_5	LOI	Sum
2002-1	98.26	<.20	.51	<.10	.03	<.01	<.01	<.05	<.15	<.50	<.01	<.02	.39	99.28
2002-2a	98.07	<.20	.55	<.10	.02	<.01	<.01	<.05	<.15	<.50	<.01	<.02	.44	99.08
2002-3	62.01	.58	20.09	.16	.31	.07	.04	<.05	.39	<.50	<.01	<.02	15.75	99.82
2002-4a	19.81	.47	43.67	.10	.14	.14	.02	<.05	<.15	<.50	<.01	<.02	34.49	99.19
2002-4b	46.88	1.23	27.94	.27	.45	.07	.02	<.05	<.15	.90	<.01	<.02	21.77	99.61
2002-5a	55.96	.41	23.42	.11	.22	.07	.02	<.05	<.15	<.50	<.01	<.02	18.67	99.51
2002-5b	91.53	.95	2.26	.44	.44	<.01	.04	<.05	<.15	<.50	<.01	<.02	2.81	98.79
2002-6a	18.98	1.03	43.47	.21	.32	.11	.04	<.05	.25	.60	<.01	<.02	34.25	99.56
2002-6b	58.77	6.42	11.55	1.42	2.25	.03	.22	3.53	.45	1.71	.01	.02	11.96	98.34

Na_2O <.50

Trace elements

Sample	Pb	Zn	Ba	Zr	Sr
2002-1	<20	45	<20	<20	<10
2002-2a	36	245	<20	<20	<10
2002-3	<20	203	194	<20	66
2002-4a	<20	315	51	<20	101
2002-4b	41	193	125	22	114
2202-5a	51	364	180	<20	30
2002-5b	34	113	359	20	30
2002-6a	20	226	298	22	159

Cu, Co, Ni, Ga, Bi, Mo, Sb, Cd, As <20 ppm
Nb, Y, Rb <10 ppm
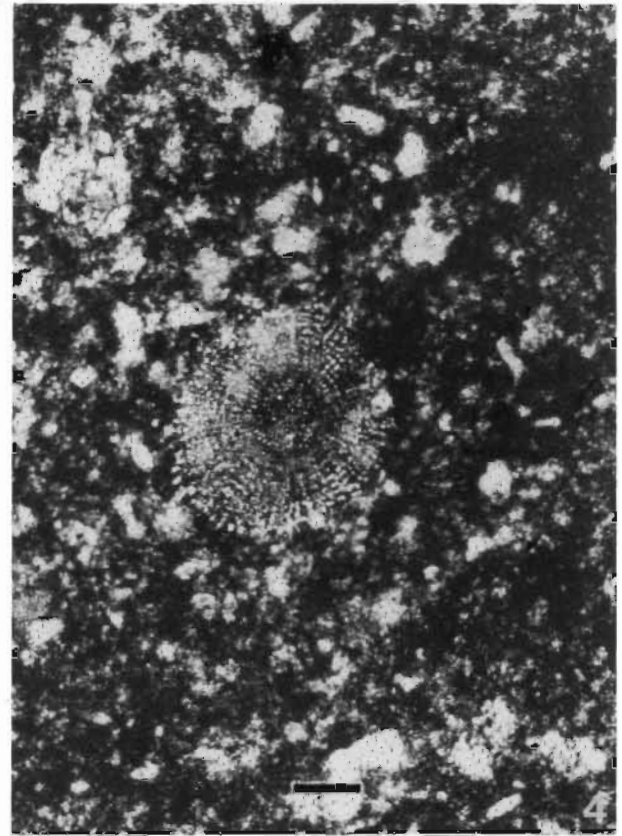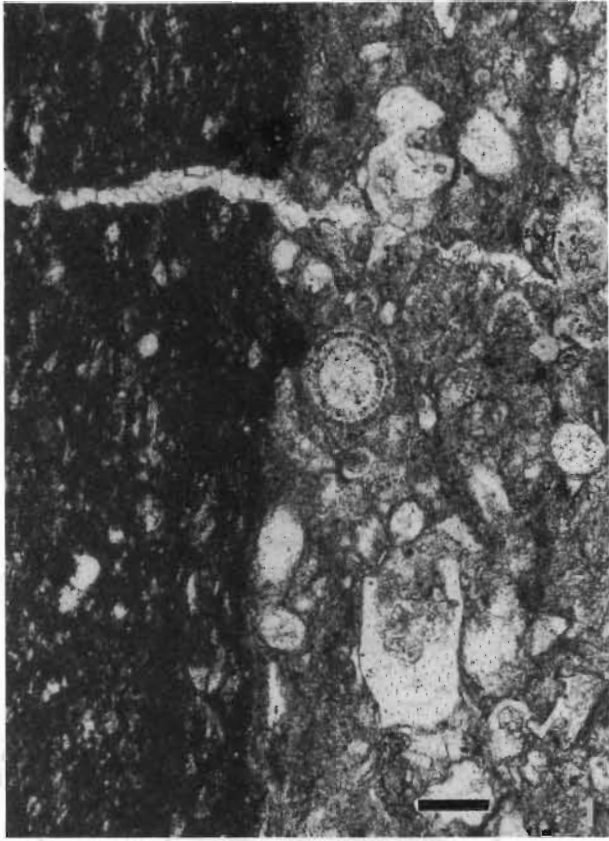
PLATE 4

