

TRANSFORMATION SEQUENCES OF COPPER SULFIDES AT VIELSALM, STAVELOT MASSIF, BELGIUM

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ABSTRACT

Bornite, chalcopyrite, idaïte, covellite, yarrowite, spionkopite, anilite, digenite, djurleite, and chalcocite have been identified in quartz veins from the Vielsalm area, Stavelot Massif, Belgium. The identification of these copper sulfides is confirmed by electron-microprobe analyses. The association of primary sulfides indicates that the bornite-bearing quartz veins crystallized above 300–350°C, whereas the chalcocite-bearing quartz veins crystallized below 200°C. Relations among sulfides indicate the occurrence of two sequences of transformation, responsible of the formation of secondary sulfides: chalcocite-*H* ⇒ chalcocite-*M* ⇒ djurleite ⇒ low digenite or (anilite + djurleite) ⇒ yarrowite + spionkopite ⇒ covellite + oxidation minerals, and bornite ⇒ idaïte + chalcopyrite ⇒ covellite + oxidation minerals. The crystallization of chalcocite-*M*, djurleite, and low digenite or (anilite + djurleite) took place between 103.5 and 72°C. The associations idaïte + chalcopyrite, yarrowite + spionkopite, and covellite + oxidation minerals, were produced under meteoric conditions. The source of Cu and of the other elements present in the quartz veins must be sought in the host chloritoid-bearing schists.

Keywords: copper sulfides, transformation sequences, Vielsalm, Stavelot Massif, Belgium.

SOMMAIRE

L'observation des sections polies, réalisées dans les sulfures de cuivre provenant de veines de quartz de la région de Vielsalm, Massif de Stavelot, Belgique, a permis de reconnaître la bornite, la chalcopyrite, l'idaïte, la covellite, la yarrowite, la spionkopite, l'anilite, la digénite, la djurléite et la chalcocite. L'identification de ces minéraux est confirmée par des analyses chimiques à la microsonde électronique. Les paragenèses des sulfures primaires indiquent que les veines de quartz minéralisées en bornite se sont mises en place à des températures supérieures à 300–350°C, alors que les veines de quartz minéralisées en chalcocite se sont formées en-dessous de 200°C. Les relations pétrographiques parmi les sulfures de cuivre ont permis de mettre en évidence deux séquences de transformation, qui sont responsables de la formation des sulfures secondaires: chalcocite-*H* ⇒ chalcocite-*M* ⇒ djurleite ⇒ digénite ou (anilite + djurleite) ⇒ yarrowite + spionkopite ⇒ covellite + minéraux d'oxydation, et bornite ⇒ idaïte + chalcopyrite ⇒ covellite + minéraux d'oxydation. La cristallisation de la chalcocite-*M*, de la djurleite, et de la digénite ou (anilite + djurleite), s'est produite entre 103.5 et 72°C. Les associations idaïte + chalcopyrite, yarrowite + spionkopite, et covellite + minéraux d'oxydation, se sont formées en conditions météoriques. L'origine du cuivre, mais aussi des autres éléments chimiques exotiques observés dans les veines de quartz, serait à chercher dans les phyllades à chloritoïde encaissants.

Mots-clés: sulfures de cuivre, séquences de transformation, Vielsalm, Massif de Stavelot, Belgique.

INTRODUCTION

An association of many sulfides of copper is developed along the southern border of the Stavelot Massif, Belgium, in quartz veins cross-cutting chloritoid-bearing schists of Ordovician age. These sulfides have long been known to occur here (Hatert *et al.* 2002), but there are few mineralogical descriptions. Dumont (1847–1848) mentioned the presence of chalcocite and bornite at Vielsalm, whereas de Koninck (1871) reported the chemical composition of bornite from this locality and described the relations between bornite and covellite.

In Salmchâteau, Buttgenbach (1921) observed chalcocite in the schists, and du Ry *et al.* (1976) identified digenite and djurleite in a quartz vein.

The present paper, part of a mineralogical study of sulfides from several localities in the Stavelot Massif (Hatert 1996, 2003), focuses on the copper sulfides occurring at Salmchâteau and Vielsalm (Fig. 1), which show unusual textural relations. The aim of this paper is to provide an inventory of the sulfides and associated minerals from this area, to report results of new electron-microprobe analyses of the copper sulfides, and to describe their textural relations. These mineralogical

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descriptions also provide new data on the transformation sequences of copper sulfides, when they are submitted to supergene oxidizing conditions.

ANALYTICAL METHODS

Chemical analyses were performed with a CAMECA SX50 electron microprobe operating in wavelength-dispersion mode, at the Louvain-la-Neuve University (Belgium). Measurement conditions were 20 kV acceleration voltage, 20 nA beam current, 16–20 s counting time per element. Pyrite (Fe, S) and pure metallic Cu were used as standards. Matrix corrections were performed with the PAP method (Pouchou & Pichoir 1984a, b). The elements occurring in very low amounts, below the detection limits of the instrument, were not considered in the chemical analyses. Arsenic, Au, Bi, Cd, Co, Ge, Ni, Pb, Sn, and Te were also sought, but not detected in significant amounts.

Powder X-ray-diffraction patterns were recorded with a Philips PW-3710 diffractometer using $\text{FeK}\alpha$ radiation ($\lambda = 1.9373 \text{ \AA}$).

GEOLOGICAL SETTING

The Venn–Stavelot Massif, Belgian Ardennes, represents a large accumulation of Cambro-Ordovician

metasedimentary units belonging to the Rhenohercynian of the Variscan orogenic belt. Located in the southeastern portion of the massif, the Salm syncline shows, between Vielsalm and Salmchâteau, a geological section containing schists of the Salm Group, of Lower Ordovician age (Verniers *et al.* 2001). This area was first affected by an episode of very low-grade metamorphism during the Caledonian orogeny. Fluid-inclusion measurements made on quartz veins of Caledonian age by Ferket *et al.* (1998) indicate P–T conditions of 0.8–3 kbar and 280–380°C. The episode of low-grade metamorphism, which occurred during the Hercynian orogeny, is responsible for the crystallization of the metamorphic minerals observed in the quartz veins and in the schists (Schreyer 1975). The presence of andalusite, chloritoid and spessartine, as well as a white

