The Canadian Mineralogist
Vol. 34, pp. 503-512 (1996)

COBALTITE–GERSDORFFITE SOLID SOLUTION AS A PRIMARY MAGMATIC PHASE IN SPESSARTITE, LACAUNE AREA, MONTAGNE NOIRE, FRANCE

DIDIER BÉZIAT, PIERRE MONCHOUX AND FRANCIS TOLLON

Laboratoire de Minéralogie et Cristallographie, UMR 5563, Université Paul Sabatier,
39, Allées Jules Guesde, 31000 Toulouse Cedex, France

ABSTRACT

A cobaltite–gersdorffite solid solution occurs in spessartite sills from the Lacaune area, Montagne Noire, southern France, enclosed within phenocrysts and found in the matrix. It commonly encloses rounded grains of pyrrhotite with lamellae of pentlandite. Compositional variation of cobaltite–gersdorffite$_{ss}$ is represented mainly by a Co-for-(Ni + Fe) substitution; the core is cobaltiferous, and the rim, nickeliferous. Atomic proportions in the structural formula, as obtained from over 80 analyses, vary within the following ranges: $(Co_{0.05-0.59}Ni_{0.27-0.66}Fe_{0.14-0.32})As_{0.97-1.07}S_{0.89-0.97}$. The Ni/Fe value is near 2, which could indicate the presence of a $(Ni_{0.66}Fe_{0.33})AsS$ component with a Ni–Fe order in the Ni site. Textural evidence and compositional data support an igneous rather than secondary origin. Cobaltite–gersdorffite$_{ss}$ can crystallize by separation of an early immiscible sulfarsenide liquid from a calc-alkaline lamprophyric magma. These sills could represent an attractive target for Au prospecting in the Montagne Noire area.

Keywords: cobaltite, gersdorffite, solid solution, primary, spessartite, Montagne Noire, France.

SOMMAIRE

Une solution solide de cobaltite–gersdorffite se rencontre dans un sill de spessartite de la région de Lacaune, Montagne Noire, partie sud de la France, soit inclus dans les phénocristaux, soit dans la pâte. Ce minéral renferme fréquemment en inclusion des grains arrondis de pyrrhotite avec des lamelles de pentlandite. Sa variation en composition est représentée essentiellement par une substitution Co–(Ni + Fe), avec un coeur cobaltifère et une bordure nickélifère. Les formules structurales, obtenues à partir de 80 résultats d'analyses, varient dans les intervalles suivants: $(Co_{0.05-0.59}Ni_{0.27-0.66}Fe_{0.14-0.32})As_{0.97-1.07}S_{0.89-0.97}$. Le rapport Ni/Fe est toujours voisin de 2, ce qui pourrait indiquer l'existence d'un composant $(Ni_{0.66}Fe_{0.33})AsS$ avec mise en ordre de Ni et Fe sur le site Ni. Leur composition et leur relation avec les minéraux primaires magmatiques indiquent qu'ils sont le résultat d'un processus igné plutôt qu'hydrothermal. Les solutions solides cobaltite–gersdorffite cristalliseraient à partir d'un liquide sulfo-arsénié, séparé précocement par immiscibilité du magma lamprophyrique calco-alcalin. Ces sills de spessartite peuvent représenter une cible intéressante pour la prospection de l'or en Montagne Noire.

Mots-clés: cobaltite, gersdorffite, solution solide, primaire, spessartite, Montagne Noire, France.

INTRODUCTION

The occurrence of cobaltite–gersdorffite solid-solution in basic and ultrabasic rocks is generally considered to be of hydrothermal origin (Oen *et al.* 1971, Petruk *et al.* 1971, Oen 1973, Besson & Picot 1975, Leblanc 1986, Gervilla 1990, Prichard *et al.* 1994). Occasionally, lamprophyric rocks may contain primary magmatic sulfides, generally pyrrhotite, pentlandite and chalcopyrite (Grosser 1966, Rohde 1972), but magmatic cobaltite–gersdorffite$_{ss}$ has never been reported.

In this paper, we report new information (compositional variations and zoning) on sulfarsenide minerals found in sills of spessartite from the Lacaune area, Montagne Noire, in southern France. Features of unusual occurrence will be used to discuss their origin: is the cobaltite–gersdorffite$_{ss}$ a primary magmatic phase or a hydrothermal phase?

THE HOST SPESSARTITE

The cobaltite–gersdorffite$_{ss}$ occurs in spessartite emplaced in Lower Cambrian carbonate formations in the Lacaune area, Montagne Noire, southern France. Béziat *et al.* (1993) have described the geology, mineralogy and geochemistry of the host spessartite, and proposed that it could have been derived by partial melting of a metasomatically enriched garnet + phlogopite ± amphibole lherzolite. The water-rich nature of the magma is clearly indicated by the presence of hydrous mafic phenocrysts and by plagioclase occurring only in the groundmass (*cf.* Burnham 1979, Allan & Carmichael 1984).

Spessartite belongs to the calc-alkaline suite. It contains amphibole (magnesio-hastingsite to pargasite) and phlogopite as phenocrysts, both commonly including microphenocrysts of chromian rutile, zincian chromite and cobaltite–gersdorffite$_{ss}$, with occasional inclusions of pyrrhotite. However, sulfarsenide–sulfide grains and oxide grains occur in separate inclusions. The groundmass comprises plagioclase, light brown mica, quartz and apatite. Ocelli of light brown mica, commonly including microcrystals of cobaltite–gersdorffite$_{ss}$ in their core, also are found. These ocelli are interpreted as the product of transformation of relict olivine phenocrysts during the ascent of the magma.

A very subordinate, secondary assemblage, with colorless amphibole, talc, chlorite, white mica, carbonate and pyrite, is found only near the veinlets within the fresh rock.