«Schalenblende» with rhythmically layered crusts of sphalerite (dark grey) and pyrite (ligth grey). Thermae 2002-2, 241.0-242.5 m. Bar = 1 mm.
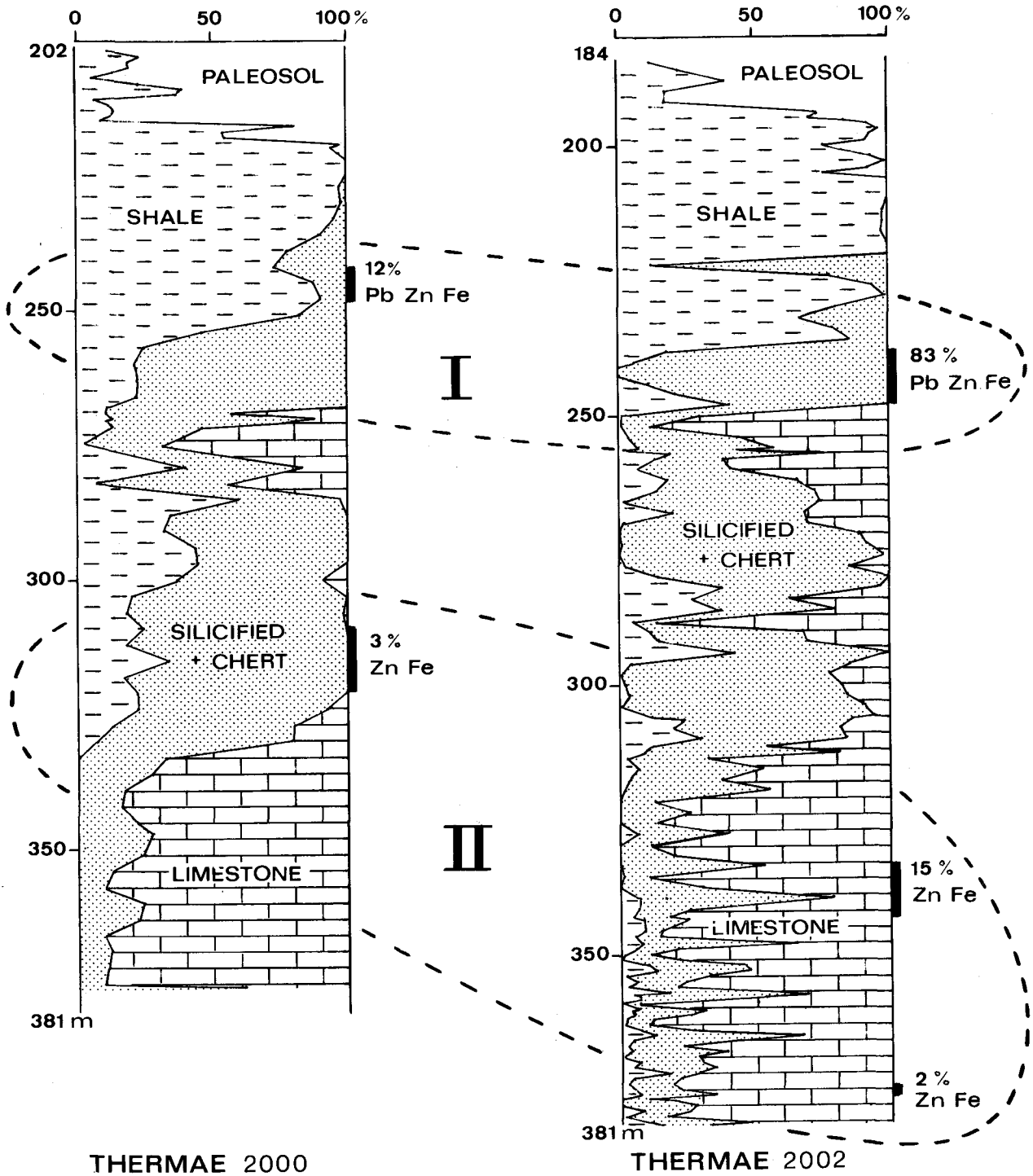

Figure 1 - Quantitative composition of rock in the Dinantian sequence of Thermae 2000 and Thermae 2002 and occurrence of sulfide minerals. Note that in both boreholes a downward decrease of sulfide ore percentages occurs although important variations between the two wells can be observed.
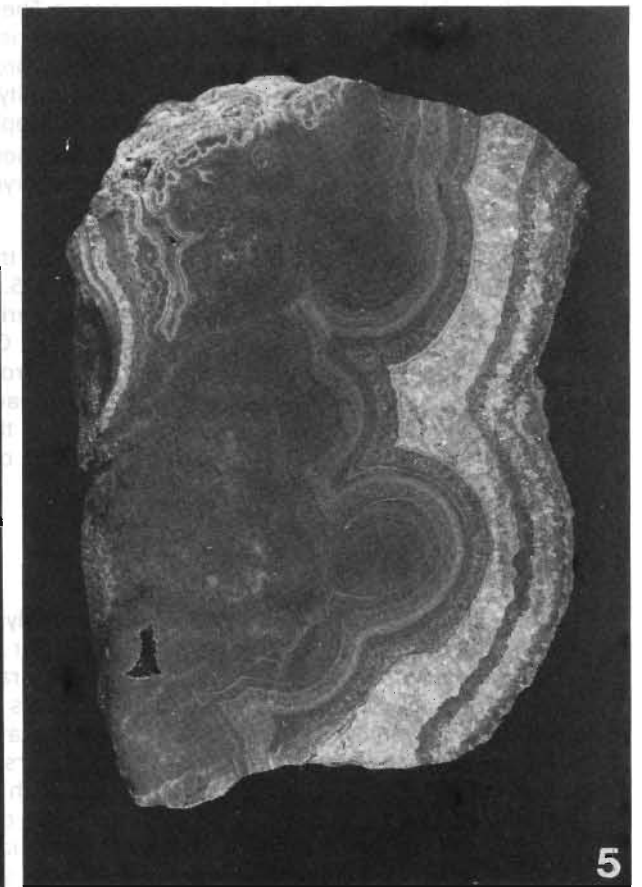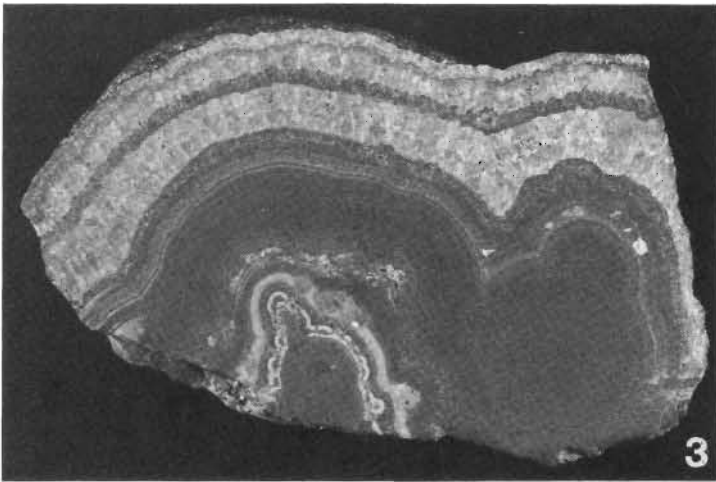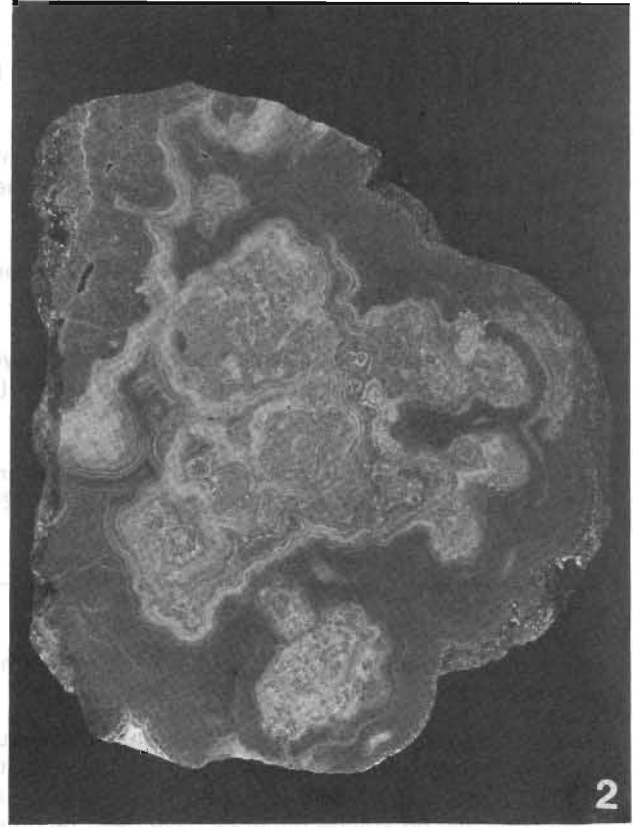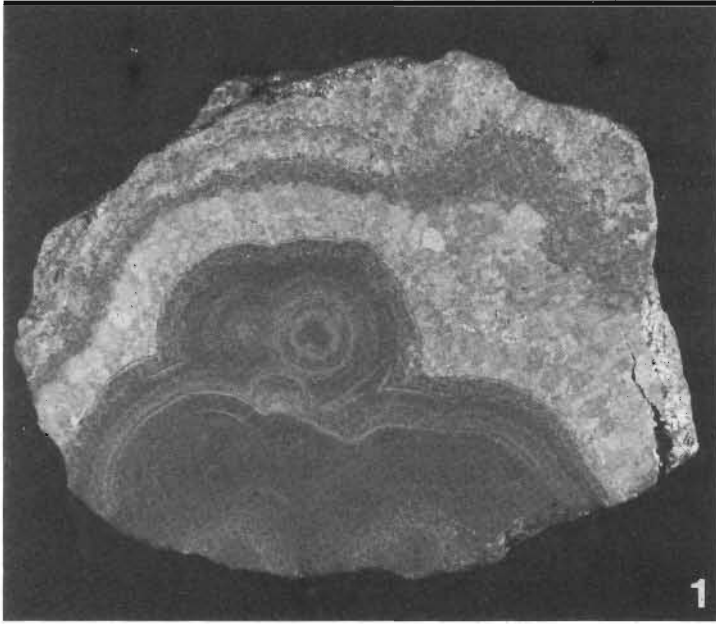
PLATE 5