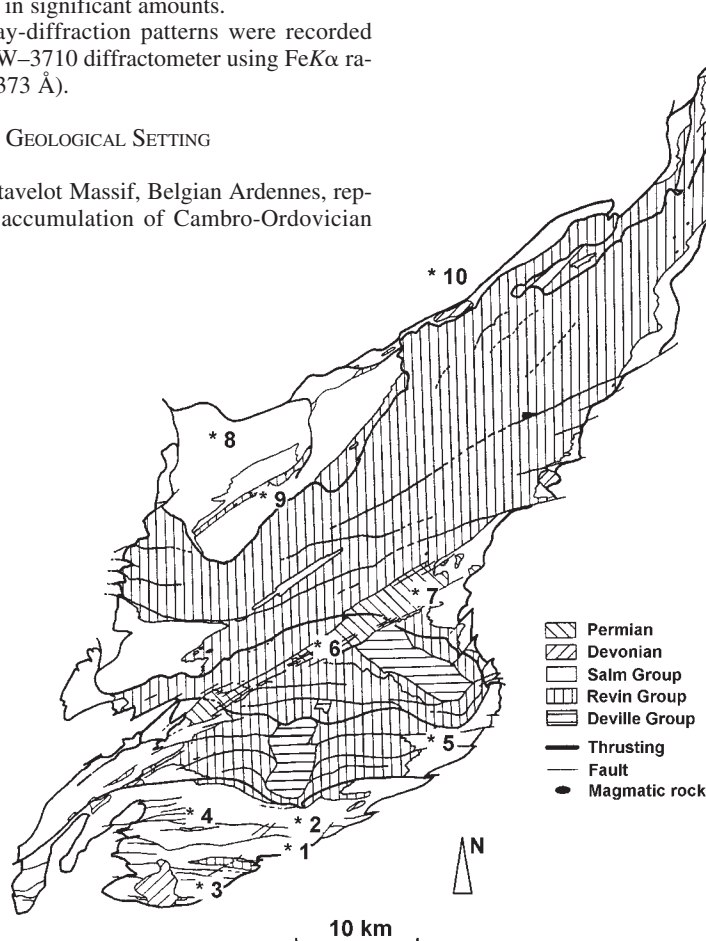


FIG. 1. Geological map of the Stavelot Massif, Belgium (after Geukens 1999). 1: Salmchâteau, 2: Vielsalm, 3: Bihain, 4: Lierneux, 5: Recht, 6: Stavelot, 7: Malmédy, 8: Theux, 9: Spa, 10: Eupen.

K-dominant mica, lead to an estimate of P–T conditions of 2 kbar, 360–420°C (Kramm 1982, Kramm *et al.* 1985). Similar P–T conditions, 1.75–2.8 kbar, 300–415°C, were obtained by Ferket *et al.* (1998) from fluid-inclusion measurements on Hercynian quartz veins.

The quartz veins formed at the end of the Hercynian episode of metamorphism. The circulation of fluids along fractures, coupled with metasomatic processes, resulted in the mobilization of numerous elements, such as Cu, Mn, Te, and Mo, in the quartz veins (Michot 1954–1955, de Béthune & Fransolet 1986, Hatert 1996). This setting explains the diversity of minerals discovered in this area (Hatert *et al.* 2002): copper sulfides, which constitute the main topic of the present paper, Mn-bearing aluminosilicates, such as davreuxite and otrérite (Fransolet & Bourguignon 1976, Fransolet 1978, Hanson 1983, Fransolet *et al.* 1984, Theye & Fransolet 1994), and manganese oxides, such as lithiophorite, cryptomelane, nsutite, and hollandite–strontiomelane (Fransolet 1979, Schreyer *et al.* 2001, Gustine 2002). As shown in Figure 2, the quartz veins investigated in the present study cross-cut the green to violet chloritoid-bearing schists of the Colanhan Member (Middle Salm Group, Sm 2c).

The rocks of the Les Plattes Member (Middle Salm Group, Sm 2b, see Fig. 2) are well known for the occurrence of coticule, which has been used for many years as whetstone. This rock, which occurs as creamy layers

parallel to the stratification of the host red schists, consists of spessartine crystals reaching 20 µm, included in a matrix of phyllosilicates and quartz (Lessuisse 1981). Another rock similar to coticule occurs in the Colanhan Member (Middle Salm Group, Sm 2c, see Fig. 2), but the spessartine grains are much larger, reaching 100 µm, and are included in a matrix consisting essentially of quartz (Bossiroy 1984). This rock is here called *pseudocoticule*, because it cannot be used as whetstone despite its mineralogy similar to that of coticule (Theunissen 1971, Bossiroy 1984).

The copper sulfides occur in several quartz veins in the region of Vielsalm and Salmchâteau, in pseudocoticules, as coatings on schists, and as disseminations in schists. The nomenclature of the copper sulfides is given in Table 1, and the sample locations are shown on Figure 2.

DESCRIPTION OF THE COPPER SULFIDE OCCURRENCES

Quartz veins

The quartz veins, which cross-cut the green to violet chloritoid-bearing schists of the Colanhan Member (Fig. 2), have a thickness of 1 to 30 cm, and contain quartz with accessory chlorite, hematite, rutile, and sulfides. The copper sulfides are the most abundant among the sulfides, but small inclusions of galena, wittichenite, and

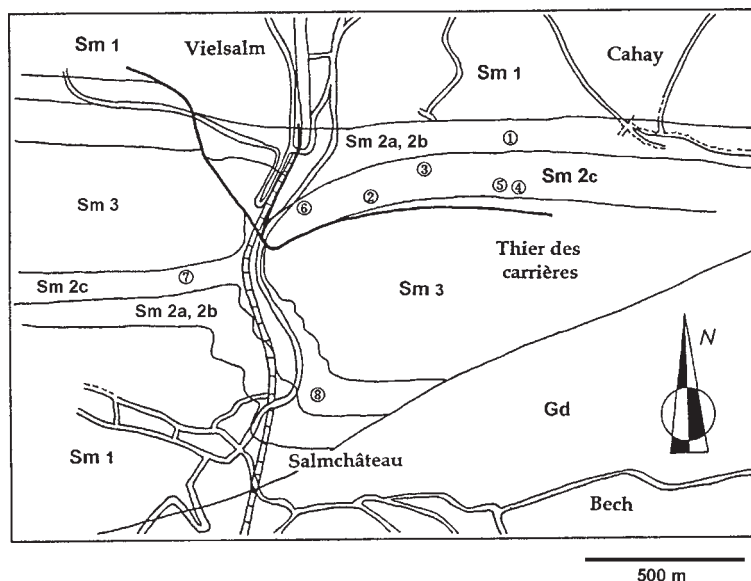


FIG. 2. Location of the copper sulfide mineralization in the Vielsalm–Salmchâteau area. Sm 1: Jalhay Formation, Sm 2a: Meuville Member, Sm 2b: Les Plattes Member, Sm 2c: Colanhan Member, Sm 3: Bihain Formation. The numbers correspond to those given in Table 1. Geological map after Fourmarier (1944), stratigraphy after Geukens (1999) and Verniers *et al.* (2001).

tellurides also have been observed. Under oxidizing supergene conditions, secondary copper-bearing oxides, carbonates, sulfates, phosphates, and arsenates crystallized. The associations of sulfide minerals and minerals diagnostic of oxidation, which occur in the quartz veins and associated occurrences in the area of Vielsalm and Salmchâteau, are shown in Tables 2 and 3, respectively.