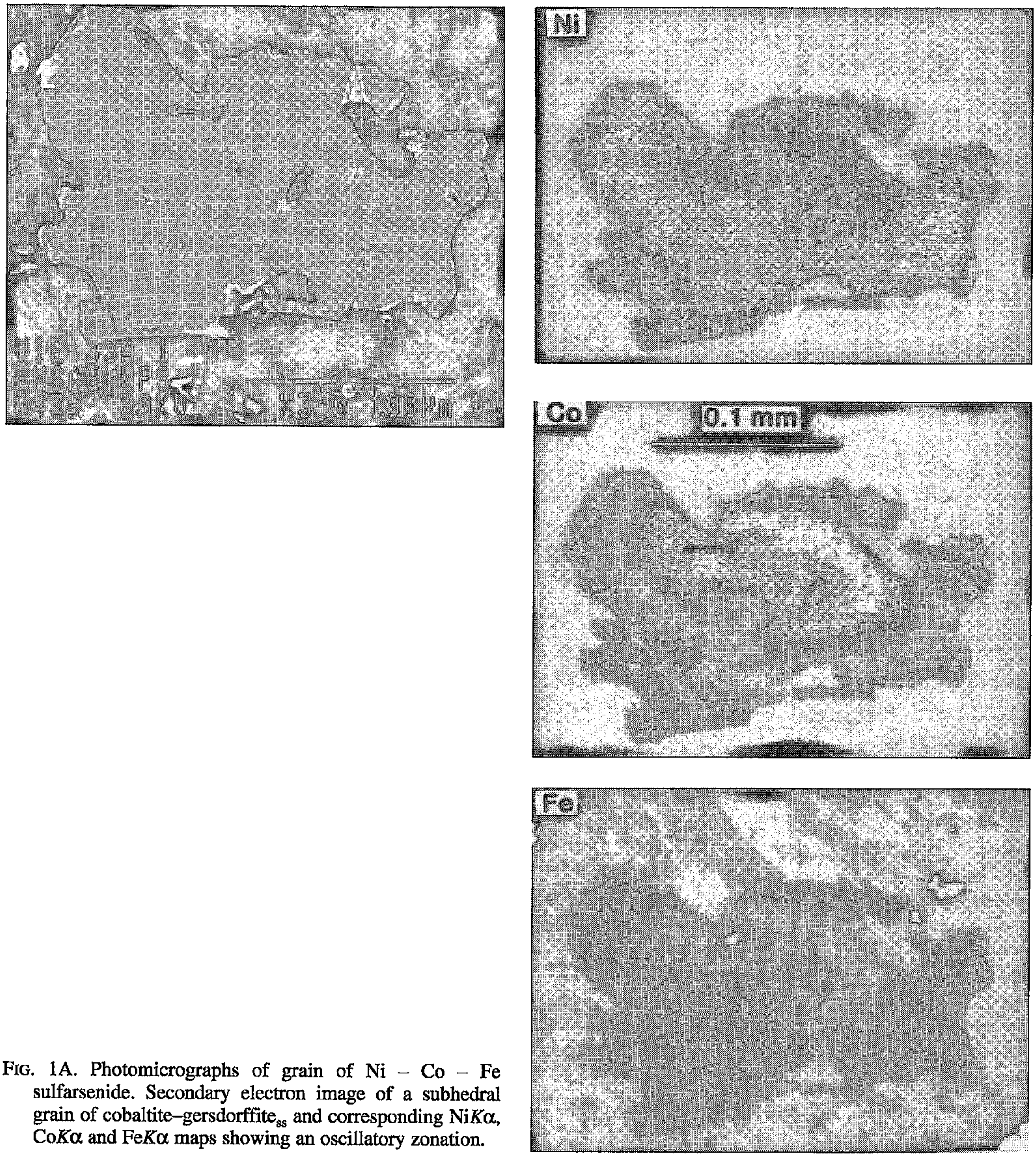

FIG. 1A. Photomicrographs of grain of Ni – Co – Fe sulfarsenide. Secondary electron image of a subhedral grain of cobaltite–gersdorffite$_{ss}$ and corresponding Ni*K*α, Co*K*α and Fe*K*α maps showing an oscillatory zonation.

COBALTITE–GERSDORFFITE$_{SS}$

Mineralogy and textures

The average spessartite contains less than 0.1% by volume of cobaltite–gersdorffite$_{ss}$. It occurs as inclusions 50 to 250 μm across within amphibole and, more rarely, within phlogopite phenocrysts, in the ocelli of light brown mica, and also in the matrix. The grains of cobaltite–gersdorffite$_{ss}$ appear white, with high reflectance and weak anisotropism. They occur as euhedral to subhedral single crystals (Figs. 1A, D) or in small aggregates and, more rarely, as subspherical grains (Fig.1B). No evidence of exsolution is visible, even at 500× magnification with the scanning electron microscope, in secondary-electron images (Figs. 1A, C). The crystals of cobaltite–gersdorffite$_{ss}$ occasionally contain amphibole and phlogopite crystals as inclusions, as well as rounded grains of pyrrhotite with lamellae of pentlandite (Fig. 1C).

Mineral chemistry

More than eighty electron-microprobe analyses were done using a CAMEBAX SX50 at the Laboratory of Mineralogy, Toulouse (beam current of 20 nA, 25 kV, with a counting time of 10 s at the peak positions and 5 s for symmetrical backgrounds). The following standards were used: pure elements for Ni and Co, $CuFeS_2$ for Cu, Fe and S, FeAsS for As, and Sb_2S_3 for Sb. The data were corrected using PAP (SX50) procedures. Concentrations of major elements are accurate to ±1 wt% of the element present, whereas concentrations of minor elements are less accurate, but are reproducible to ±0.1 wt%.

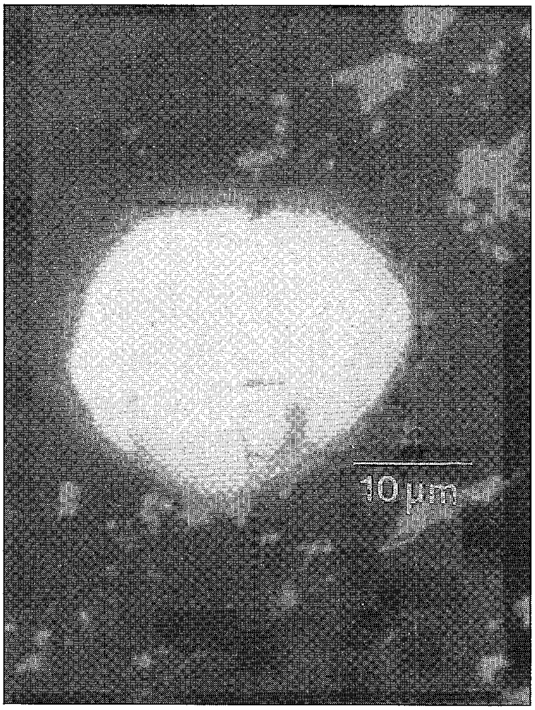

FIG. 1B. Photomicrograph of subspherical grain of cobaltite–gersdorffite$_{ss}$.