1   Layers of botryoidal sphalerite («Schalenblende» : light grey) intergrown with pyrite layers (white) characterized by idiomorphic pyrite to the left. Cavities are black. Thermae 2002-1, 240.0-241.0 m. Bar = 200 μm.

2   Rhythmically layered crusts of «Schalenblende» showing radiating fibrous forms in alternating light and dark layers. Oil immersion, crossed nicols. Thermae 2002-1, 240.0-241.0 m. Bar = 100 μm.

3   Colloform pyrite (white) containing thin layers of arseniferous pyrite (light grey) and idiomorphic grains of marcasite (light grey). Crossed nicols (polars slightly decrossed), oil immersion. Thermae 2002-1, 240.0-241.0 m. Bar = 100 μm.

4   Rhythmically layered pyrite (white) intergrown with sphalerite (dark grey). Outer crust to the left is (melnikovite-) pyrite (white). Thermae 2002-1, 240.0-241.0 m. Bar = 100 μm.

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cular, whereas the host rock yielded 51 ppm Pb and 364 ppm Zn.

Most remarkable is the fact that cores from Heugem-1 contain more than 5000 ppm Zn (even up to 30.040 ppm) and up to 1449 ppm Pb although macroscopically no sulfide minerals have been recognized. Maybe this is explained by accepting that sulfide minerals mainly precipitated in karst cavities in Thermae 2000 and Thermae 2002 whereas the metal-rich solutions hardly penetrated the host rock (high porosity maybe not matched by high permeability), whereas in Heugem these solutions may have deeply penetrated the extremely porous and permeable host rock (permeability up to 52 md) producing microcrystalline, finely dispersed mineralization.

In this context it is noticed that one sample of the host rock from Thermae 2002 (2002-4b, 335.5-337.5 m) contains chalcopyrite and idiomorphic pyrite with low contents of As, but relatively high Ni and Cu contents, whereas the pyrite in the sulfide ore from the karst cavities is rich in As (table III). This clearly indicates that the pyrite in the host rock and the pyrite in the «schalenblende-ore» from the karst cavities have been derived from different sources.

3. ORE MINERALS

Ore microscopic, microprobe and chemical analysis of the sulfide minerals have been carried out for all samples indicated in table I. The sulfide ore is characterized by colloidal textures and mainly consists of rhythmically layered marcasite and sphalerite (plates 4-7). Concentric shells of very thin (< 1 mm) layers of sphalerite varying in colour from white-yellowish to dark-brown are very common. These variations can be caused either by changes in chemistry (especially in iron content) or by changes in the growth rate and content of inclusions and pores.

3.1. SPHALERITE

As shown in plates 4-7 rhythmic precipitation is a very common feature of sphalerites. It is beautifully developed in the «schalenblende» which consists of sphalerite as the dominant constituent and in part of wurtzite. Marcasite, pyrite and galena may also occur within the «schalenblende».

Close to the intercalated layers of iron sulfides sphalerite becomes more crystalline and often consists of euhedral grains. A similar texture has been observed near cavities filled with quartz. The dark-coloured layers of «schalenblende» very often contain anisotropic fibrous crystals similar to wurtzite as being observed in many other occurrences of «schalenblende» type in the Aachen-Stolberg-Moresnet district (Gussone 1964).

Microprobe studies reveal that the variation in colour of alternating layers of light and dark sphalerite of a «schalenblende» crust is caused by different chemical composition. The dark layers contain up to 3.76 weight-% Fe whereas the light-coloured layers are very low in Fe (about 0.01 weight-%). Cadmium also varies from layer to layer with maximum values of 0.7 weight-% in the light ones.

