

A COBALT-BEARING SULFIDE – ARSENIDE ASSEMBLAGE FROM THE NORD MINE (FINNSHYTTEBERG), SWEDEN: A NEW OCCURRENCE OF CLINOSAFFLORITE

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ABSTRACT

Three mineral assemblages have been recognized in the Nord mine, a small abandoned iron-ore deposit at the western edge of the Proterozoic Bergslagen province in central Sweden. The arsenide-bearing assemblage (clinosafflorite, cobaltite, bismuth, molybdenite and siegenite) and the magnetite-bearing assemblage with pyrite, pyrrhotite and chalcopyrite are regarded as the early phases of the mineralization. Later mobilization of cobalt and its reaction with the primary iron sulfides resulted in the formation of a cobalt-bearing thiospinel–disulfide assemblage with carrollite–linnaeite, cattierite and cobaltian pyrite. The average composition of clinosafflorite, as determined by electron-microprobe analysis is Co 27.4, Ni 0.7, Fe 0.4, As 70.4, S 0.4, total 99.3 wt. %. Optically, clinosafflorite is very similar to safflorite; reflectance (nm, %): 470, 58.3–58.0; 546, 55.3–57.8; 589, 52.8–56.2; 650, 48.7–53.2; its microhardness VHN_{100} is in the range 724–933.

Keywords: clinosafflorite, thiospinels, cattierite, cobalt minerals, electron-microprobe analysis, Bergslagen, Sweden.

SOMMAIRE

Trois assemblages minéralogiques ont été identifiés à la mine Nord, petit gisement de fer abandonné, situé à l'extrémité ouest de la province Protérozoïque de Bergslagen dans la partie centrale de la Suède. L'assemblage clinosafflorite, cobaltite, bismuth, molybdénite, siegenite et l'assemblage magnétite, pyrite, pyrrhotine, chalcopyrite sont considérés comme phases précoces de la minéralisation. La mobilisation subséquente du cobalt et sa réaction avec les sulfures de fer primaires ont donné un assemblage cobaltifère à thiospinelles–disulfures avec carrollite–linnaeite, cattierite et pyrite cobaltifère. La composition moyenne de la clinosafflorite, déterminée à la microsonde électronique, est: Co 27.4, Ni 0.7, Fe 0.4, As 70.4, S 0.4, pourcentage pondéral total 99.3. La clinosafflorite est optiquement très semblable à la safflorite; réflectance (nm, %): 470, 58.3–58.0; 546, 55.3–57.8; 589, 52.8–56.2; 650, 48.7–53.2; microdureté VHN_{100} entre 724 et 933.

Mots-clés: clinosafflorite, thiospinelles, cattierite, minéraux de cobalt, analyses à la microsonde électronique, Bergslagen, Suède.

INTRODUCTION

In the course of regional metallogenic investigations carried out between 1975 and 1980 in the Hällefors area, western Bergslagen, central Sweden, our attention was drawn to the Nord mine because of a remark of Magnusson (1929) about the occurrence there of economic quantities of native bismuth. In spite of a search of the dumps, native bismuth was found only as microscopic inclusions in samples containing cobalt minerals (Zakrzewski *et al.* 1980). These minerals include cobaltite, members of the carrollite–linnaeite series, siegenite of unusual composition, members of the cattierite–cobaltian pyrite series, and the rare mineral clinosafflorite.

GEOLOGICAL SETTING

The Nord mine is a small iron deposit in the Finnsyttteberg ore field (Fig. 1), southern Nordmark district of the western Bergslagen metallogenic province. The Finnsyttteberg ore field is located in an isolated enclave (1500 × 700 m) of supracrustal rocks surrounded by the postorogenic Filipstad granite. The entire enclave is literally covered with dumps from the iron mines; very few outcrops are present. The general geology and the ore deposits of the district have been studied by Magnusson (1929), and his views are summarized here.

The supracrustal rocks are the oldest rocks of the area; they consist of felsic metavolcanic rocks of quartz-keratophyric to rhyolitic composition (called leptine in Sweden) with intercalations of greenstone, limestone, skarn and iron ore. The present state of these metasedimentary and metavolcanic rocks is the result of repeated folding and metamorphism related to the intrusion of granite bodies of several generations.