Representative compositions of cobaltite–gersdorffite$_{ss}$ and sulfides are given in Table 1. The cobaltite–gersdorffite$_{ss}$ is a solid-solution series between (Ni,Fe)-rich cobaltite and gersdorffite. Compositional ranges of Co, Ni, Fe, As and S, as obtained from 80 analyses (Fig. 2), are $(Co_{0.05–0.59}Ni_{0.27–0.66}Fe_{0.14–0.32})As_{0.97–1.07}S_{0.89–0.97}$.

Sb contents invariably are low (maximum 0.5 wt%). Sb enters the cobaltite–gersdorffite$_{ss}$ structure by substitution for S (Fig. 3). As shown in Figure 4, the degree of substitution of As for S increases with increasing (Ni + Fe) contents, in agreement with the experimental results of Maurel & Picot (1974).

Depending upon the silicate assemblage in which they occur (phenocrysts, ocelli, groundmass), cobaltite–gersdorffite$_{ss}$ shows distinct compositions (Fig. 2). The grains in the groundmass are Sb-poor to Sb-bearing gersdorffite (0.13–0.50 wt%), with a As/S value greater than 1.06. They are poorly zoned, with a core slightly more Co-rich than the rim (anal. 5 and 6, Table 1). The grains trapped in the phenocrysts or in the ocelli of light brown mica generally exhibit a normal and discontinuous zonation between a large core of Sb-poor, (Ni,Fe)-rich cobaltite with an As/S value less than 1.06 and a narrow rim of gersdorffite (Fig. 1D, anal. 1 to 3 in Table 1). More rarely, they exhibit, in addition, a narrow external rim that is more cobaltiferous than gersdorffite, or even oscillatory zonation (Fig.1A). The maximum intragrain variation (*e.g.*, anal. 1a to 1d in Table 1) is as wide as the intergrain variation.

The solvi in the system NiAsS – CoAsS – FeAsS have been experimentally determined by Klemm (1965). There is complete miscibility between gersdorffite and cobaltite above 550°C. On the contrary, miscibility between arsenopyrite and cobaltite and between arsenopyrite and gersdorffite is limited, particularly at low temperatures, because of differences in the crystal structures, pseudo-orthorhombic for arsenopyrite, pseudocubic for cobaltite and gersdorffite (Permingeat 1991). As

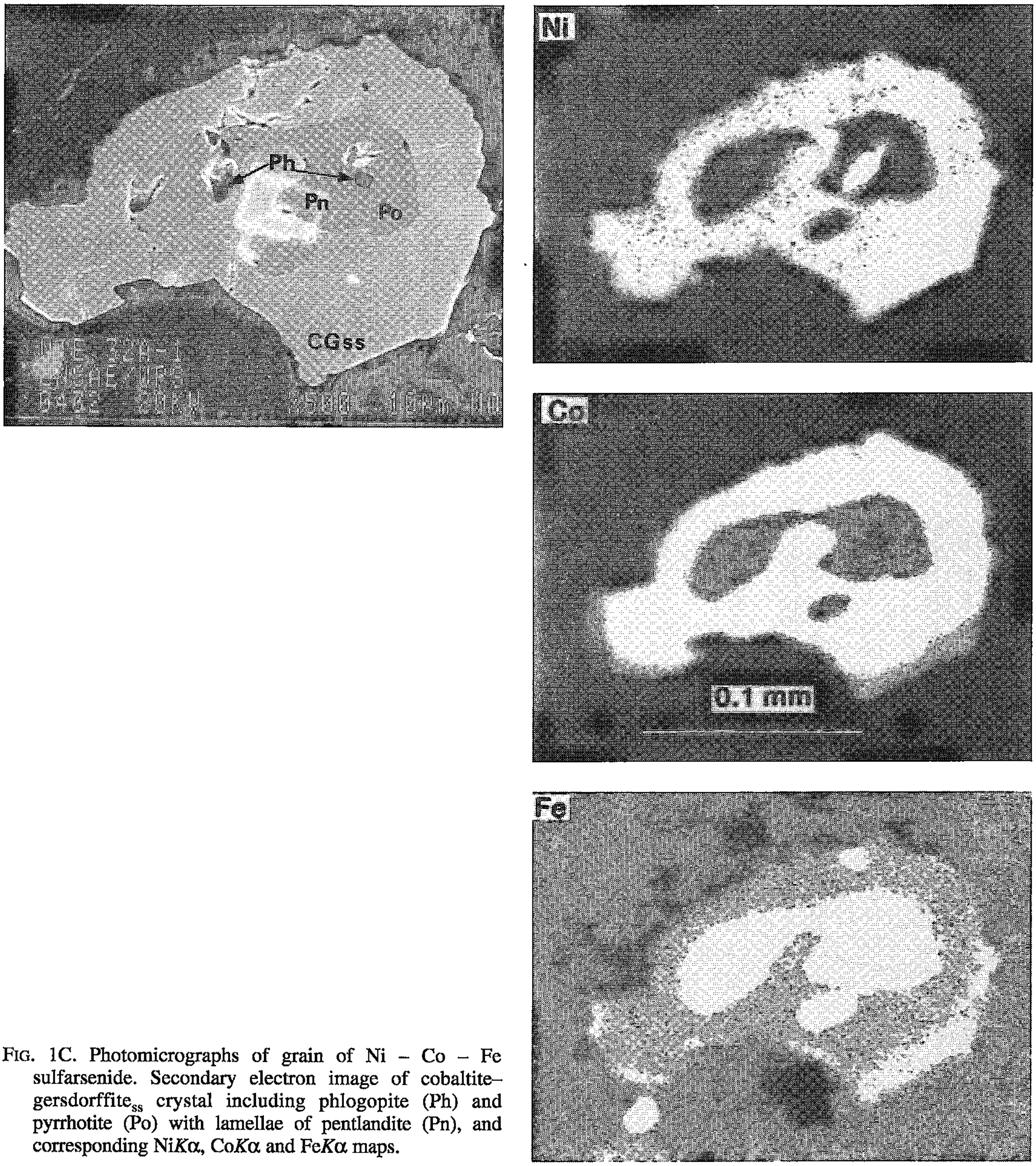

FIG. 1C. Photomicrographs of grain of Ni – Co – Fe sulfarsenide. Secondary electron image of cobaltite–gersdorffite$_{ss}$ crystal including phlogopite (Ph) and pyrrhotite (Po) with lamellae of pentlandite (Pn), and corresponding Ni*K*α, Co*K*α and Fe*K*α maps.

shown in Figure 2, our compositions of cobaltite–gersdorffite$_{ss}$ plot, with few exceptions, in a region that would be in a single-phase field at 500°C, and thus suggest that crystallization occurred at high temperatures (≥500°C).