On the basis of their mineralogical content and of their degree of deformation, two different types of quartz veins can be distinguished. The first type contains bornite as dominant copper sulfide, in some cases associated with chalcopyrite (BOR1, BOR2 and TCVB; Tables 1, 2). These veins, which can reach a width of 30 cm, show signs of very important deformation, for example the presence of boudinage (BOR1), or a lenticular shape (BOR2). The strong deformation is also responsible for the brecciated aspect of these quartz veins, which contain broken and corroded quartz crystals cemented by a bornite matrix.

The second type of quartz veins contain chalcocite as the dominant copper sulfide (FRDR, FRGA, MSFRa,

TCVF, TCVC and SALM; Tables 1, 2), and are thinner than the bornite-bearing quartz veins (1 to 10 cm). They are affected by a weak deformation, as indicated by their rectilinear nature; they are parallel to the schistosity. It is important to note that the quartz vein from Salmchâteau (SALM) does not fit this classification, as it is mineralized in chalcocite and shows signs of very strong deformation.

Pseudocoticles

The pseudocoticles containing copper sulfides (MSFRb and OLRC; Table 1) have a thickness of 3 to 5 cm, and are parallel to the stratification. Their thickness is rather constant, but they are folded and can be used as an indicator of deformation. Because quartz veins are parallel to the schistosity and pseudocoticles are parallel to the stratification, quartz veins in some cases cross-cut the pseudocoticle layers (MSFR).

The pseudocoticles contain chalcocite as dominant copper sulfide (Table 2). This mineral occurs in the

TABLE 1. NOMENCLATURE AND LOCATION OF THE COPPER SULFIDE OCCURRENCES IN THE VIELSALM-SALMCHÂTEAU AREA, BELGIUM

Code	Location	Description
VIEL (1)	Dumps of the quarry "Thier des Carrières"	Disseminations in schists
FRDR (2)	Quartz veins located on the right side of the entrance to the "Fosse-Roulette" quarry	Two linear undeformed quartz veins, 1 to 5 cm in thickness, separated by 10 to 20 cm of schist
FRGA (2)	Quartz vein localized on the left side of the entrance of the "Fosse-Roulette" quarry	Quartz vein 8 to 15 cm in thickness, weakly deformed
FRPH (2)	Schist located between the two quartz veins "FRDR" in the "Fosse-Roulette" quarry	Disseminations in chloritoid- and spessartine-bearing schist
MSFRa (3)	Quartz vein, old mine under the "Fosse-Roulette" quarry	Quartz vein 5 to 10 cm in thickness, weakly deformed
MSFRb (3)	Pseudo-coticle, old mine under the "Fosse-Roulette" quarry	Pseudocoticle 3 to 5 cm in thickness, strongly deformed and parallel to the stratification. This pseudocoticle cross-cuts the MSFRa quartz vein
BOR1 (4)	First bornite-bearing quartz vein occurring in the quarry "Thier des Carrières"	Quartz vein 10 to 20 cm in thickness, affected by a strong deformation. Boudinage observed, as well as a brecciated aspect
BOR2 (5)	Second bornite-bearing quartz vein occurring in the quarry "Thier des Carrières"	Quartz vein of 5 to 30 cm in thickness, affected by a strong deformation. Lenticular and brecciated aspect
TCVF (6)	Thin quartz vein occurring in the old "TCVN6" mine	Linear non-deformed quartz vein, 1 to 2 cm in thickness
TCVC (6)	Chalcocite-bearing quartz vein occurring in the old "TCVN6" mine	Linear non-deformed quartz vein, 2 to 5 cm in thickness
TCVB (6)	Bornite-bearing quartz vein occurring in the old "TCVN6" mine	Quartz vein ~10 cm in thickness, affected by a strong deformation; brecciated aspect
OLRP (7)	Pyrite-bearing coatings occurring in the "Old Rock" mine	Coatings on the schists
OLRC (7)	Pseudocoticle occurring in the "Old Rock" mine	Pseudocoticle 3 to 5 cm in thickness, strongly deformed and parallel to the stratification
SALM (8)	Quartz vein localized above the Salmchâteau cemetery	Quartz vein of 5 to 10 cm in thickness, affected by a strong deformation

The numbers in parentheses correspond to the numbers of Figure 2. *: The "TCVN6" mine is described by Caubergs (1991).

TABLE 2. SULFIDE MINERALS OCCURRING IN THE VIELSALM-SALMCHÂTEAU AREA

Type of occurrence	code	Bn	Cp	Ida	Cv	Yar + Spi	Dg + Ani	Cc + Dju	Alt	Apy	Cbt	Gn	Mln	Mlb	Py	Sp	Tb	Te	Wtc
Pseudocoticule	MSFR	-	-	-	-	xx	xx	xxxx	-	-	-	-	-	-	-	-	-	-	-
Dissemination	VIEL	xxxx	xxx	xx	-	-	x	xxxx	-	xxxx	-	x	-	x	-	x	-	-	-
Dissemination	FRPH	xxx	xxx	xx	xx	xxx	xxx	xxxx	-	-	-	-	-	xx	-	-	-	x	-
Coating	OLRP	xxx	xx	-	-	xx	xxxx	-	-	-	-	-	-	-	xxxx	-	-	-	-
Cc-bearing vein	FRDR	xxx	xx	-	xxx	xxx	xxxx	xxx	-	-	-	-	-	x	-	-	xx	xx	-
Cc-bearing vein	FRGA	xx	xx	-	xxx	xx	xxxx	xxxx	-	-	-	-	-	-	-	-	-	xx	-
Cc-bearing vein	MSFRa	x	-	-	xxx	x	xxxx	xxxx	-	-	-	-	-	-	-	-	-	x	-
Cc-bearing vein	TCVF	xxx	xx	x	xxx	xx	xxxx	xxxx	-	-	-	-	-	-	-	-	-	xx	-
Cc-bearing vein	TCVC	xxx	xx	-	-	-	xx	xxxx	-	-	-	-	-	-	-	-	-	xx	-
Cc-bearing vein	SALM	x	x	-	xxx	xxx	xxxx	xx	-	-	-	-	-	-	-	-	-	-	-
Bn-bearing vein	BOR1	xxxx	xx	xx	xxx	xxx	xxx	-	-	-	-	xx	-	-	-	-	-	-	-
Bn-bearing vein	BOR2	xxxx	xx	x	xxx	xxx	xxx	-	xx	-	x	x	-	x	-	-	-	-	xx
Bn-bearing vein	TCVB	xxxx	xxx	-	-	-	xxx	xx	-	-	-	-	xx	-	-	-	-	-	-