3.2. IRON SULFIDE

The iron sulfides consist of alternating zones of pyrite as the main constituent and marcasite. Two types op pyrite have been observed :
1 - massive pyrite sometimes containing euhedral pyrite with varying grain size from a few microns to a few millimeters, and
2 - «melnikovite pyrite».
The euhedral pyrites often occur at the top of iron-sulfide layers growing into the overlying «schalenblende». Melnikovite pyrite is characterized by extreme fineness of grain size and colloform structure which may have been formed by crystallization from
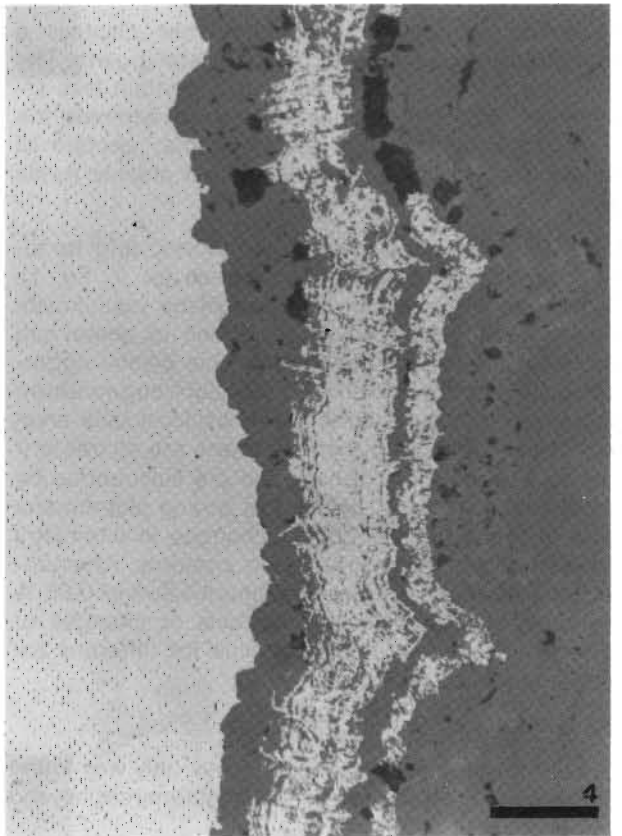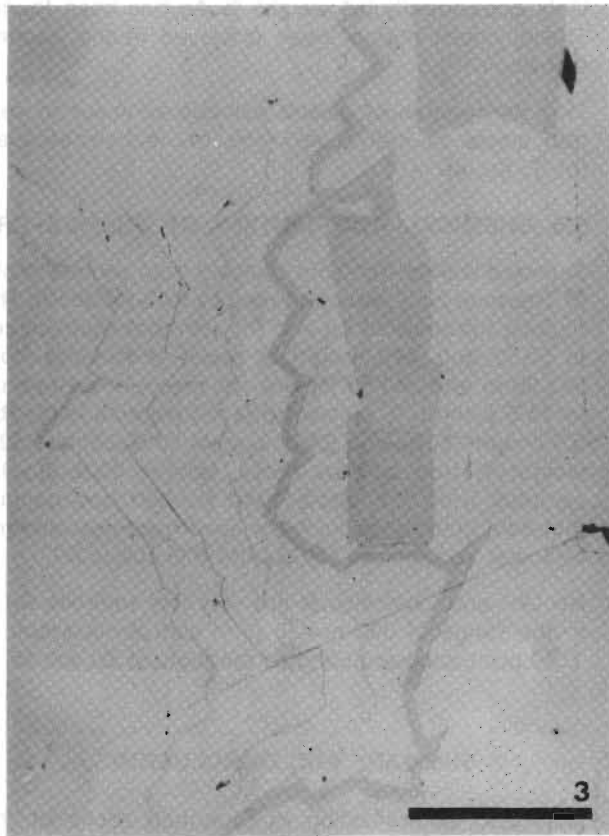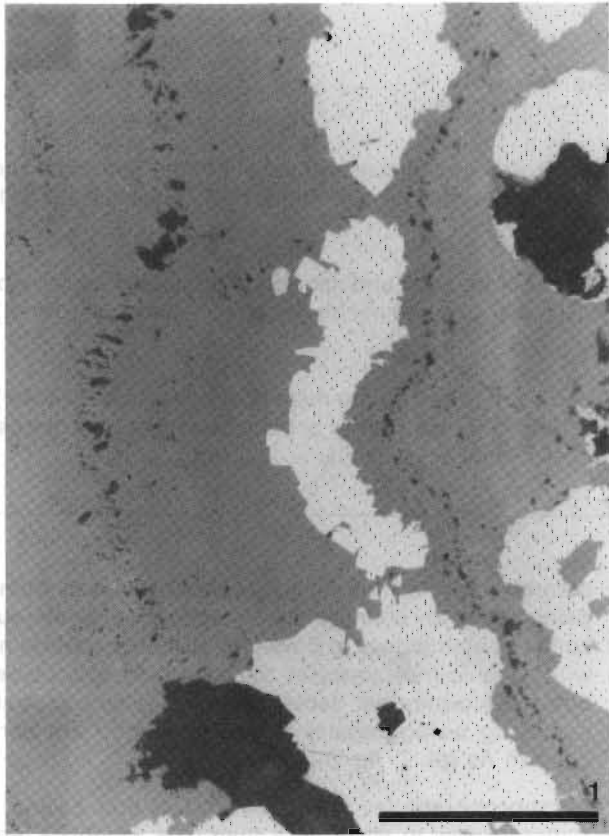
PLATE 6

1   Pyrite (white) intergrown with sphalerite (dark grey). Pyrite shows concentrical shell-like structure and idiomorphic grains. Crust to the right is melnikovite pyrite (white). Oil immersion. Thermae 2002-1, 240.0-241.0 m. Bar = 100 μm.

2   Melnikovite pyrite (white to light grey) forming rhythmic-botryoidal and spheroidal textures in layers of sphalerite («Schalenblende» ; dark grey to whitish grey). Crossed nicols (polars slightly decrossed). Thermae 2002-1, 240.0-241.0 m. Bar = 100 μm.

3-4   Rhythmically layered crusts of «Schalenblende» (dark grey) with pyrite-melnikovite-marcasite (white). The melnikovite-marcasite layer to the left is characterized by concentric colloidal textures and marcasite twins. Fig. 4 with crossed nicols. Thermae 2002-1, 240.0-241.0 m. Bar = 300 μm.

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colloidal gels. The structure of these aggregates varies from rhythmic-concentric layers to rhythmic-botryoidal and spheroidal (pl. 6, fig. 2). Melnikovite pyrite may also occur as crusts surrounding thin layers with euhedral pyrites. Within layers of melnikovite pyrite the colour varies from light-yellowish to brownish. Microprobe studies have shown that dark, brownish-coloured layers contain considerable amounts of arsenic (up to 4.8 weight-% As) and nickel (up to 0.63 weight-% Ni).