The average Ni/Fe value near 2 (Fig. 2) could indicate a solid-solution series between CoAsS and $(Ni_{0.66}Fe_{0.33})AsS$. For gersdorffite, three crystal structures corresponding to the space groups $P2_13$, $Pca2_1$ and $Pa3$ have been described, based upon different types of As–S ordering (Bayliss 1982b). For cobaltite, only the $Pca2_1$ structure has been determined (Bayliss 1982a). Bayliss invoked a chemical reason to explain the order of As and S: "Since Fe (acid) may be classified as harder than Ni, and S (base) is probably harder than As, it is possible that Ni may occur in an As-rich environment and Fe in a S-rich environment". Nevertheless, according to the crystallographic data obtained for these specimens, he comes to the conclusion that Ni and Fe are randomly distributed

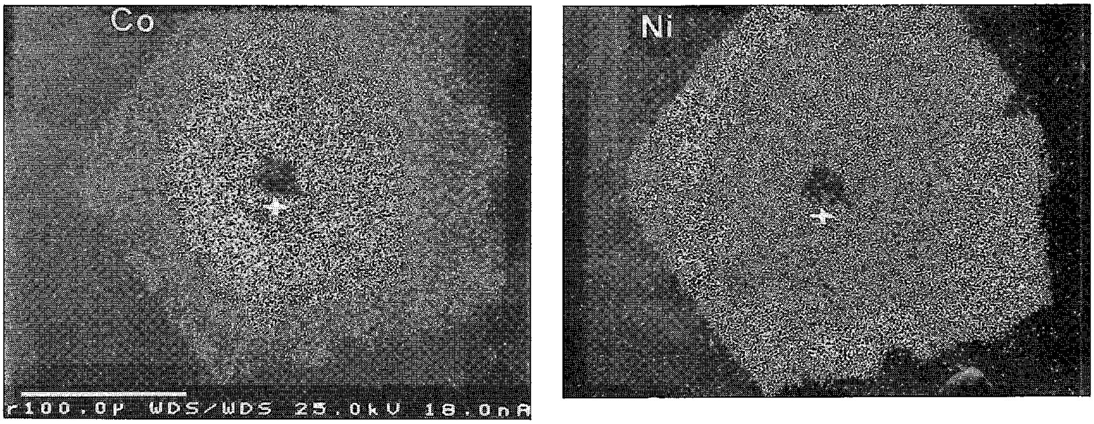

FIG. 1D. Photomicrographs of grain of Ni – Co – Fe sulfarsenide. Ni*K*α and Co*K*α maps of a euhedral grain of cobaltite–gersdorffite$_{ss}$ showing a normal, discontinuous zonation. Scale bar: 100 μm.

among the four metal sites. However, the samples used by Bayliss come from different localities and show different values of the Ni/Fe ratio. On the other hand, our cobaltite–gersdorffite$_{ss}$ data, just as the data of Vinagradova and Kroutov (quoted in Kostov & Minceva-Stefanova 1981) and those of Gervilla *et al.* (1996), plot very close to the Ni/Fe = 2 line; the $(Ni_{0.66}Fe_{0.33})AsS$ component can be interpreted to have a $Pca2_1$ structure, with Ni–Fe order at the Ni site.

In comparison with available compositions of cobaltite–gersdorffite$_{ss}$ taken from the literature, our cobaltite–gersdorffite$_{ss}$ data mostly overlap those of Vinagradova and Kroutov (quoted in Kostov & Minceva-Stefanova 1981), and those from the Málaga province, Spain (Oen *et al.* 1971, 1973, Gervilla 1990, Gervilla & Rønsbo 1992) and the Cobalt–Gowganda district, Ontario (Petruk *et al.* 1971). On the other hand, the cobaltite–gersdorffite$_{ss}$ from Lacaune clearly differs from that in Morocco (Permingeat 1991) by its higher Fe contents (Fig. 2).

Because the fine grain-size of pyrrhotite, contamination by the host cobaltite–gersdorffite$_{ss}$ is possible. However, analyses of relatively large grains (40 μm) of pyrrhotite indicate the systematic presence of Ni and

TABLE 1. REPRESENTATIVE RESULTS OF ELECTRON–MICROPROBE ANALYSES, COBALTITE–GERSDORFFITE$_{ss}$ AND ASSOCIATED SULFIDES FROM THE LACAUNE AREA, MONTAGNE NOIRE

Anal. Phase Host	1a Co/c O	1b Co/c O	1c Ge/r O	1d Ge/r O	2a Co/c O	2b Ge/r O	3a Co/c Ph	3b Ge/r Ph	4a Ge/c Amph	4b Ge/r Amph	5a Ge/c M	5b Ge/r M	6a Ge/c M	6b Ge/r M	7 Po/c CG$_{ss}$	8 Po/c CG$_{ss}$	9 Po/c CG$_{ss}$	10 Pn/c Po
Ni	9.83	11.87	21.32	22.85	10.83	14.60	10.30	17.01	15.86	20.67	19.09	21.01	23.15	22.83	1.10	0.61	1.11	30.82
Co	21.39	18.84	3.10	2.36	19.52	14.40	10.49	9.28	12.53	3.37	6.29	4.13	1.97	2.12	0.07	n.d.	n.d.	0.46
Fe	4.96	5.47	10.59	9.97	5.97	6.98	5.75	9.27	7.72	10.86	9.82	10.03	10.14	9.97	57.70	58.75	58.36	34.00
Sb	0.21	0.13	0.26	0.41	0.14	0.12	0.08	0.10	0.15	0.19	0.26	0.13	0.32	0.37	0.00	0.00	0.00	0.00
As	45.35	45.52	46.83	46.82	45.73	45.73	45.50	46.07	45.75	47.14	45.75	46.46	46.82	47.28	2.72	1.00	0.58	1.33
S	19.04	19.06	18.33	17.93	18.76	18.50	18.99	19.01	18.55	18.30	18.22	17.82	17.32	17.85	38.94	39.12	39.30	33.84
Total	100.78	100.89	100.43	100.34	100.95	100.33	101.11	100.74	100.56	100.53	99.43	99.58	99.72	100.42	100.53	99.48	99.35	100.45
									Atoms per formula unit									
Ni	0.27	0.33	0.60	0.64	0.30	0.40	0.28	0.47	0.44	0.58	0.53	0.59	0.65	0.64	0.01	0.01	0.02	2.13
Co	0.59	0.51	0.09	0.06	0.53	0.40	0.56	0.26	0.34	0.09	0.18	0.11	0.05	0.06	0.00	–	–	0.03
Fe	0.14	0.16	0.31	0.29	0.17	0.20	0.16	0.27	0.22	0.32	0.29	0.30	0.30	0.30	0.83	0.85	0.85	2.47
As	0.98	0.98	1.03	1.03	0.98	0.99	0.97	1.00	0.98	1.04	1.00	1.02	1.03	1.05	0.03	0.01	0.01	0.07
S	0.96	0.96	0.94	0.92	0.94	0.93	0.95	0.97	0.93	0.95	0.94	0.91	0.89	0.92	0.97	0.99	0.99	4.29