Symbols: Bn: bornite, Cpy: chalcopyrite, Ida: idaite, Cv: covellite, Yar + Spi: yarrowite + spionkopite, Dg + Ani: digenite + anilite, Cc + Dju: chalcocite + djurleite, Alt: altaite, Apy: arsenopyrite, Cbt: cobaltite, Gn: galena, Mln: melonite, Mlb: molybdenite, Py: pyrite, Sp: sphalerite, Tb: tellurobismuthite, Te: tellurium, Wtc: wittichenite. xxx: dominant mineral, xx: abundant mineral, x: not so abundant mineral, -: rare mineral. Data from Hatert (1996) and Hatert *et al.* (2002).

TABLE 3. SECONDARY MINERALS ASSOCIATED WITH THE COPPER SULFIDES FROM THE VIELSALM-SALMCHÂTEAU AREA

Type of occurrence	code	Azu	Bro	Ccm	Chp	Cnl	Cup	Del	Gt	Lgt	Lib	Mal	Mim	Par	Pha	Psm	Tei	Tor	Wul
Pseudocoticule	OLRC	-	xxx	-	-	x	x	-	xx	xxx	-	xxx	-	-	-	-	-	x	-
Dissemination	VIEL	-	xxx	-	-	x	xx	-	xx	xxx	-	xxx	x	-	x	-	-	-	-
Coating	OLRP	-	xxx	-	-	-	-	-	-	xxx	-	xx	-	-	-	x	-	-	-
Cc-bearing vein	FRDR	-	xx	-	-	-	x	-	-	x	xx	xx	-	-	-	xxx	-	-	-
Cc-bearing vein	MSFRa	-	xxx	-	-	x	-	-	x	xxx	-	xx	-	-	-	xx	-	-	-
Cc-bearing vein	TCVF	-	xxx	-	-	x	-	-	-	xxx	-	xx	-	-	-	-	-	-	-
Cc-bearing vein	TCVC	-	xxx	-	-	-	-	x	-	xxx	-	xxx	-	-	-	-	-	-	-
Cc-bearing vein	SALM	x	xx	x	-	-	x	x	-	xx	xx	xxx	-	x	-	xx	x	-	-
Bn-bearing vein	BOR1	-	xxx	-	x	x	-	-	-	xx	xx	xxx	-	-	-	x	-	-	-
Bn-bearing vein	BOR2	-	xx	-	-	-	-	-	-	-	xx	xxx	-	-	-	xx	-	-	x
Bn-bearing vein	TCVB	-	xxx	-	-	-	x	-	xx	xxx	-	xxx	-	-	-	-	-	-	-

Symbols: Azu: azurite, Bn: bornite, Bro: brochantite, Ccm: chalcoalumite, Cc: chalcocite, Chp: chalcophyllite, Cnl: connellite, Cup: cuprite, Del: delafossite, Gt: goethite, Lgt: langite, Lib: libethenite, Mal: malachite, Mim: mimetite, Par: paratellurite, Pha: pharmacosiderite, Psm: pseudomalachite, Tei: teineite, Tor: torbernite, Wul: wulfenite. xxx: abundant mineral, xx: not so abundant mineral, x: rare mineral. Data from Hatert (1996) and Hatert *et al.* (2002).

quartz matrix, between the grains of spessartine, thus indicating that the crystallization of copper sulfides in this type of rocks took place after the peak of Hercynian metamorphism. The supergene oxidation of copper sulfides also led to the crystallization of secondary minerals, mainly brochantite, langite, and malachite (Table 3).

Disseminations

Copper sulfides are disseminated in schist of the Colanhan Member; they are found in the dumps of the old "Thier des Carrières" quarry (VIEL), and between the two thin quartz veins of the old "Fosse-Roulette"

TABLE 4. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF COPPER SULFIDES FROM THE VIELSALM-SALMCHÂTEAU AREA

<i>n</i>	Bornite 18	Chalcopyrite 5	Idaite (*) 3	Covellite 10	Yarrowite 13	Spionkopite 15	Anilite 21	Digenite 4	Djurleite 19	Chalcocite 8
Cu wt. %	62.66(41)	34.38(21)	52.81(08)	66.82(68)	68.50(29)	73.24(143)	76.88(79)	77.96(37)	78.69(72)	79.60(77)
Fe	11.02(16)	29.58(27)	13.80(24)	0.11(22)	0.28(17)	0.05(05)	0.04(06)	0.03(00)	0.08(13)	0.01(01)
S	25.57(18)	34.79(08)	32.79(29)	33.05(45)	30.87(22)	26.10(108)	22.26(19)	21.97(27)	20.76(21)	20.05(22)
Total	99.25	98.75	99.40	99.98	99.65	99.39	99.18	99.96	99.53	99.66
Cu <i>apfu</i>	4.95(3)	1.00(1)	3.25(1)	1.02(1)	8.96(4)	39.64(77)	6.97(7)	8.95(4)	30.61(28)	2.00(2)
Fe	0.99(1)	0.98(1)	0.97(2)	tr.	0.04(3)	0.03(3)	tr.	tr.	0.03(6)	tr.
S	4.00(3)	2.00(1)	4.00(4)	1.00(1)	8.00(6)	28.00(116)	4.00(3)	5.00(6)	16.00(16)	1.00(1)
Cu/S	-	-	-	1.02(2)	1.12(1)	1.42(9)	1.74(3)	1.79(3)	1.91(4)	2.00(4)

Analyst: J. Wautier. The number of point analyses *n* is indicated; standard deviations are shown in parentheses. Cation numbers were calculated on the basis of 4 (bornite, idaite, anilite), 2 (chalcopyrite), 1 (covellite, chalcocite), 8 (yarrowite), 28 (spionkopite), 5 (digenite), and 16 (djurleite) sulfur atoms per formula unit (*apfu*). (*): Sample M402-a (Hatert 2003).

quarry (FRPH; Table 1). Arsenopyrite crystals, described in detail by Hatert (1997), are associated with the copper sulfides from the "Thier des Carrières". Chalcocite, which is the dominant copper sulfide occurring in the schists from "Fosse-Roulette", has crystallized in the matrix, between the crystals of spessartine and chloritoid. This indicates again that the copper sulfides have crystallized after the peak of metamorphism.

