

## REPLACEMENT PHENOMENA IN ZN-PB DEPOSITS OF THE VERVIERS AND NAMUR SYNCLINORIA, BELGIUM<sup>1</sup>

by

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(1 table and 2 plates)

**RESUME.**- De nombreuses minéralisations sulfurées des synclinoriums de Verviers et de Namur comportent une sphalérite très poreuse. Cette texture poreuse est liée au remplacement sélectif d'oolithes, de crinoïdes et d'autres bioclastes tandis que les ciments sparitiques ne sont peu ou pas remplacés.

Il est suggéré que la présence d'une microporosité et d'une phase organique dispersée au sein de ces bioclastes ainsi que 0,5-1 % poids de Zn incorporé dans leurs structures ont permis leur remplacement préférentiel par la sphalérite. Ce remplacement provoque la libération d'une quantité proportionnelle de CO<sub>2</sub> qui permet la dissolution des carbonates encaissants. Les cavités formées ainsi sont ensuite envahies par des sulfures rubanées.

**ABSTRACT.**- Part of the sulfide mineralization in the Verviers and Namur synclinoria occurs as a very porous sphalerite. This texture is associated with a selective replacement of oolites, crinoids and other bioclasts by sphalerite, while sparry calcite shows only minor, if any, replacement. Microporosity, organic matter dispersed in bioclasts and 0.5-1 wt % of Zn introduced into the structure of carbonates are suggested as a reason for the replacement by sphalerite. Replacement of carbonates by sphalerite released proportional amounts of CO<sub>2</sub>. This agent caused leaching of the host carbonates and produced large cavities filled by banded massive sulfides.

### INTRODUCTION

The Vesder and Namur synclinoria contain the most important Zn-Pb deposits in Belgium. Most of them are situated in the carbonate rocks of the folded Carboniferous. Mineralization is controlled by faults (Variscan NE-SW faults and post-Variscan transverse faults with a NNW-SSE strike), and by lithological contacts between carbonates (Dinantian) and siliciclastics (Upper Devonian, Namurian . . .). The geological setting of the deposits has been described by Dejonghe & Jans (1983).

These epigenetic deposits consist often of open space fillings where banded sulfides of sphalerite, galena and pyrite/marcasite were precipitated. However, part of the mineralization also formed as replacement of the carbonate rocks. Little attention has been paid to this phenomenon. The aim of this paper is to discuss the texture resulting from the replacement of the host carbonates by sphalerite mineralization.

### MATERIALS AND METHODS OF INVESTIGATION

Since all mining activities of Pb-Zn mineralization ceased several decades ago, sampling of the mineralization in situ is not possible. Therefore the study is based on the investigation of ~ 90 samples, of which the locality is known, from museum and private collections.

After inspection of the hand specimens, polished sections were prepared and examined. Microprobe analysis were made with a Jeol 733 probe. The probe was operated at 20 kV using the following spectral lines and synthetic compounds: MgK $\alpha$ (MgCO<sub>3</sub>), KK $\alpha$  and AlK $\alpha$  (KAlSi<sub>3</sub>O<sub>8</sub>), MnK $\alpha$  and SiK $\alpha$  (MnSiO<sub>3</sub>), FeK $\alpha$  and SK $\alpha$  (FeS<sub>2</sub>), ZnK $\alpha$

1. Manuscript received on November 1988.

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(ZnS). All of the detected sulfur was assumed to be balanced by Zn. The carbonate Zn has been calculated by a difference between the total and the sulfidic zinc.

## MACROTEXTURES OF THE SULFIDE MINERALIZATION

Generally five major macrotextures of the sulfide ore can be distinguished :

### 1. Veins and veinlets

They are mainly composed of sphalerite, marcasite, wurtzite, galena, melnikovite, calcite, dolomite, quartz and locally Ni minerals and nickeloan pyrite-melnikovite. A typical structure is formed by curved microbands.

### 2. Sulfide cemented breccias

Fragments are composed of the host carbonates, argillaceous carbonates or argillites. The matrix is formed by sulfides. A structure is represented by banded overgrowths on the clasts and by fillings of sulfides.

### 3. Finely dispersed mineralization

Fine-grained sulfides are dispersed in the host carbonates. Part of this texture may also be controlled by stylolite-guided fillings and by replacements.