Structural formulae, expressed in atoms per formula unit, were calculated on the basis of (1) Ni + Co + Fe = 1 atom (Permingeat 1991) for solid solutions (CG$_{ss}$) between cobaltite (Co) and gersdorffite (Ge), (2) S + As = 1 atom for pyrrhotite, and (3) a total of 9 atoms for pentlandite. Points analyzed: core (c) and rim (r) of cobaltite–gersdorffite$_{ss}$ crystal included in phlogopite (Ph) and amphibole (Amph) phenocrysts, ocelli (O) and matrix (M); n.d.: not detected. The proportion of constituents is reported in weight %.

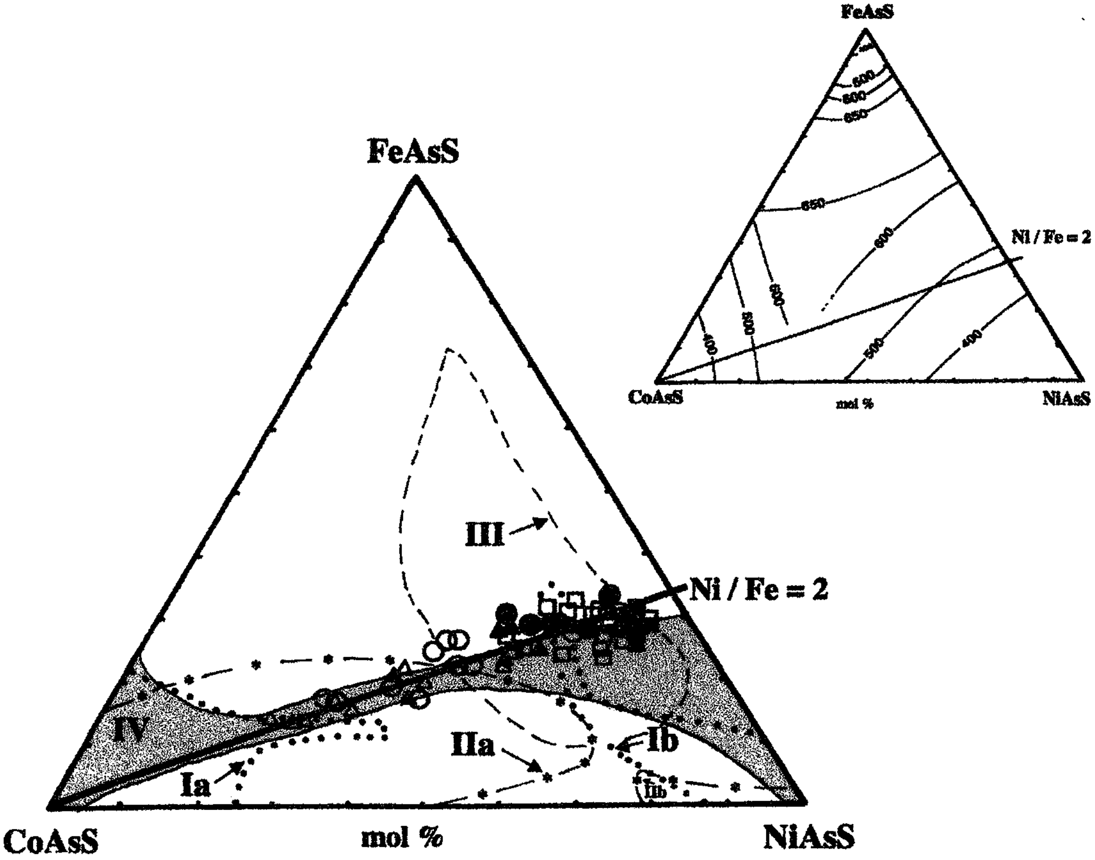

FIG. 2. Compositional plot of cobaltite–gersdorffite$_{ss}$ in the CoAsS – FeAsS – NiAsS system. Solvus lines at 400°, 500°, 600° and 650°C (inset) are taken from Klemm (1965). Legend: core (○) and rim (●) of cobaltite–gersdorffite$_{ss}$ included in amphibole or phlogopite phenocrysts; core (Δ) and rim (▲) of cobaltite–gersdorffite$_{ss}$ included in ocelli in mica; (□) cobaltite–gersdorffite$_{ss}$ included in the groundmass. Fields Ia and Ib: cobaltite–gersdorffite$_{ss}$ from Morocco (Permingeat 1991), IIa and IIb: cobaltite–gersdorffite$_{ss}$ from Cobalt–Gowganda (Petruk *et al.* 1971), III: cobaltite–gersdorffite$_{ss}$ from Màlaga (Oen *et al.* 1971, 1973, Gervilla 1990, Gervilla & Rønsbo 1992), IV: stippled field, data of Vinagradova and Kroutov (in Kostov & Minceva-Stefanova 1981).

As (0.5 to 1.1 wt% Ni, 0.5 to 2.7 wt% As, Table 1) and the absence of Co. Very fine-grained pentlandite (5 μm) shows a fairly constant composition, with a Ni/Fe value near 0.9 (Table 1).

DISCUSSION

The occurrence of cobaltite–gersdorffite$_{ss}$ in basic and ultrabasic rocks is generally attributed to a hydrothermal process except, for instance, in lherzolite from the Málaga province, where Gervilla & Rønsbo (1992) related the Fe-rich cobaltite–gersdorffite$_{ss}$ to a late-magmatic process, with a temperature of crystallization as high as 700°C.