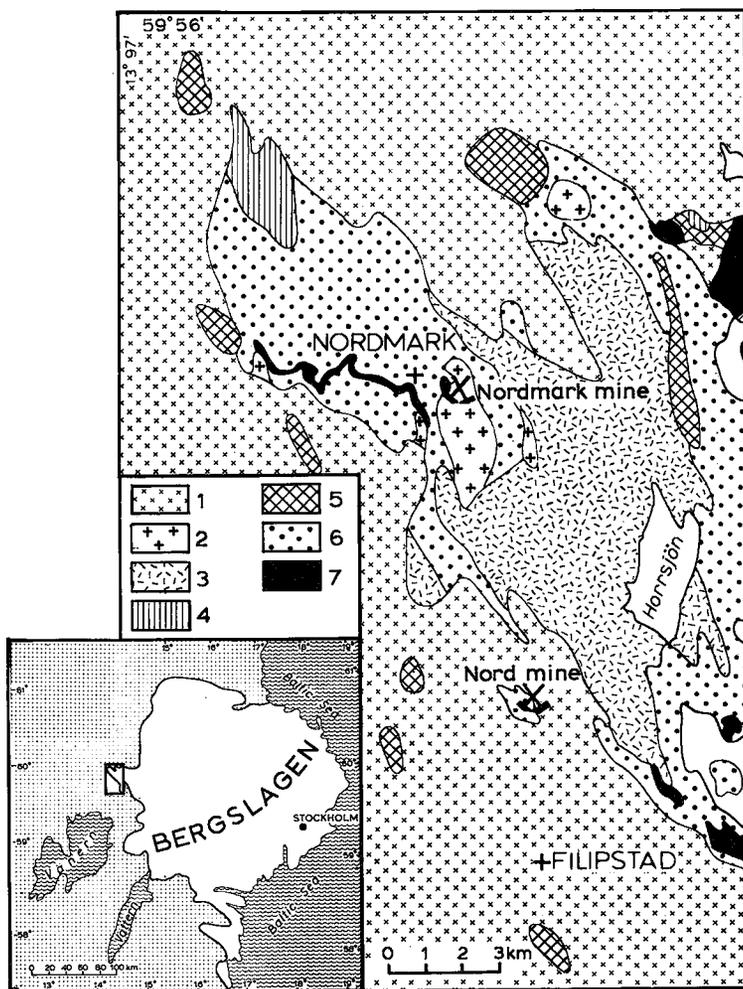


Fig. 1. Location of the Bergslagen province and geological map of the Filipstad area, simplified after Magnusson (1925). (1) postorogenic granite, (2) late-orogenic palingenetic granite, (3) synorogenic granite, (4) metasedimentary rocks, (5) greenstone, (6) leptite, (7) limestone and dolomite.

According to Magnusson (1929), the oldest synorogenic granite gave rise to the occurrence of magnetite and garnet-pyroxene skarns, to the so-called "magnesia-metasomatic process", which formed a number of Mg-rich minerals, and to the "invasion" of the sulfides chalcopyrite, galena, pyrite, pyrrhotite and sphalerite. This synorogenic granite is exposed 1.5 km east of the Nord mine (Fig. 1). The younger late-orogenic palingenetic granite (1841 Ma: Oen *et al.* 1982) is, in Magnusson's view, the cause of formation of more skarn minerals and of the sulfide mineralization in the Nordmark mine

(Fig. 1). As the association of elements in the Nordmark and Nord mines is identical, it should also be possible to relate the mineralization of the Nord mine to this palingenetic granite. However, the distance to the nearest body of this granite, 6 km, makes such an assumption dubious. In the Finnshytteberg ore field; the postorogenic Filipstad granite of Gothian age (1655 Ma: Welin *et al.* 1977) caused the alteration of garnet-pyroxene skarn to hornblende-epidote skarn and of anthophyllite and cummingtonite to hypersthene; the formation of grossular-hedenbergite-wollastonite skarn, scap-

olite, brucine-spotted limestone, spinel and mica is also related to this granite (Magnusson 1970).