### 4. Cavity fillings

Cavities of various sizes are filled by banded sulfides and internal sediments composed of clasts of banded sulfides cemented by silica. This texture also includes sulfide stalactites. The cavities probably resulted from the dissolution of the host carbonates by hydrothermal fluids circulating via vein cavities (de Magnée, 1967; Bartholomé & Gérard, 1976). Some of these cavity fillings at Seilles and Engis might have been formed by circulation of meteoric waters (Balcon, 1981).

### 5. Stratiform mineralization

The stratiform texture is formed by replacement of the carbonate host by sphalerite. A typical microtexture is formed by phantoms of oolites and bioclasts replaced by sphalerite (Pl. 1 : 1, 2 and 3). Voids and cavities up to a few mm in size are ubiquitous and a characteristic feature of this type of massive sphalerite. The microtextures, described and discussed in the next sections, are connected mainly with this macrotexture. Replacement of the carbonate host by sphalerite was observed in samples from La Calamine, Schmalgraf, Engis, Corphalie and Andenne.

## REPLACEMENT OF CARBONATES BY SULFIDES : MICROTEXTURES AND GEOCHEMISTRY

Some of the studied samples are entirely composed of sphalerite replacing the host carbonates (Pl. 1 : 1 and 2); some represent a contact zone between the host rock and massive banded sulfides (Pl. 1 : 3). The replacive sphalerite has one persistent feature : it always contains numerous empty spaces and voids ranging in size from a few  $\mu\text{m}$  to 1 cm (Pl. 1).

Replacement is a very selective feature in the studied samples. The most prone to replacement are oolites and bioclasts. Usually these carbonate components are entirely replaced and only a few recrystallized relics of carbonates, embedded in replacive sphalerite can be seen. In contrast, sparry calcite cement often forms recognizable fillings between bioclasts and oolites replaced by sphalerite (Pl. 1 : 5). Only in most massive sphalerite sparry calcite is also affected by replacement. In it phantoms of bioclasts and oolites (Pl. 1 : 7 and 8) can be recognized under crossed nicols in otherwise massive sphalerite.

The process of replacement produces a characteristic distribution of elements in micro-areas. Some Zn is present in the carbonate matrix and may not be balanced by sulfur. Iron is irregularly distributed in replacive sphalerite; it often concentrates at the edges of ZnS grains (Pl. 2 : 10; Fe). Silicon forms inclusions in both the carbonate matrix and the replacive sphalerite (Pl. 2 : 10; Si), but it also forms a distinct rim surrounding some of the calcite as well as the sphalerite grains.

Considering the chemical composition of carbonates (table 1), a distinct difference exists only between micritic infill of shelter porosity in bioclasts and other recrystallized carbonates. The first are distinctly richer in Al, Si and S due to minute inclusions of clay minerals and organic matter. Their metal content is low. The second ones are enriched in Mn and Zn. There is a positive correlation between the grain size of carbonates and the concentration of some metals. This may suggest that recrystallization might have been a major factor controlling the introduction of metals into the structures of the carbonates.

The discussed replacement produces two different types of sphalerite. A more abundant variety consists of fine-grained sphalerite with grain size varying around a few  $\mu\text{m}$ . Plain polarized light shows numerous small black voids (Pl. 1 : 4, 5 and 7) and minute inclusions of clay minerals (Pl. 1). This sphalerite type mimics shapes of crinoids (Pl. 1 : 4) molluscs and/or bivalves and oolites (Pl.

Table 1.- Microprobe composition of carbonates and associated replacive sphalerite; average (wt %) of N, number of microprobe analysis.

	<i>Crystal size (<math>\mu\text{m}</math>)</i>	<i>Mg</i>	<i>Al</i>	<i>Si</i>	<i>S</i>	<i>Ca</i>	<i>Mn</i>	<i>Fe</i>	<i>Carbonate Zn</i>	<i>Sulfide Zn</i>
Micrite in shelter porosity of bivalves N=15	3-35	0.05	0.08	0.64	0.12	36.31	0.37	0.16	0.36	0.25
Recrystallized bivalve shell N=3	25-140	0.04	$\leq 0.02$	$\leq 0.02$	0.06	38.86	0.65	0.22	1.01	0.12
Recrystallized oolite relics N=6	70-100	0.05	$\leq 0.02$	0.33	0.05	39.74	0.45	0.08	0.51	0.10
Recrystallized sparry calcite N=33	14-150	0.04	$\leq 0.02$	0.38	0.05	37.18	0.47	0.11	0.47	0.10
Relics in calcite spar N=6	3-20	0.08	$\leq 0.02$	0.32	$\leq 0.04$	38.20	0.50	0.20	0.18	$\leq 0.05$
Recrystallized crinoids N=12	50-120	0.03	$\leq 0.02$	$\leq 0.02$	0.10	39.54	0.54	0.19	0.41	0.20
Sphalerite replacing bioclasts N=5	3-20	$\leq 0.04$	0.25	0.15	33.28	0.05	$\leq 0.04$	0.25		65.14
Sphalerite replacing oolites N=10	3-20	$\leq 0.04$	0.20	0.34	33.01	0.05	$\leq 0.04$	0.39		65.07
Sphalerite fillings N=5	40-80	$\leq 0.04$	$\leq 0.04$	$\leq 0.04$	33.40	$\leq 0.04$	$\leq 0.04$	0.75		65.18