Coatings

In the "Old Rock" mine, a coating mineralized in copper sulfides and pyrite covers the schists of the Colanhan Member (Table 1). The copper sulfides are very altered in these coatings, and chalcocite is completely replaced by digenite-anilite (Table 2). Moreover, the oxidation minerals brochantite, langite, and malachite are very abundant in these samples (Table 3).

MINERALOGICAL DESCRIPTIONS OF THE COPPER SULFIDES

Bornite, Cu_5FeS_4

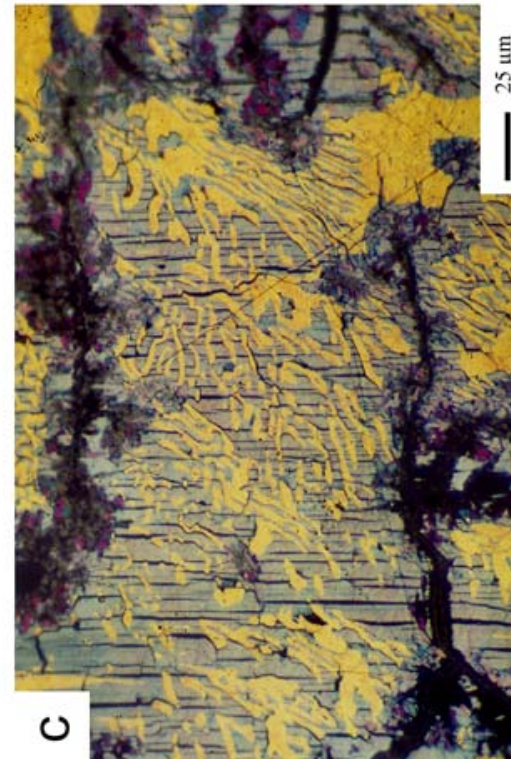
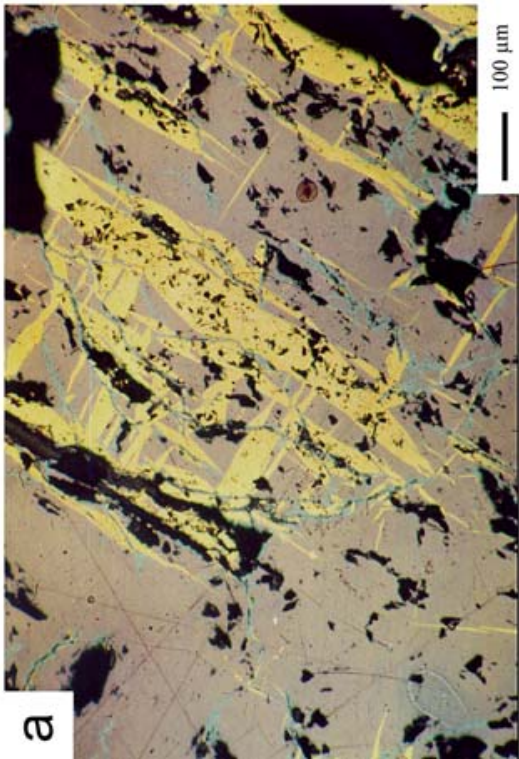
Found in quartz veins, in disseminations, and in coatings (Table 2), bornite is isotropic in reflected light and exhibits pinkish colors. This mineral contains lamellae of chalcopyrite (TCVB, Fig. 3a) or forms a symplectitic intergrowth with chalcocite + djurleite or with yarrowite + spionkopite (VIEL, BOR2, Figs. 3b, c). Some samples of bornite contain inclusions of galena, wittichenite, cobaltite, and tellurides (Hatert 1996; see Table 2), which are still under study. The composition of bornite from Vielsalm is shown in Table 4.

In the more altered parts of the BOR1 quartz vein, another type of bornite has been observed, which exhibits an orange color and a weak yellowish to greenish anisotropy (Figs. 3c, 4a). The optical properties of this mineral correspond to those of "anomalous bornite" described by Sillitoe & Clark (1969) from Copiapó, Chile, whereas the electron-microprobe analyses of Hatert (2003) show a composition poor in Cu, between those of bornite and idaite.

Chalcopyrite, $CuFeS_2$

Chalcopyrite forms yellow lamellae with a weak anisotropy, included in bornite or in idaite. Lamellae are generally less than 5 μm wide (BOR1, Fig. 3d), but in some cases, they reach 100 μm (TCVB, Fig. 3a). Their

FIG. 3. a. Chalcopyrite lamellae (yellow) included along the {100} directions of bornite (pink). Fractures filled with digenite + anilite (blue) cross-cut both minerals. Reflected light microscopy, plane-polarized light (sample TCVB-001). b. Symplectitic intergrowth of bornite (pink) and chalcocite + djurleite (bluish). Reflected light microscopy, plane-polarized light (sample VIEL-001). c. Symplectitic intergrowth of "anomalous bornite" (orange) and lamellae of spionkopite + yarrowite (blue). Grains of covellite (purple) occur on the border of fractures cross-cutting the symplectitic structure. Reflected light microscopy, plane-polarized light, oil immersion (sample BOR2-001). d. Idaite grain (orange to brownish) containing small lamellae of chalcopyrite (yellow) aligned along the {100} and {111} directions of parent bornite. Reflected light microscopy, plane-polarized light (sample BOR1-001).



orientations indicate that they have crystallized along the {100} and {111} directions of bornite.

Idaite, Cu₃FeS₄

Idaite occurs in the more altered parts of the BOR1 quartz vein, as millimeter-sized metallic grains with a bronze color. Under reflected light, this mineral exhibits a yellowish to brownish pleochroism, and a strong yellow to green anisotropy. Small lamellae of chalcopyrite are also included in idaite (BOR1, Fig. 3d).