According to the hydrothermal hypothesis, cobaltite–gersdorffite$_{ss}$ could represent original magmatic Fe–Ni-sulfides that have been modified by a As–Co-rich fluid penetrating along the cleavage planes of the phenocrysts, and probably responsible for the very subordinate secondary assemblage present in the spessartite. Pyrrhotite and pentlandite enclosed in cobaltite–gersdorffite$_{ss}$ would be relics of this magmatic stage. We can also suggest a reaction between a high-temperature ore fluid and the water-rich lamprophyric magma. However, such a hypothesis does not explain both intragrain and intergrain variations, *i.e.*, neither the systematically highest Co content of the core of the grains nor its systematic partition between cobaltite, for the grains trapped in the phenocrysts and the ocelli, and gersdorffite for those hosted in the matrix. In addition, in the hydrothermal hypothesis, one would expect that additional

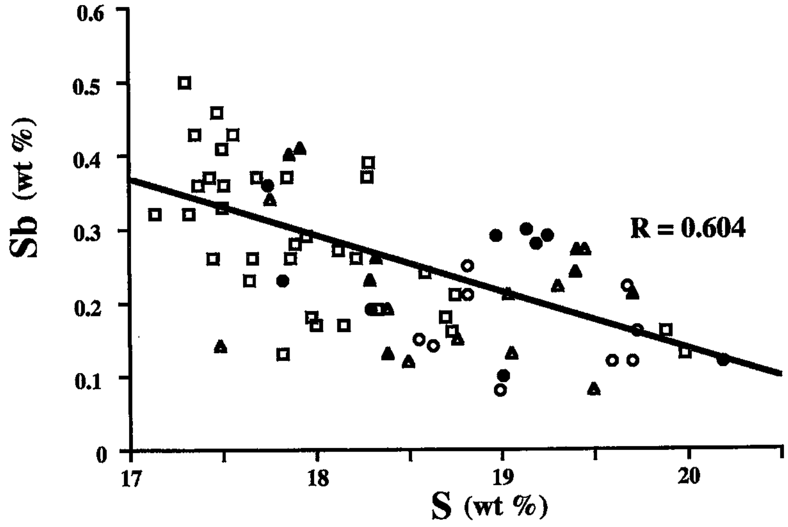

FIG. 3. Plot with regression coefficient describing the relationship between weight percent Sb and S in cobaltite–gersdorffite$_{ss}$. We use wt% instead of atomic proportions because of the low contents of Sb.

chalcophile and siderophile elements would be carried by the fluid phase (Fleet 1977, Leblanc 1986, Stone *et al.* 1989).

A magmatic origin for the cobaltite–gersdorffite$_{ss}$ of Lacaune could theoretically account for the following features: (1) the presence of cobaltite–gersdorffite$_{ss}$ grains enclosed by primary magmatic amphibole and phlogopite phenocrysts, associated with high-T phases like pyrrhotite, pentlandite, chromite and Cr-rich rutile, (2) its occurrence in an undeformed rock showing a panidiomorphic texture, (3) the large and regular compositional variation (Fig. 2) between the cobaltite hosted in the phenocrysts and the gersdorffite hosted in the matrix, reflecting a temperature decrease related to a magmatic trend, from "early" Co-rich to "late" Ni-rich crystals, (4) the crystallochemical features of the associated zincian chromite (with up to 4.5 wt% ZnO); Naldrett (1979) has shown that in hydrothermal ores, Zn is preferentially partitioned with Cu and Fe into sulfide phases, whereas in orthomagmatic ores,

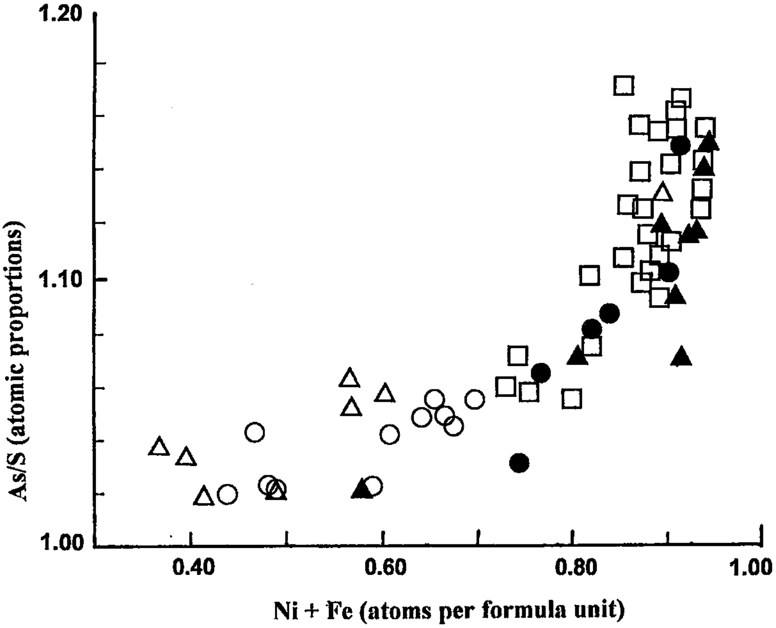

FIG. 4. Relationship between As/S and (Ni + Fe) in cobaltite–gersdorffite$_{ss}$.

it is preferentially partitioned into chromian spinel. Zn-rich chromite associated with Fe–Ni sulfides and Ni–Co arsenides in ultrabasic rocks have been described in several ore deposits (Klemm & Weiser 1965, Groves *et al.* 1977, Oen & Kieft 1977, Leblanc 1986, Gervilla 1990). Johan (1980) has proposed a crystallochemical model for spinel that allows us to discriminate between that occurring in Ni–Cu-mineralized complexes and that in barren mafic intrusions, based on their mg-number and Al–Cr contents. According to this model, the chromite of Lacaune would correspond to spinel in mineralized complexes (Béziat *et al.* 1993).

Moreover, experimental studies on gersdorffite (Yund 1962) and cobaltite (Maurel & Picot 1974) have shown that these phases can be stable at temperatures as high as 700° and 1000°C, respectively, and 850°C for the $Pca2_1$ crystal-structure (Kostov & Minceva-Stefanova 1981).

Gervilla *et al.* (1992) observed separate associations of arsenides and sulfides in the ore deposit associated with ultramafic rocks of Beni Bousera, in Morocco. They suggested that this could be the result of immiscibility and gravity separation of the denser As-liquid from the S-dominant liquid, inducing the early crystallization of arsenides. Contrary to the Beni Bousera ultramafic rocks, the cobaltite–gersdorffite$_{ss}$ in the Lacaune lamprophyre suggests a crystallization from a single liquid. Accepting the model of magmatic segregation, these different textural relationships could be explained by a different timing of crystallization: after the unmixing of the As–S liquid in the Beni Bousera ore, before at Lacaune. According to the water-rich character of the silicate magma (*cf.* Naldrett 1969), the cobaltite crystallized early from the As–S liquid, and was present at the onset of crystallization of the hydrous mafic phenocrysts. Before the trapping by the phenocrysts, the Ni-rich residual As–S liquid would have been partially removed during the magma's ascent and would have crystallized later, contemporaneously with the matrix, thus forming the gersdorffite. Such a hypothesis supports the observed discontinuous zonations, these being preserved by the rapid cooling.