1: 5, 6, 7 and 8). Phantoms of carbonate components are richer in Al and Si (table 1). This type of sphalerite has dull grey-brownish internal reflections forming under crossed nicols a characteristic pattern composed of small dots and flakes (Pl. 1: 6 and 8). This sphalerite was produced by direct replacement of carbonates.

The second sphalerite type is coarsely crystalline with crystal sizes between 40 and 80  $\mu\text{m}$  and honey-coloured internal reflections. In plain polarized light it is free of voids (Pl. 1: 5 and 7) and the only detected admixture is formed by Fe (table 1). This sphalerite has been introduced as fillings of moldic porosity and as an infill of interparticle porosity (Pl. 1: 5 and 7). This variety of sphalerite does not occur frequently.

## DISCUSSION

Oolites, crinoids, molluscs and/or bivalves are the major replaced carbonate allochems. Oolites are presumably composed originally of aragonite or high Mg-calcite, echinoderms of high Mg-calcite and molluscan shells of layers which are

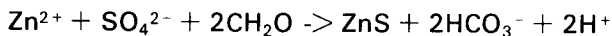
either all aragonite or interlayered aragonite and calcite (Bathurst, 1975). Grainstones composed of these components have an original porosity of 40 to 60 % and are very permeable. The discussed carbonate allochems, because of their original mineralogy, are metastable during diagenesis and are subjected to polymorphic transformations and recrystallization or are leached leaving moldic porosity (Bathurst, 1975).

Additionally, the original microporosity of bioclasts and oolites is high (Bathurst, 1975) and may be preserved during diagenesis. In contrast sparry calcite cement has very little, if any, microporosity. Therefore bioclasts and oolites with their high microporosity are much more prone to be affected by mineralizing fluids.

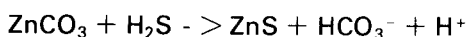
Replacement of carbonates by sulfides reduces the volume of reacting phases, releases  $\text{CO}_2$  and involves leaching. These processes may retain a high permeability in the ore zone over an extended period of time. Therefore such a leaching may focus on a smaller scale the flow and discharge of the ore fluids within the same volume of the ore zone and, by replacement of carbonates and sulfide fillings, may eventually produce a high-grade ore. Advanced replacement of metal-

bearing carbonates may release amounts of CO<sub>2</sub> large enough to produce solution cavities in the host carbonates. In this way replacement, mineralization and creation of open spaces could be a one reciprocal process (Kucha & Czajka, 1984). This may also provide an explanation of the process of cavity-creation by the hydrothermal fluids proposed by de Magnée (1967) and Bartholomé & Gérard (1976).

A similar replacive process of mollusc shells but by pyrite was also observed in the Lower Oxford clay, England (Fisher, 1986). This replacement is ascribed to a reducing micro-environment provided by the shells themselves. In the process bacteria are reducing sulphate ions at the expense of organic substances present in the shells. There exist a balance between the precipitation of pyrite and carbonate depending on the availability of iron. Analogous reasoning can be applied to the replacement of bioclasts and oolites by sphalerite :



or for carbonate Zn :



The potential H<sup>+</sup> ions change the carbonate equilibria, allowing the solution of carbonate. Three features are important in the studied samples :

- 1) open pore spaces in the mineralized sections, involving carbonate host replacement, are much more abundant than in laterally equivalent host away from the mineralization;
- 2) carbonate cement textures in the mineralized sections resemble sparry cement in carbonate grainstones away from the mineralization;
- 3) Zn content in carbonates in the mineralized sections is usually above microprobe detection limit, while away from the mineralization is below.