As mentioned above pyrite sometimes displays a strong tendency towards euhedral crystal growth. The newly formed single crystals usually contain less arsenic and nickel than colloform pyrite, whereas the idiomorphic pyrite in the host rock may contain Ni values of up to 1.26 weight-% without arsenic (table III).

Marcasite also forms banded structures, ring textures, cockades and agate-like textures (pl. 7, fig. 1). They often occur within layers of pyrite melnikovite showing well-developed single grains of some mm size and - more commonly - very fine crystal aggregates. Crustations with fibrous structure and reniform aggregates also have been observed. Marcasite crystals occurring in the outermost layers are characterized by a pronounced zoning and are surrounded by colloform pyrite (pl. 7, fig. 2). The zoning phenomena seen in marcasite are due to changes in chemistry especially to variation in arsenic contents. Arseniferous marcasite zones have maximum value of 0.66 % As (table III). Rhythmic interruptions or changes of growth process may be responsible for different zoning features (pl. 5, fig. 3).

3.3. BRAVOIT

Bravoit forming single zoned crystals only was found occasionally within layers of pyrite-marcasite and «schalenblende».

3.4. GALENA

Galena often occurs as single crystals or thin bands of idiomorphic grains within layers of «schalen-blende». Zoning has been observed and was found being due to changes in chemistry. Arseniferous zones containing up to 2 weight-% As are alternating with arsenic-free zones in the micron range. Sometimes the outermost darker zones of galena crystals occurring as aggregates within sphalerite are enriched in As (pl. 7, fig. 3).

Microprobe studies have also shown that galena is generally low in silver (less than 0.04 weight-% Ag). Only occasionally 0.1 weight-% Ag has been found. These values match those observed in the Aachen district.

Tiny aggregates of galena sometimes occur in very thin zones of individual layers of «schalenblende» (pl. 7, fig. 4).

3.5. CHEMICAL COMPOSITION OF SULFIDE ORE

Selected sulfide-rich chip samples from various depth of Thermae 2002 were analysed by AAS (table IV). The highest contents of Zn and Pb with maximum values of 50.72 and 4.76 weight-% occur in samples from 241.00 m and 242.50 m. Ore samples can contain up to 75.6 weight-% sphalerite (ZnS) (sample 2002-2b), 5.5 weight-% galena (PbS, sample 2002-2a) and 53.9 weight-% iron sulfides (FeS$_2$, sample 2002-3). Ore samples from the upper zone contain less gangue minerals than those from the lower part documented by lower contents of CaCO$_3$ and SiO$_2$ (table IV).

Ni- Co- and Cu-contents are very low whereas Cd is in the range of 390 to 470 ppm with a maximum of 1120 ppm corresponding to the highest Zn values.

SUMMARY AND CONCLUSIONS

Lead-zinc mineralization in Dinantian rocks of the Valkenburg area, Southern Netherlands, has been discovered in 1985-1986 by two boreholes which were drilled in order to explore the possible occurrences of thermal water. The mineralization is characterized by colloform sphalerite (schalenblende) and
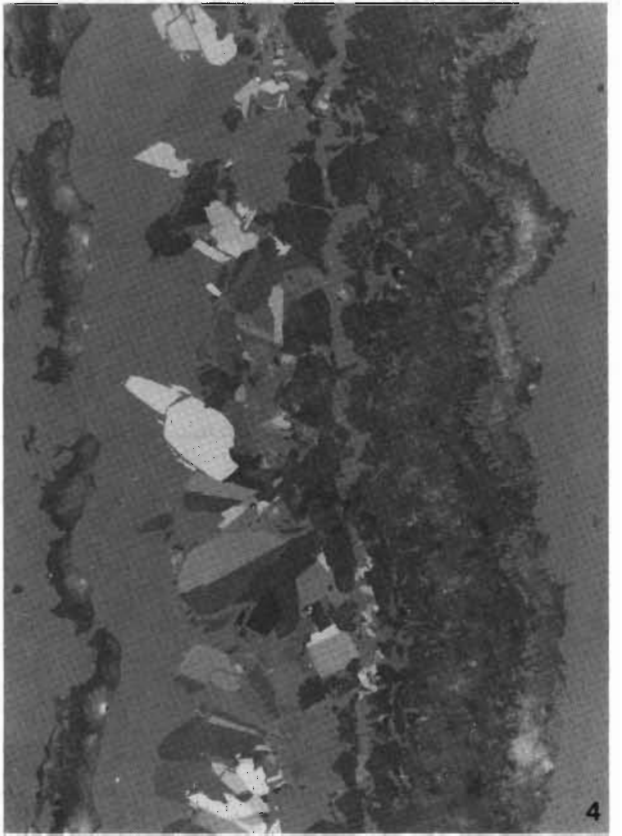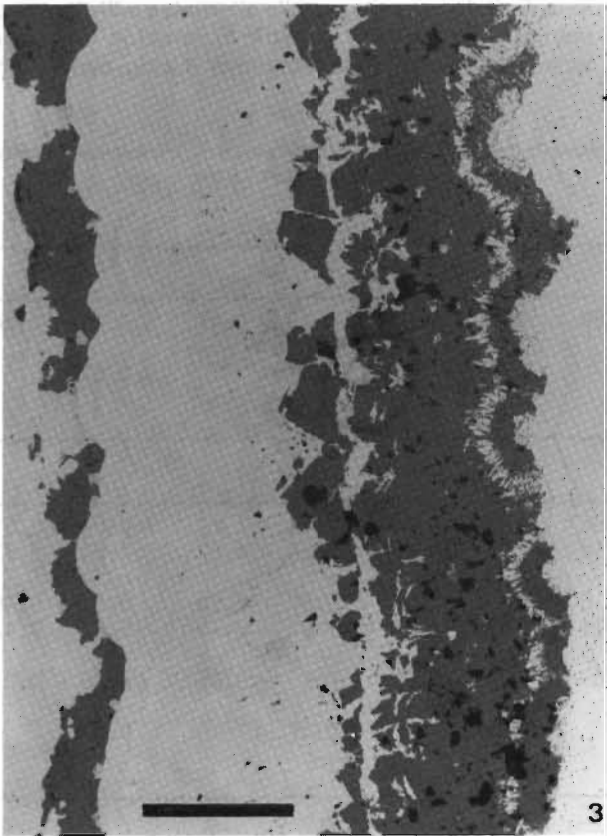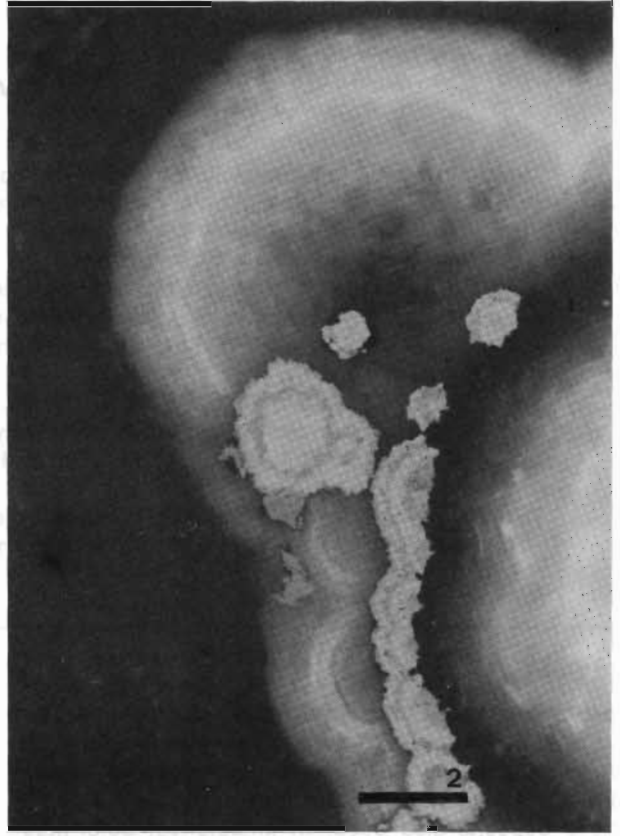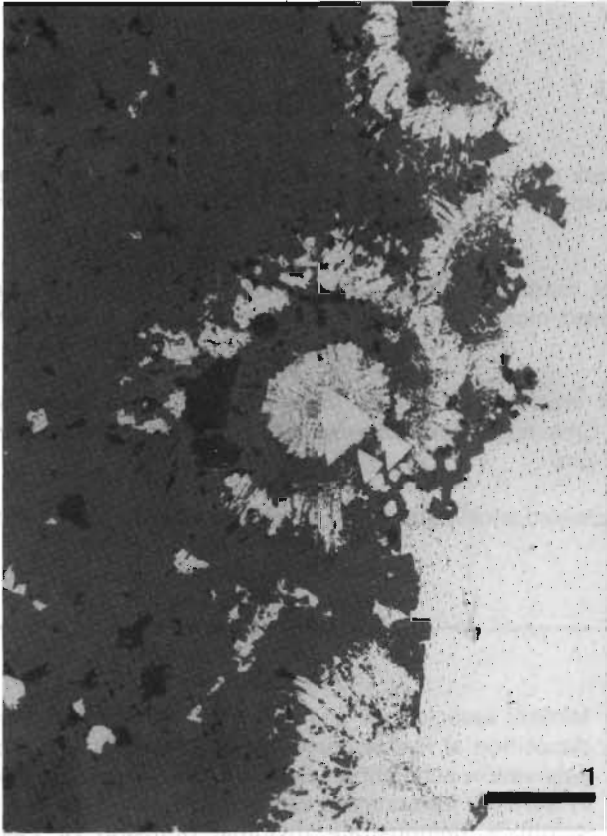
PLATE 7