Idaite from Vielsalm has recently been investigated in detail by Hatert (2003), who demonstrated that the crystal structure of this mineral is similar to that of stannite, Cu₂FeSnS₄. The powder-diffraction pattern of idaite has been indexed on a tetragonal unit-cell, with *a* 5.279(4), *c* 10.47(2) Å. The electron-microprobe data for idaite (Table 4) lead to the chemical formula Cu_{3.25}Fe_{0.97}S_{4.00}, which is significantly enriched in Cu, compared with the ideal composition of idaite, Cu₃FeS₄ (Lévy 1967, Sillitoe & Clark 1969, Constantinou 1975, Hatert 2003).

Covellite, CuS

Covellite crystallizes along the rim of the copper sulfide grains, or in the fractures cross-cutting these minerals (BOR1, BOR2, Figs. 3c, 4a, and 4b). The strong dark blue to light blue pleochroism, and the strong pinkish to orange anisotropy, are characteristic in reflected light. Nevertheless, the difference between covellite and yarrowite + spionkopite is only noticeable in oil immersion. In these conditions, covellite grains exhibit a pinkish to purple pleochroism (BOR2, Fig. 3c), whereas yarrowite + spionkopite lamellae show a blue to pinkish pleochroism. The electron-microprobe data for covellite (Table 4) reveal a chemical composition very close to the ideal composition CuS, thus confirming the identity of the mineral.

Yarrowite, Cu₉S₈, and spionkopite, Cu₃₉S₂₈

Yarrowite and spionkopite were described by Goble (1980) in the area of Yarrow Creek and Spionkop Creek, Alberta, Canada. These minerals were previously observed by Frenzel (1959), who named them "blaubleibender Covellin" because their optical properties are similar to those of covellite. In the area of Vielsalm, yarrowite and spionkopite occur as lamellae intergrown with digenite + anilite (MSFRb, Fig. 4c), or forming a symplectitic intergrowth with bornite (BOR2, Fig. 3c). In oil immersion, the blue to pinkish pleochroism allows one to distinguish these minerals from covellite. Electron-microprobe data (Table 4) indicate Cu/S ratios of 1.12 and 1.42 for yarrowite and spionkopite, respectively, which are close to the ideal values of 1.13 and 1.39. The powder-diffraction pattern, measured on the lamellar copper sulfides associated with bornite from

Vielsalm, confirms the identification of covellite, yarrowite, and spionkopite.

Digenite, Cu₉S₅, and anilite, Cu₇S₄

Digenite, an isotropic phase with bluish colors, is well known to occur in the quartz veins from Vielsalm (Table 2). This mineral occurs in lamellae associated with yarrowite + spionkopite (MSFRb, Fig. 4c) or forms small veinlets cross-cutting bornite and chalcopyrite (TCVB, BOR1, Figs. 3a, 4d). Electron-microprobe analyses (Table 4) show that some samples have a Cu:S ratio of 1.79, close to the ideal value of 1.80. Nevertheless, other grains show a Cu:S ratio of 1.74, which better corresponds to the Cu:S ratio of anilite, ideally 1.75. Because the Cu:S ratio of digenite cannot be lower than 1.77 at low temperature (Roseboom 1966), the mineral that shows a Cu:S ratio of 1.74 probably corresponds to anilite. However, this identification is subject to caution because anilite transforms to a phase similar to digenite during the polishing process (Morimoto *et al.* 1969).

Chalcocite, Cu₂S, and djurleite, Cu₃₁S₁₆

Chalcocite and djurleite, which exhibit similar optical properties, occur in large grains of white color, forming a symplectitic intergrowth with bornite (VIEL, Fig. 3b). Electron-microprobe data (Table 4) show the existence of two minerals, with Cu/S values of 1.91 and 2.00, values that are very close to the ideal Cu/S values of djurleite (1.94) and chalcocite, (2.00). The powder-diffraction pattern of these sulfides is generally in good agreement with that of chalcocite-*M*, but the presence of djurleite was confirmed by this technique in samples from the TCVC quartz vein.

DISCUSSION

Interpretation of the textural relations

The textural relations among the copper sulfides from the Vielsalm area lead to a better understanding of the genesis of these minerals. The large lamellae of chalcopyrite, which occur along the {100} direction of bornite (TCVB, Fig. 3a), can be understood as an exsolution texture, and the symplectitic intergrowths of bornite and chalcocite (VIEL, Fig. 3b) indicate that these two minerals have crystallized together. For this reason, bornite, chalcopyrite and chalcocite are considered the primary sulfides.

The quartz veins occurring in the old mines (MSFRa, TCVF, TCVC, TCVB) are less affected by meteoric oxidation than the veins occurring in the quarries (VIEL, FRDR, FRGA, BOR1, BOR2, SALM). Observations on the sulfides from the old mines show that under these conditions, bornite and chalcopyrite are both stable, whereas chalcocite + djurleite transform progressively

to digenite + anilite, then to yarrowite + spionkopite, indicating a progressive leaching of copper. Evidence of this transformation is shown in Figure 4c, where digenite + anilite is replaced by blue lamellae of yarrowite + spionkopite. The lamellar texture of yarrowite + spionkopite, compared with the massive texture of digenite + anilite (Fig. 4c), indicates a volume decrease upon transformation. As a result of this decrease, the textures shown in Figure 3c appear: "anomalous bornite" forms a symplectitic intergrowth with lamellae of yarrowite + spionkopite. This texture was originally a symplectitic intergrowth of bornite with chalcocite + djurleite, in which the latter pair transformed progressively to digenite + anilite, and then to yarrowite + spionkopite, whereas bornite transformed to "anomalous bornite". The transformation into yarrowite + spionkopite is accompanied by a contraction, which leads to the formation of lamellae separated by quartz infillings.

In the quartz veins occurring in the quarries (BOR1, BOR2), which are more exposed to meteoric alteration, the evolution of the copper sulfides is different. The first stage of transformation of copper sulfides is the formation of digenite + anilite veins cross-cutting bornite (Fig. 4d). The fractures associated with the latter veins permitted the circulation of fluids, which promoted the crystallization of oxidized minerals, such as goethite, an amorphous Cu-Fe-bearing oxide, and malachite or brochantite (Fig. 4a). Small grains of covellite, produced by the alteration of digenite + anilite, appear along the border of these veins (Figs. 4a, b). Bornite, which is located between the fractures filled with oxidation-induced minerals, also is affected. As shown in Figure 4a, some grains of bornite exhibit an orange color, thus indicating a progressive transformation to "anomalous bornite", and then to idaite. This transformation is accompanied by the growth of small lamellae of chalcopyrite, which are aligned along the {100} and {111} directions of the parent bornite (Fig. 3d; Hatert 2003). Finally, the intense oxidation leads to an important enlargement of the network of fractures, thus isolating relics of bornite and idaite included in oxidation-induced minerals (Fig. 4b). Small residual grains of covellite also occur in the oxidation minerals (Fig. 4b).