The observed textures and microtextures of the mineralization can be achieved in two ways :

#### 1) Infill of porosity after dissolved carbonate allochems

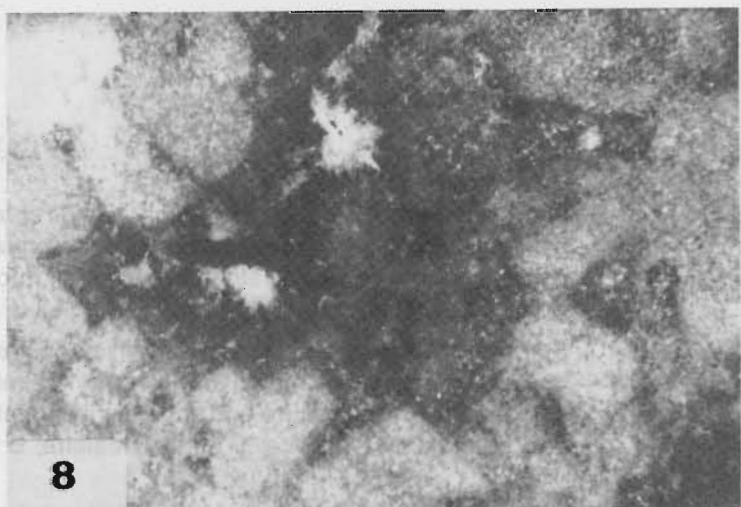
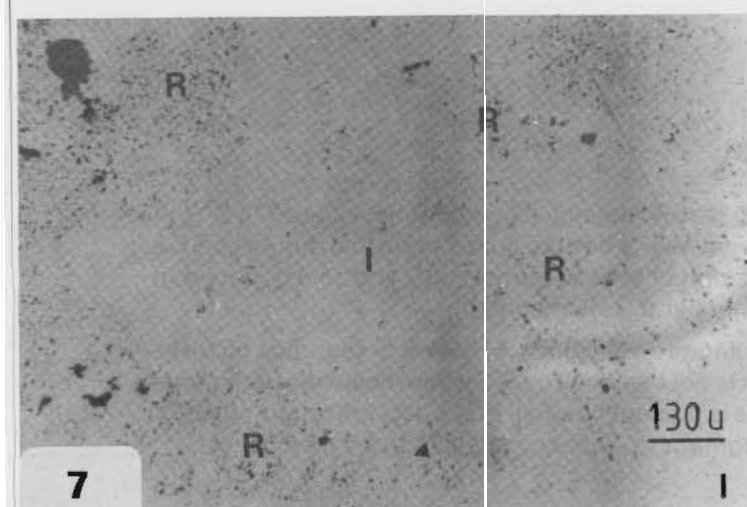
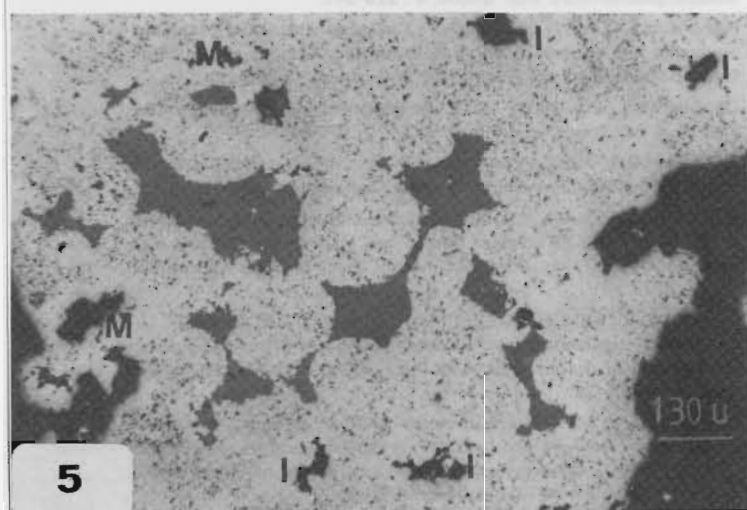