1   Idiomorphic zoned marcasite crystals (light to dark grey) and slightly anisotropic pyrite (medium grey shades). Crossed nicols (polars slightly decrossed), oil immersion. Thermae 2002-4, 335.5-337.5 m. Bar = 100 μm.

2   Colloform structure of ironsulfide. In the center marcasite (various grey shades), with surrounding melnikovite pyrite. Sphalerite is dark grey. Crossed nicols (polars slightly decrossed), oil immersion. Thermae 2002-1, 240.0-241.0 m. Bar = 100 μm.

3   Aggregates of galena (light grey) with rims of arseniferous galena (medium grey) surrounded by polycentrically banded sphalerite (whitish grey). Crossed nicols (polars slightly decrossed), oil immersion. Thermae 2002-1, 240.0-241.0 m. Bar = 100 μm.

4   Banded sphalerite (medium to light grey) with dispersed small particles of galena (white). Oil immersion. Thermae 2002-1, 240.0-241.0 m. Bar = 100 μm.

colloform iron sulfides (gelpyrite and melnikovite-pyrite) very common in other lead-zinc deposits in Europe (especially in the Aachen-Altenberg/Vieille Montagne lead-zink district) and in North America. These deposits also occur in limestones, dolomites and calcareous shales, usually filling open spaces in zones of brecciation, crevices or joints enlarged by solution.

Mineral associations and colloform textures indicate deposition at low temperatures. Alternating white or pale yellow schalenblende with brown layers caused by different iron content varying from about 0.4 to 4.0 weight-% demonstrate rhythmic diffusion of Fe^{2+} ions. Colloform pyrite usually alternates with layers of marcasite, suggesting a rhythmic variation from acid to weakly acid or basic solutions during deposition.

Tab. III - Distribution of trace elements in sphalerite, pyrite, marcasite and galena (microprobe analysis, values in weight-%, n = number of analysis).

MINERAL	OCCURRENCE	n	Fe	Cu	Cd	Mn
Spalerite	ore	78	0.01 - 3.76	0.00 - 0.03	0.00 - 0.74	0.00 - 0.04
Detection limit			0.03	0.05	0.11	0.03

MINERAL	OCCURRENCE	n	Co	Ni	As	Cu
Pyrite (idiomorphic)	ore	30	0.02 - 0.06	0.01 - 0.04	1.76 - 3.22	0.00 - 0.01
Pyrite (colloform)	ore	24	0.02 - 0.10	0.01 - 0.63	2.68 - 4.82	0.00 - 0.03
Pyrite (idiomorphic)	host rock	27	0.01 - 0.10	0.03 - 1.26	0.00 - 0.09	0.00 - 0.49
Pyrite (xenomorphic)	host rock	14	0.02 - 0.11	0.03 - 0.24	0.00 - 0.19	0.00 - 0.42
Marcasite	ore	16	0.02 - 0.08	0.00 - 0.05	0.00 - 0.66	0.00 - 0.01
Detection limit			0.03	0.03	0.30	0.03