Crystallization temperatures of the copper sulfides

A relation between the intensity of deformation of the quartz veins and the minerals that crystallize in these veins has been observed in the Vielsalm area. Quartz veins containing bornite are affected by an important deformation, characterized by boudinage and by a brecciated aspect, whereas the veins mineralized in chalcocite + djurleite and digenite + anilite are linear and do not seem to be affected by deformation (Table 1). According to Kramm (1982), the peak of Hercynian metamorphism occurred just before the beginning of deformation, thus indicating that the quartz veins con-

taining bornite should be of higher temperature than those containing chalcocite + djurleite and digenite + anilite.

This deduction is confirmed by the temperatures estimated from the associations of copper sulfides. In the TCVB quartz vein, bornite is associated with 10 to 15% of exsolution-induced lamellae of chalcopyrite (Fig. 3a). The experimental investigations of the Cu-Fe-S system by Yund & Kullerud (1966) and Sugaki *et al.* (1975) have shown that this composition of bornite corresponds to a single homogeneous phase above 300–350°C; it begins to exsolve chalcopyrite below this temperature. As a consequence, we can consider that the bornite-bearing quartz veins from the Vielsalm area have crystallized above 300–350°C (Fig. 5).

The chalcocite-bearing quartz veins contain 0 to 20% of bornite, which forms a symplectitic intergrowth with chalcocite or with products of its transformation (Fig. 3b). The experimental investigations show that this composition of chalcocite corresponds to a single homogeneous phase above *ca.* 200°C; it begins to exsolve bornite below this temperature (Yund & Kullerud 1966, Sugaki *et al.* 1975). Because the symplectitic intergrowths indicate that bornite and chalcopyrite have crystallized together, and because no exsolution textures have been observed, we can consider that the chalcocite-bearing quartz veins have crystallized below *ca.* 200°C (Fig. 5).

Under these hypogene conditions, the stable sulfide crystallizing with bornite was hexagonal chalcocite, which transformed at 103.5°C to the monoclinic phase, low chalcocite (Fig. 5; Potter 1977). The leaching of copper out of the sulfides then led to the crystallization of djurleite, digenite, spionkopite + yarrowite, and covellite, respectively (Fig. 5). Djurleite is stable below 93°C, whereas low digenite and spionkopite + yarrowite are metastable phases (Potter 1977). Morimoto & Koto

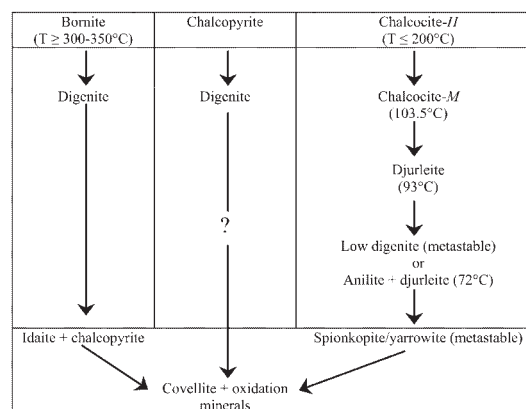
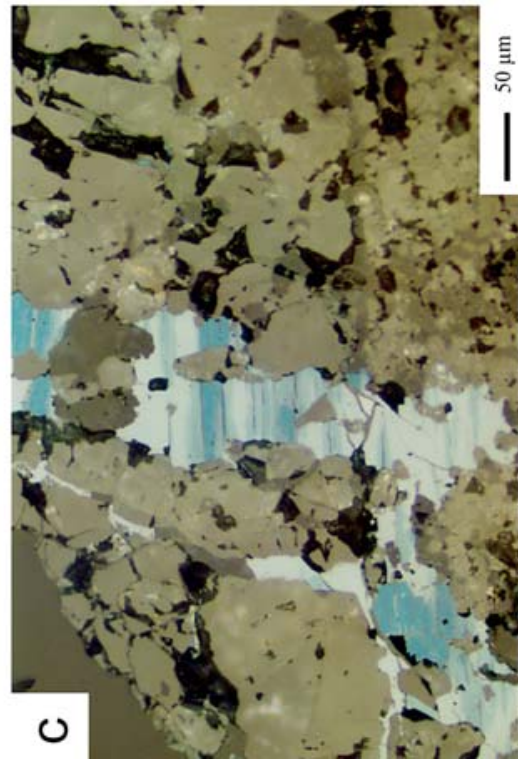
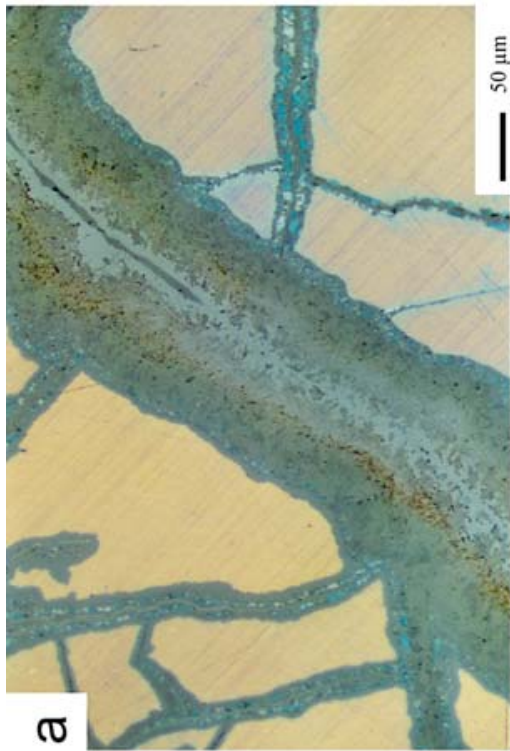
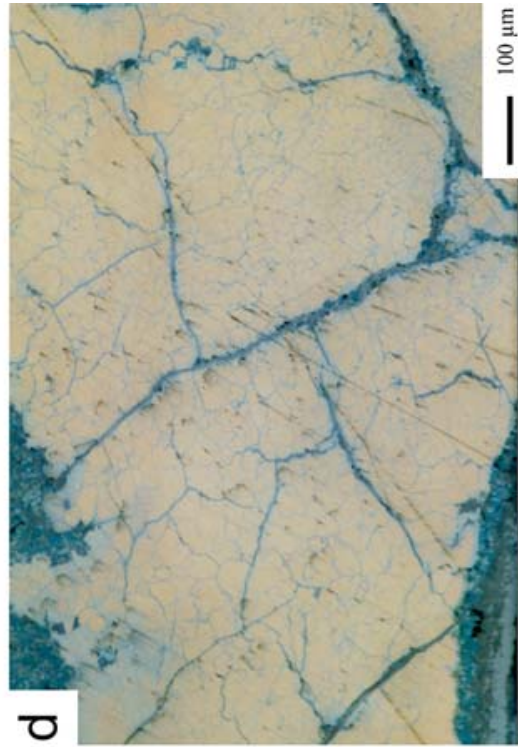
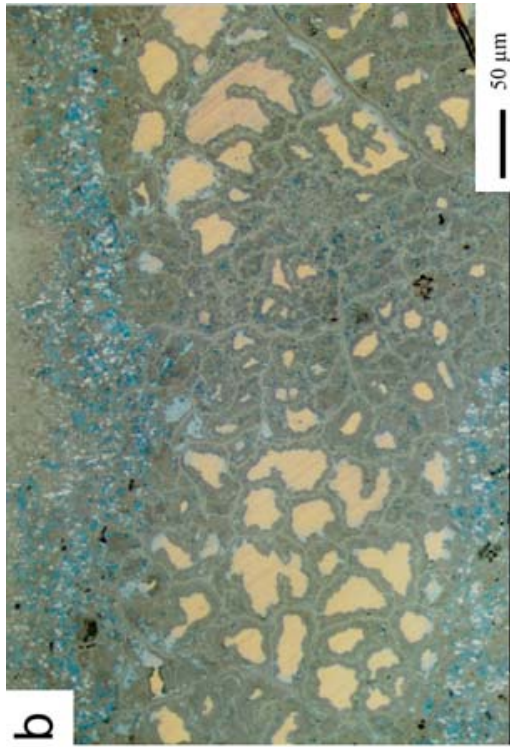