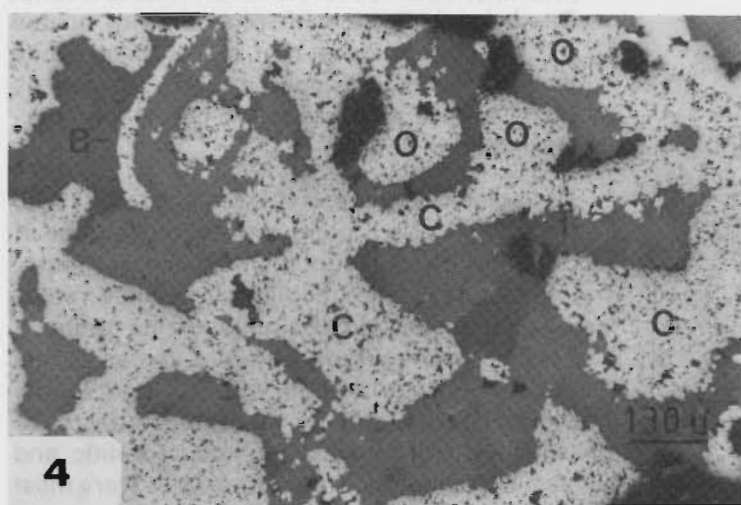
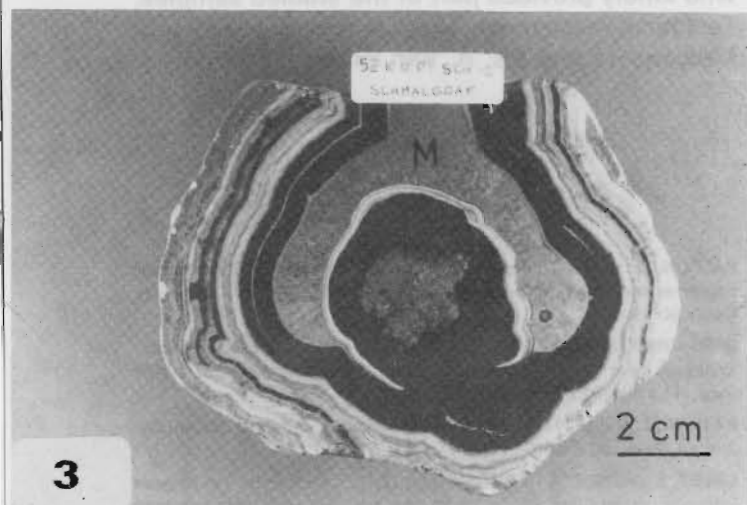
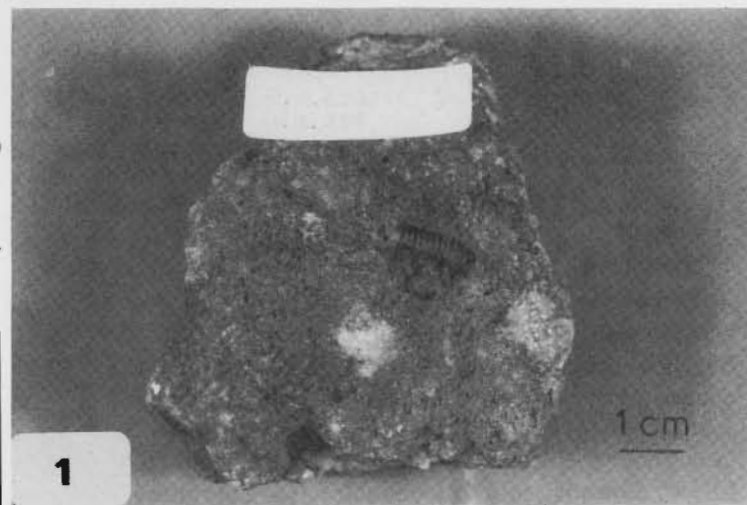
However, in the studied samples molds after oolites and bioclasts filled with coarse-crystalline honey sphalerite are rare (Pl. 1 : 5 and 6).