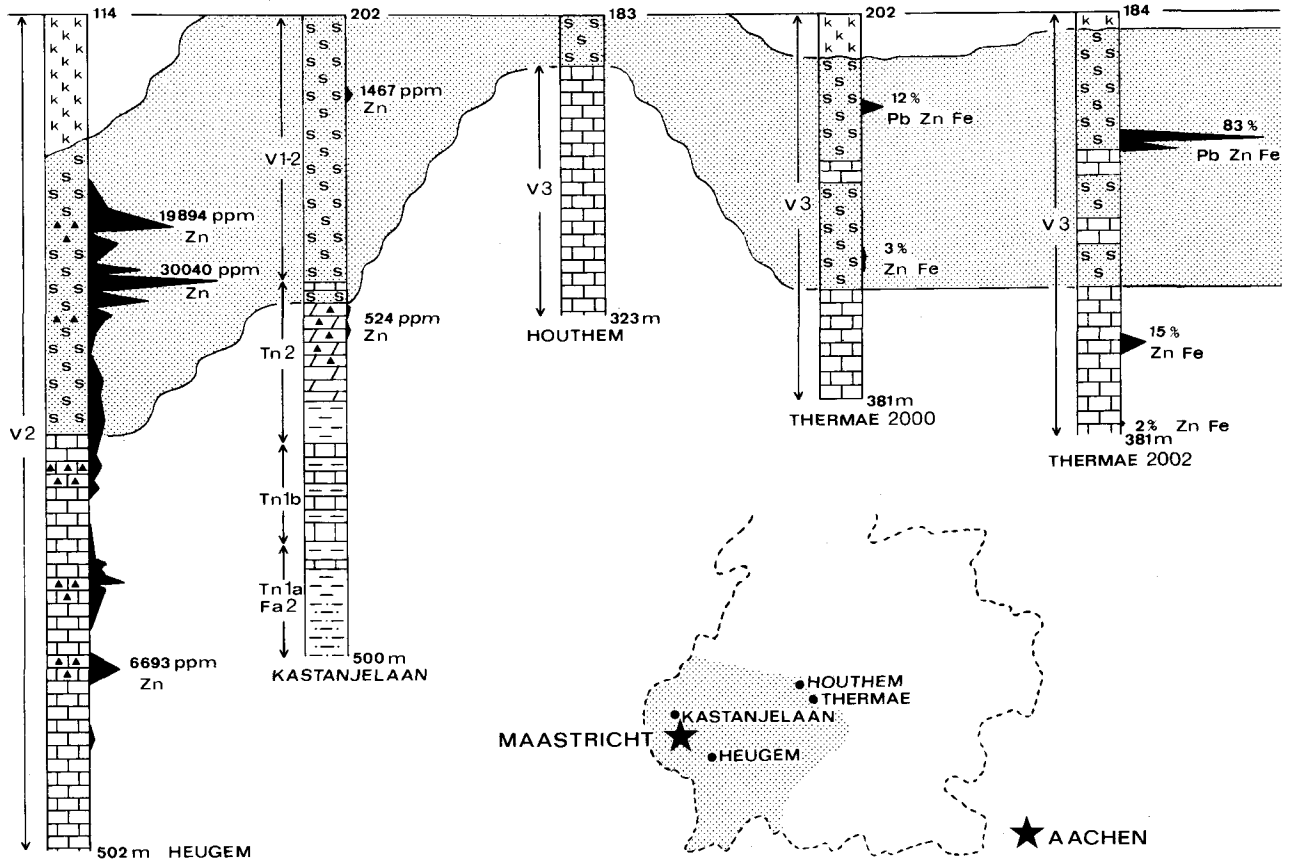| MINERAL	OCCURRENCE	n	As	Sb	Ag	Bi
Galena	ore	41	0.00 - 2.32	0.00 - 0.49	0.00 - 0.10	0.00 - 0.16
Detection limit			0.20	0.03	0.04	0.05
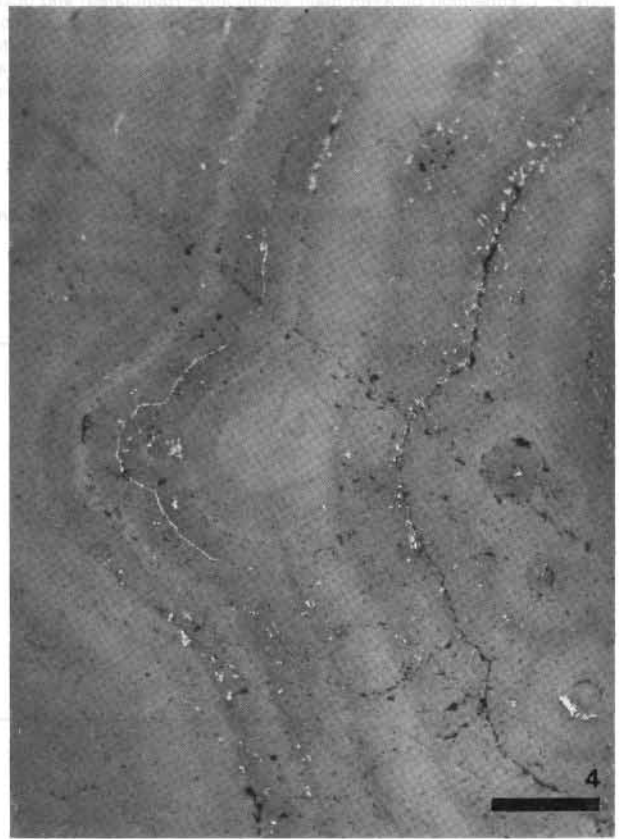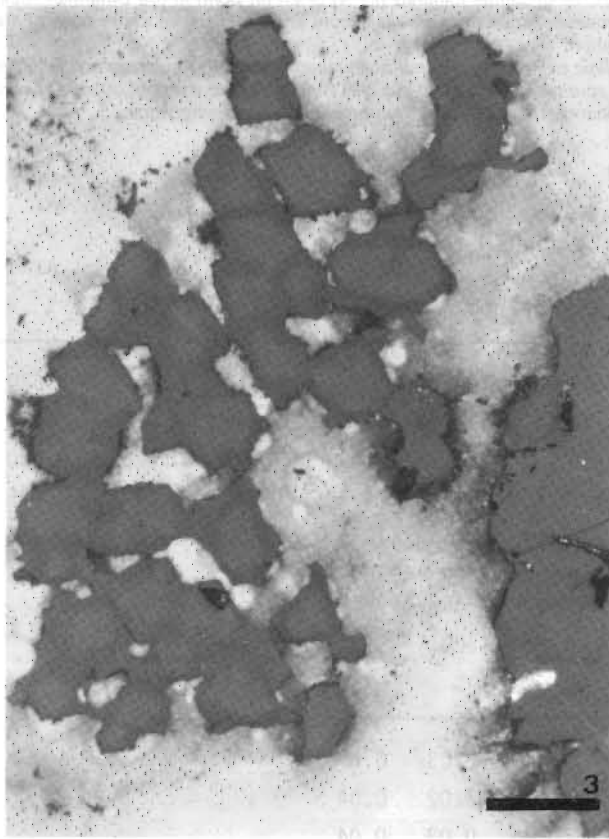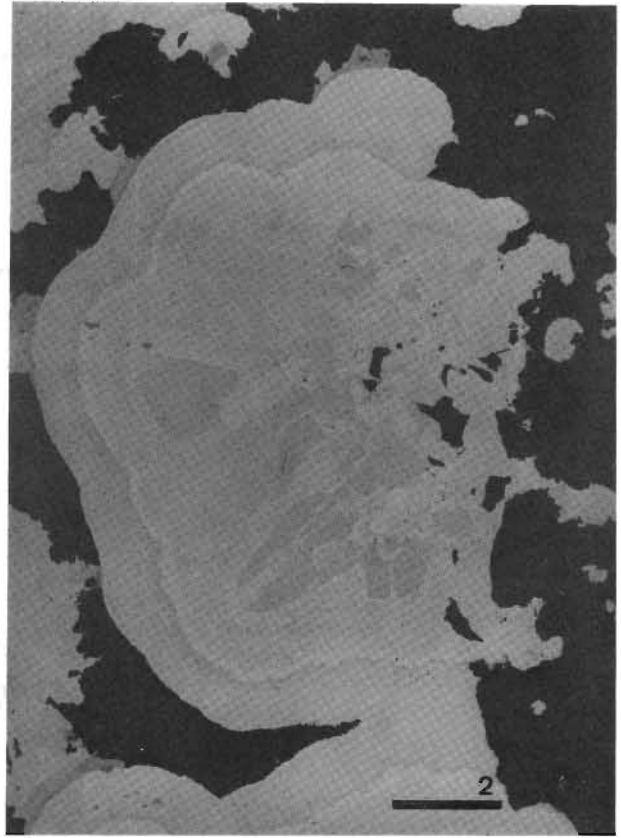
Figure 2 - Comparison between main silicification (punctated) and occurrence of sulfide minerals (in %) or Zn (in ppm) in the Dinantian rocks of some selected boreholes in South-Limburg. Note that emplacement of main mineralization always occurs at some distance above base of main silicification.