Fig. 5. Sequences of transformation in the copper sulfides from the Vielsalm-Salmchâteau area.



(1970) have shown that low digenite can be stable below 70°C where it contains approximately 1% Fe, a composition very different from that of digenite from the Vielsalm area, which only contains 0.03% Fe (Table 4). The phase diagram for the system Cu–S (Potter 1977) also shows that the composition of digenite lies within a domain occurring below 72°C, in which anilite and djurleite coexist. The blue mineral, identified as digenite and showing a very variable composition (Table 4), may therefore consist of submicroscopic intergrowths of anilite and djurleite. As shown in Table 2, spionkopite + yarrowite are very abundant in the quartz veins more affected by oxidation, in which the association idaite + chalcopyrite also occurs. These minerals thus have crystallized simultaneously during the late meteoric oxidation, which took place at very low temperatures (Fig. 5). The occurrence of metastable spionkopite + yarrowite, in place of the stable assemblage covellite + anilite, is due to the difficulty of nucleating covellite, which has a hexagonal closest-packed structure (Potter 1977).

Finally, it is important to note that the temperature above 300–350°C obtained for the bornite-bearing quartz veins is in good agreement with the temperatures deduced from the mineralogical content of similar quartz veins found in the schists of the Otré Formation. For example, the occurrence of sudoite in the Otré quartz vein indicates a maximum temperature of 370–390°C (Fransolet & Schreyer 1984), whereas otrérite, which occurs at the contact between the quartz veins and the host rock, crystallized at a temperature lower than 350°C (Theye & Fransolet 1994). These temperatures are confirmed by fluid-inclusion studies and by geothermometric data inferred from the chemical compositions of chlorite-group minerals occurring in several quartz veins from the Stavelot Massif (Zhang *et al.* 1997).

Origin of the sulfides

As demonstrated by Michot (1954–1955) and de Béthune & Fransolet (1986), metasomatic processes are responsible for the formation of the quartz veins, as well as for the migration of chemical elements from the host rock to the quartz veins. The occurrence of unusual minerals, such as Mn-bearing aluminosilicates (Fransolet & Bourguignon 1976, Fransolet 1978, Fransolet *et al.* 1984), manganese oxides (Schreyer *et al.* 2001), and copper sulfides (Hatert 1996, 2003), probably results from the transport and the concentration of Mn, As, V, Ba, Sr, Cu, Mo, and Te in the quartz veins.

The elements observed in the quartz veins at Vielsalm are similar to those occurring in the quartz veins associated with the metatonalite of La Helle (Van Wambeke 1954, Weiss *et al.* 1980, Hatert 1996, Godfroid 1999). Nevertheless, the origin of the elements is different; the quartz veins of La Helle ultimately have a magmatic origin, whereas the quartz veins from Vielsalm have a metamorphic origin (Hatert 1996). Because the quartz veins cross-cut the green chloritoid-bearing schists of the Colanhan Member in the area of Vielsalm (Fig. 2), the origin of the exotic elements observed in the veins must be sought among these host rocks.

In the Colanhan Member, pseudocoticules occur in association with the copper sulfides (Tables 1, 2). The occurrence of rocks similar to coticule in these schists permits a comparison with the rocks of the Les Plattes Member, which exhibit an unusual geochemistry related to hydrothermal exhalations during the sedimentation process (Krosse & Schreyer 1993). A detailed geochemical study of the rocks of the Colanhan Member clearly needs to be carried out.

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- FIG. 4. a. Fracture filled with oxidation minerals (gray), localized between bornite (pink) and a grain of “anomalous bornite” (orange). Small grains of covellite (blue) occur along fractures. Reflected light microscopy, plane-polarized light (sample BOR1–001). b. Residual grains of bornite (pink), included in oxidation minerals (gray). Small grains of covellite (blue) also are visible along the edge of the photograph. Reflected light microscopy, plane-polarized light (sample BOR1–001). c. Replacement of digenite + anilite (light blue) to lamellar yarrowite + spionkopite (dark blue). These sulfides have crystallized between the spessartine grains of a pseudocoticule. Reflected light microscopy, plane-polarized light (sample MSFR–002). d. Network of digenite + anilite (light blue) cross-cutting bornite (pink). Reflected light microscopy, plane-polarized light (sample BOR1–001).
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