Various genetic models have been proposed for the origin of sulfur and arsenic in magmas (Oen 1973, Haughton *et al.* 1974, Rajamani & Naldrett 1978, Naldrett 1981, Stone *et al.* 1989, Gervilla & Leblanc 1990, Leblanc *et al.* 1990). For instance, Duke (1990) proposed that crustal sulfur was assimilated at depth, prior to fractional crystallization, whereas Garuti *et al.* (1984) preferred a mantle origin, as did Lorand (1987) and Gervilla & Leblanc (1990). The mineralogical and chemical features of the Lacaune lamprophyre are consistent with a primary magma derived from a metasomatically enriched phlogopite + garnet ± amphibole lherzolite (Béziat *et al.* 1993). Since low-field-strength elements can concentrate in these types of magma (*e.g.*, Perfit *et al.* 1980), and although arsenic-rich mantle-derived magmas have never been reported, we suggest that arsenic and sulfur could have been introduced during metasomatism of the mantle source by fluids derived from a subducted slab.

Rock *et al.* (1989) have discussed the common link between gold mineralization and lamprophyres. Tollon (1969) and Béziat & Monchoux (1991) also pointed out the presence of metabasic rocks with chromian and zincian spinel in the gold-bearing As–S mineralization of the Salsigne district. As the result of geochemical prospecting carried out in Montagne Noire (Michard 1990), two zones with As and Au anomalies were discovered, one obviously centered on the Salsigne district, the other on the Lacaune area. Hence, the spessartite sills from the latter area, with higher contents of gold and arsenic (2.9–5 ppb and 300–450 ppm, respectively) than common basic rocks, and the associated surficial As–Au anomalies, constitute a potential exploration guide for Au–As–S mineralization.

CONCLUSIONS

Results of our study indicate that the occurrence of cobaltite–gersdorffite$_{ss}$ in basic rocks like spessartite can result from orthomagmatic segregation, through formation of an early immiscible sulfo-arsenide liquid from a nearly primitive, calc-alkaline lamprophyric magma, as well as by secondary (hydrothermal) processes. Textural relationships and compositional features of cobaltite–gersdorffite$_{ss}$ suggest that the cobaltite crystallized early as high-temperature solid-solution crystals, and then the gersdorffite formed contemporaneously with the matrix, and quenched upon cooling. Such an early crystallization of cobaltite–gersdorffite$_{ss}$ could be due to the water-rich character of the magma.

ACKNOWLEDGEMENTS

The authors are grateful to M. Benvenuti, J. Guha and D.C. Harris for critical comments and corrections. We also thank the referees, Y. Moëlo, Z. Johan and R.F. Martin, for the numerous comments that greatly improved the manuscript.

REFERENCES

ALLAN, J.F. & CARMICHAEL, I.S.E. (1984): Lamprophyric lavas in the Colima graben, SW Mexico. *Contrib. Mineral. Petrol.* **88**, 203-216.

BAYLISS, P. (1982a): A further crystal structure refinement of cobaltite. *Am. Mineral.* **67**, 1048-1057.

________ (1982b): A further crystal structure refinement of gersdorffite. *Am. Mineral.* **67**, 1058-1064.

BESSON, M. & PICOT, P. (1975): Métallogénie du gisement d'Aghbar district de Bou-Azzer (Maroc). *C.R. Acad. Sci. Paris* **281**, 1553-1556.

BÉZIAT, D., JORON, J.L. & MONCHOUX, P. (1993): Spessartites in the Montagne Noire, France: mineralogical and geochemical data. *Eur. J. Mineral.* **5**, 879-891.

________ & MONCHOUX, P. (1991): Les spinelles chromozincifères du district aurifère de Salsigne (Montagne Noire, France). *Eur. J. Mineral.* **3**, 957-969.

BURNHAM, C.W. (1979): The importance of volatile constituents. *In* The Evolution of the Igneous Rocks (H.S. Yoder, Jr., ed.). Princeton Univ. Press, Princeton, New Jersey (439-482).

DUKE, J.M. (1990): Mineral deposit models: nickel sulfide deposits of the Kambalda type. *Can. Mineral.* **28**, 379-388.

FLEET, M.E. (1977): Origin of disseminated copper–nickel sulfide ore at Frood, Sudbury, Ontario. *Econ. Geol.* **72** 1449-1456.

GARUTI, G., GORGONI, C. & SIGHINOLFI, G.P. (1984): Sulfide mineralogy and chalcophile and siderophile element abundances in the Ivrea–Verbano mantle peridotites (Western Italian Alps). *Earth Planet. Sci. Lett.* **70**, 69-87.

GERVILLA, F. (1990): *Mineralizaciones magmaticas ligadas a la evolución de las rocas ultramáficas de la Serrania de Ronda (Málaga, Espana).* Doct. thesis, Univ. Granada, Granada, Spain.

________, FENOLL, P., LEBLANC, M. & TORRES-RUIZ, J. (1992): Evidencias texturales de inmiscibilitad entre liquidos magmaticos sulfurados y arseniurados (Amasined, Beni Bousera, Marruecos). *Actas del Tercero Congresso Geologico de España (Salamanca)* **3**, 123-125.

________ & LEBLANC, M. (1990): Magmatic ores in high-temperature alpine-type lherzolite massifs (Ronda, Spain, and Beni Bousera, Morocco). *Econ. Geol.* **85**, 112-132.

________, ________, TORRES-RUIZ, J. & FENOLL HACH-ALÍ, P. (1996): Immiscibility between arsenide and sulfide melts: a mechanism for the concentration of noble metals. *Can. Mineral.* **34**, 485-502.

________ & RØNSBO, J. (1992): New data on (Ni,Fe,Co) diarsenides and sulfarsenides in chromite–niccolite ores from the Málaga Province, Spain. *Neues Jahrb. Mineral., Monatsh.*, 193-206.

GROSSER, P. (1966): Differentiation in Lamprophyren der Lausitz. *Neues Jahrb. Mineral., Abh.* **105**, 133-160.