#### 2) Direct replacement

The majority of observed phantoms of carbonate allochems consists of a very fine-grained sphalerite with dull grey-brownish internal reflections. The phantoms have increased concentrations of Al and Si, and contain detectable amounts of Ca (table 1). The first two are present as minute inclusions of clay minerals, the second one is related to

## PLATE 1

1. Sphalerite formed by replacement of the host carbonate rock. Sphalerite contains numerous black voids up to 1 cm in size. In the centre of the specimen, a replaced crinoid, is visible. Schmalgraf, sample J.G. 5232 R.N. 227 (Museum of Natural Sciences).
2. Massive sphalerite formed by replacement of oolitic limestone. White spots represent pore spaces filled by polishing powder. Sample at the top and at the bottom is overgrown by sphalerite bands. These bands grade from massive without visible oolite relics through massive with oolite ghosts to a semimassive ore formed by replacement of oolites in the inner part of the specimen. Schmalgraf.
3. Banded sphalerite (white to black) and marcasite (M) overgrowing sphalerite formed by replacement of the host carbonates (central part). This replacive sphalerite contains numerous voids and empty spaces. Schmalgraf, sample SCH 12 (P. Simons collection).
4. Photomicrograph of porous sphalerite (light grey) replacing carbonate bioclasts and allochems (mollusc or bivalve : B, crinoid ossicles : C, oolites : O). Sparry calcite (grey) is only little affected by replacement. Sample EMP 12/G, Schmalgraf, reflected light.
5. Photomicrograph of a massive sphalerite formed by replacement of oolites. Replacive sphalerite (light grey) contains numerous minute black voids and inclusions. Sphalerite formed as an infill of interparticle pores (I) is free of voids and inclusions. Sample EMP 12/C, Schmalgraf.
6. Photomicrograph of sample EMP 12/C (Pl. 1 : 5) shown under crossed nicols. Sphalerite replacing oolites is very fine-grained. Sphalerite filling porosity is darker and coarser crystalline.
7. Photomicrograph of massive sphalerite formed by replacement of oolites (R) and infill of interparticle porosity (I). Replacive sphalerite contains numerous black minute voids and inclusions, in contact with filling sphalerite. Sample EMP 12/B, Schmalgraf, reflected light.
8. Photomicrograph of sample EMP 12/B (Pl. 1 : 7) shown under crossed nicols. Two types of sphalerite are visible : brighter fine-grained replacing oolites, and darker coarsely crystalline filling interparticle porosity.



relics of calcite. Direct replacement of allochems follows probably microfabric of these carbonates. During recrystallization some Zn was introduced into the carbonate structure (table 1). This, together with microporosity and organic matter present in bioclasts, might facilitate the later process of direct replacement of carbonates by sphalerite. Sparry calcite in the studied samples shows only a minor amount of replacement by sphalerite probably because of lack of microporosity. Banded sphalerite with phantoms of oolites (Pl. 1: 2) may suggest that such a texture may develop not only in open cavities but also by infill and replacements of permeable carbonate grainstones.

Pb isotopic signature (Pasteels *et al.*, 1980; Cauet *et al.*, 1982) is compatible with a source of metals from the surrounding sedimentary rocks. The metals have been mobilized by a continuous, large scale ground water circulation (de Magnée, 1967). The circulating fluids were vented by the Variscan and transversal faults and partly discharged preferentially at the contacts of siliciclastics and carbonates, and at oolitic and bioclastic limestones. These lithologies were most susceptible for replacement by sphalerite and most prone for the contemporaneous dissolution by released  $\text{HCO}_3^-$  to produce cavities around faults. A large scale fluid circulation requires relatively high porosity-permeability values. Sphalerite introduced as filling cement in oolitic-bioclastic limestone may suggest that during the time of mineralization the host carbonates were still not entirely cemented and therefore permeable. This together with the newly created porosity by the above described mineralizing process may provide additional evidence supporting the genetic model advanced by de Magnée (1967) and Bartholomé & Gérard (1976). However, a further study of diagenetic features in these carbonates, away from the sulfide mineralization could help to refine an advanced genetic model.

## ACKNOWLEDGEMENTS

This study has been made possible by a grant from the research fund of the K.U. Leuven. We would like to express our gratitude to Dr. S. Wartel, the Museum of Natural Sciences - Brussels for the access to the Museum's samples; Prof. L. Delaey and Dr. O. Arkens, Metallurgy Department K.U. Leuven for the access to the electron probe, and to Mr. P. Simons, mineral collector (La Calamine) who kindly provided part of the studied samples. Technical assistance was provided by Mr. C. Moldenaers and Ms. A. Van Espen.

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## PLATE 2

9. Photomicrograph of sphalerite (light grey) replacing carbonate allochems, mainly oolites (O). One of the replaced oolites has in the centre a large black void after a detrital quartz grain lost during sample polishing. Two types of calcite are visible : micritic infill of shelter porosity (M) and sparry calcite in interparticle spaces (grey). Sample EMP 12/F, Schmalgraf, reflected light.
10. Scanning electron micrographs (SEM) of the area outlined on Fig. 9. Zn, S, Fe and Si scanning pictures of these elements. Some Zn in the carbonate matrix is not balanced by S. Silicon (arrowed) forms rims surrounding some calcite and sphalerite crystals. Fe is present as small pyrite dots and at the edges of ZnS crystals. M : micrite; S : sparry calcite; B : fragment of replaced shell; O : replaced oolite.