Datum line represents top Dinantian below Cretaceous overburden. A Kaolinic paleosol (k) has not been recognized in Kastanjelaan and Houthem. This may have been eroded before the Santonian. Punctated area in southwestern part of South-Limburg shows distribution of Dinantian subcrop below Upper Cretaceous. Beyond this area the Dinantian is covered by Namurian shales and sandstones.

Tab. IV - AAS-analysis of sulfide-rich samples. Compounds are calculated with respect to assumed minerals.

Sample	Zn %	Fe %	Pb %	Mn ppm	Ni ppm	Co ppm	Cu ppm	Cd ppm	Ca %	Si %	Al %
2002-1	27.60	31.42	0.400	28	<2	<10	10	400	0.012	0.040	<0.020
2002-2a	33.02	24.41	4.760	28	20	16	38	450	0.009	0.020	<0.020
2002-2b	50.72	10.63	3.060	46	8	<10	32	1120	0.009	0.020	<0.020
2002-3	20.09	34.21	0.439	70	16	<10	31	474	1.175	0.247	0.025
2002-4	26.80	24.63	0.414	408	14	<10	42	470	6.800	0.680	0.056
2002-5	16.70	31.62	0.448	446	8	14	28	390	0.740	0.100	0.024

Sample	Zns %	FeS$_2$ %	PbS %	CaCO$_3$ %	SiO$_2$ %
2002-1	41.14	49.46	0.46	0.03	0.09
2002-2a	49.22	38.42	5.50	0.02	0.04
2002-2b	75.60	16.73	3.53	0.03	0.04
2002-3	29.95	53.85	0.51	2.93	0.53
2002-4	39.95	38.77	0.48	16.98	1.46
2002-5	24.89	49.77	0.52	11.84	0.21

Colloform and idiomorphic pyrites from sulfide ore are rich in arsenic (up to 4.82 weight-% As), but relatively poor in copper (up to 0.03 weight-% Cu) and nickel (up to 0.63 weight-% Ni).

Idiomorphic pyrites also occur as small disseminations in the host rock close to the ore bearing intervals. The chemical composition of this type of pyrite differs distinctly from the above mentioned pyrite from sulfide ore : Arsenic is very low (up to 0.09 weight-% As), but copper and nickel are relatively high (up to 0.49 weight-% Cu and up to 1.26 weight-% Ni).

Two more types of pyrite were found in the Valkenburg Dinantian sequence : Framboidal pyrite in non-laminated to poorly laminated black shales and bituminous limestones of borehole Thermae 2000 (Wolf and Bless, 1987) and pyrite-marcasite concretions in the kaolinic paleosol on top of the Dinantian.

The existence of four types of pyrite in the Dinantian rocks may be important fur further genetic interpretations : The earliest type is the framboidal pyrite that is finely disseminated in the black shales. This is interpreted as early diagenetic and indicative of a reducing depositional environment. This type of pyrite has been formed more or less synsedimentary in late Visean time.

The Ni-Cu-rich pyrites occuring in the host rock close to the ore bearing intervals seem to be related to the extremely high coalification rank recently found by Wolf and Bless (1987). Since this high coalification rank also occurs in the Namurian of the Cartiels borehole near Gulpen in Southern Netherlands, this type of pyrite mineralization must be late Variscan or younger. Both the coalification and the formation of Ni-Cu-rich pyrite may be pre-ore-formation, related to the uplift of the Visé-Puth and Waubach blocks (Wolf and Bless, 1987).

The arsenic-rich pyrite occurring with sphalerite and galena in the «schalenblende-ore» is restricted to fissures and karst cavities. This ore-mineralization succeeded leaching and silicification from the surface and is therefore certainly post-Variscan. Zn, Fe, Pb, As, Cd and Sb were presumably derived from deeper-seated sources and transported by ascendent, warm saline water.

The pyrite-marcasite concretions in the kaolinic paleosol on top of the Dinantian are related to soil-forming processes. According to the existing literature this paleosol may have been formed in Jurassic to pre-Santonian times.

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