GROVES, D.I., BARRETT, F.M., BINNS, R.A. & MCQUEEN, K.G. (1977): Spinel phases associated with metamorphosed volcanic-type iron–nickel sulfide ores from Western Australia. *Econ. Geol.* **72**, 1224-1244.

HAUGHTON, D.R., ROEDER, P.L. & SKINNER, B.J. (1974): Solubility of sulfur in mafic magmas. *Econ. Geol.* **69**, 451-467.

JOHAN, Z. (1980): Possibilité de discrimination des massifs basiques minéralisés en nickel et cuivre et des massifs stériles par l'étude cristallochimique des spinelles. *Mém. B.R.G.M.* **97**, 203-218.

KLEMM, D.D. (1965): Synthesen und Analysen in den Dreieckdiagrammen FeAsS – CoAsS – NiAsS und FeS_2 – CoS_2 – NiS_2. *Neues Jahrb. Mineral., Abh.* **103**, 205-255.

________ & WEISER, T. (1965): Hochtemperierte Glanzkobalt–Gersdorffit-Mischkristalle von Outokumpo, Finnland. *Neues Jahrb. Mineral., Monatsh.*, 236-241.

KOSTOV, I. & MINCEVA-STEFANOVA, J. (1981): *Sulphide Minerals: Crystal Chemistry, Paragenesis and Systematics.* Bulgarian Acad. Sci., Sofia, Bulgaria.

LEBLANC, M. (1986): Co–Ni arsenide deposits, with accessory gold, in ultramafic rocks from Morocco. *Can. J. Earth Sci.* **23**, 1592-1602.

________, GERVILLA, F. & JEDWAB, J. (1990): Noble metals segregation and fractionation in magmatic ores from Ronda and Beni Bousera lherzolite massifs (Spain, Morocco). *Mineral. Petrol.* **42**, 233-248.

LORAND, J.P. (1987): Sur l'origine mantellaire de l'arsenic dans les roches du manteau: exemple des pyroxénites à grenat du massif lherzolitique des Beni-Bousera (Rif, Maroc). *C.R. Acad. Sci. Paris* **305**, 383-386.

MAUREL, C. & PICOT, P. (1974): Stabilité de l'alloclasite et de la cobaltite dans les systèmes Co – As – S et Co – Ni – As – S. *Bull. Soc. Fr. Minéral. Cristallogr.* **97**, 251-256.

MICHARD, A. (1990): Synthèse Montagne Noire. *Rapp. B.R.G.M.* **R30 358 DEX-DAM-90.**

NALDRETT, A.J. (1969): A portion of the system Fe–S–O between 900° and 1080°C and its applications to sulfide ore magmas. *J. Petrol.* **10**, 171-201.

________ (1979): Partitioning of Fe, Co, Ni, and Cu between sulfide liquid and basaltic melts and the composition of Ni–Cu sulfide deposits – a reply and further discussion. *Econ. Geol.* **74**, 1520-1528.

________ (1981): Nickel sulfide deposits: classification, composition, and genesis. *Econ. Geol., 75th Anniv. vol.*, 628-685.

OEN, I.S. (1973): A peculiar type of Cr–Ni mineralization; cordierite – chromite – niccolite ores of Málaga, Spain, and their possible origin by liquid unmixing. *Econ. Geol.* **68**, 831-842.

________, BURKE, E.A.J., KIEFT, C. & WESTERHOF, A.B. (1971): Ni-arsenides, Ni-rich loellingite and (Fe,Co)-rich gersdorffite in Cr-Ni-ores from Málaga province, Spain. *Neues Jahrb. Mineral., Abh.* **115**, 123-139.

——— & KIEFT, C. (1977): Chromite riche en vanadium et zinc dans un minerai de chromite–nickeline des Beni-Bousera, Maroc. *Service Géol. Maroc, Notes* **38**, 251-254.

———, ——— & WESTERHOF, A.B. (1973): Composition of chromites in cordierite- and mica-bearing Cr–Ni ores from Málaga province, Spain. *Mineral. Mag.* **39**, 193-203.

PERFIT, M.R., GUST, D.A., BENCE, A.E., ARCULUS, R.J. & TAYLOR, S.R. (1980): Chemical characteristics of island-arc basalts: implications for mantle sources. *Chem. Geol.* **30**, 227-256.

PERMINGEAT, F. (1991): Introduction à la minéralogie du Maroc. Eléments natifs et alliages (classe I). Sulfures, séléniures, tellurures, arséniures...(classe II). *Notes et Mémoires du Service Géologique du Maroc* **336**, 161-175.

PETRUK, W., HARRIS, D.C. & STEWART, J.M. (1971): Characteristics of the arsenides, sulpharsenides, and antimonides. *Can. Mineral.* **11**, 150-186.

PRICHARD, H.M., IXER, R.A., LORD, R.A., MAYNARD, J. & WILLIAMS, N.W. (1994): Assemblages of platinum-group minerals and sulfides in silicate lithologies and chromite-rich rocks within the Shetland ophiolite. *Can. Mineral.* **32**, 271-294.

RAJAMANI, V. & NALDRETT, A.J. (1978): Partitioning of Fe, Co, Ni, and Cu between sulfide liquid and basaltic melts and the composition of Ni–Cu sulfide deposits. *Econ. Geol.* **73**, 82-93.

ROCK, N.M.S., GROVES, D.I., PERRING, C.S. & GOLDING, S.D. (1989): Gold, lamprophyres and porphyries: what does their association mean? *Econ. Geol., Monogr.* **6**, 609-625.

ROHDE, G. (1972): Über Pentlanditentmischugen in Pyrrhotinen aus Lausitzer Lamprophyren. *Dtsch. Ges. Geol. Wiss. Berlin, Reihe B. Mineral. Lagerstattenforsch.* **16**, 265-269.

STONE, W.E., FLEET, M.E. & MACRAE, N.D. (1989): Two-phase nickeliferous monosulfide solid solution (mss) in megacrysts from Mount Shasta, California: a natural laboratory for nickel–copper sulfides. *Am. Mineral.* **74**, 981-993.

TOLLON, F. (1969): *Le district aurifère de Salsigne (Aude).* Thèse Doct. d'Etat, Univ. Toulouse, Toulouse, France.

YUND, R.A. (1962): The system Ni – As – S: phase relations and mineralogical significance. *Am. J. Sci.* **260**, 761-782.

Received June 15, 1995, revised manuscript accepted January 11, 1996.