OCCURRENCE

The Nord mine is located near the contact between the supracrustal rocks and the Gothian granite. Intrusion of the granite divided the original orebody into several smaller masses (Fig. 2); originally the body was lenticular, with a length of 50 m and a width of up to 12 m; mine workings reached a depth of 80 m (Tegengren 1912). The mine was closed because of technical problems in 1892 after 12 years of production that yielded (together with several smaller mines of the ore field) 65,000 tonnes of iron ore containing 52–54 wt. % Fe. Magnusson (1929) mentioned that some bismuth was found in 1890 and that the ore produced at that time gradually became more sulfide-bearing. The dumps were reworked in 1897 (Tegengren 1912); at present they contain only about 5,000 tonnes of rock. The material on the dumps consists of dark green hornblende-epidote skarn, magnetite and granite. Sulfides, mainly pyrite and pyrrhotite, are rare, and only a few blocks containing cobalt minerals have been found.

MINERAL ASSEMBLAGES AND TEXTURAL RELATIONS

The descriptions of the Nord mine by Tegengren (1912) and Magnusson (1929) shed no light on the location of the cobalt mineralization in the mine. A study of dump material provides no

TABLE 1. MINERAL ASSEMBLAGES OF THE NORD MINE

MAGNETITE-SULFIDE		ARSENIDE-SULFIDE	
EARLY	Magnetite Fe_3O_4	Clinosafflorite	CoAs_2
	Chalcopyrite CuFeS_2	Cobaltite	CoAsS
	Pyrite FeS_2	Siegenite	$(\text{Co},\text{Ni})_3\text{S}_4$
	Pyrrhotite Fe_{1-x}S	Bismuth	Bi
		Molybdenite	MoS_2
THIOSPINEL-DISULFIDE			
	Carrollite	CuCo_2S_4	
	Cattierite	CoS_2	
LATE	Cobaltian pyrite	$(\text{Fe},\text{Co})\text{S}_2$	
	Linnaeite	Co_3S_4	
	Marcasite	FeS_2	
	(Hematite)	Fe_2O_3	
	(Magnetite)	Fe_3O_4	

clues either, but enables a reconstruction of the spatial relation with regard to the iron ores. Our conclusion is that two primary assemblages (magnetite-sulfide and arsenide-sulfide) reacted to form the later thiospinel-disulfide assemblage (Table 1).

Magnetite-sulfide assemblage

Magnetite constitutes, on average, 75 vol. % of the iron ores, the remainder being the skarn minerals clinopyroxene, chlorite, feldspar and garnet. Magnetite forms equidimensional grains up to 1.5 mm in diameter. Locally it contains disk-like exsolution bodies of spinel and blebs of pyrrhotite and pyrite (Fig. 3). Nests up to 10 cm in diameter in the iron ores contain up to 30 vol. % sulfides and only 10 vol. % magnetite disseminated in dark-colored clinopyroxene

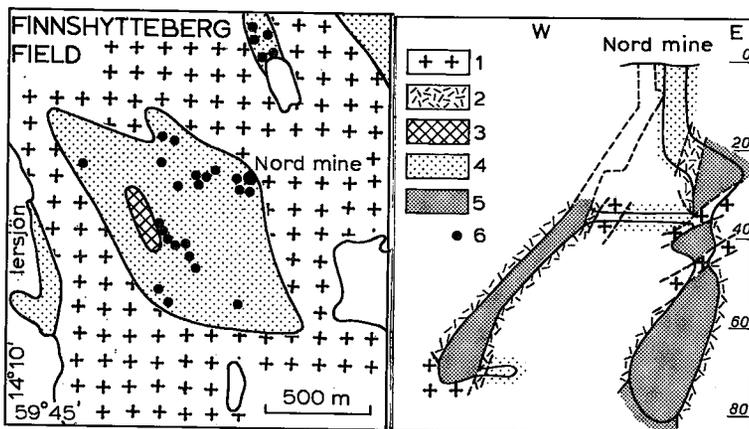


FIG. 2. Geological map of the Finnshtytteberg field and cross section through the Nord mine (after Magnusson 1929). (1) postorogenic granite, (2) skarn, (3) greenstone, (4) leptite, (5) iron ore, (6) mine.

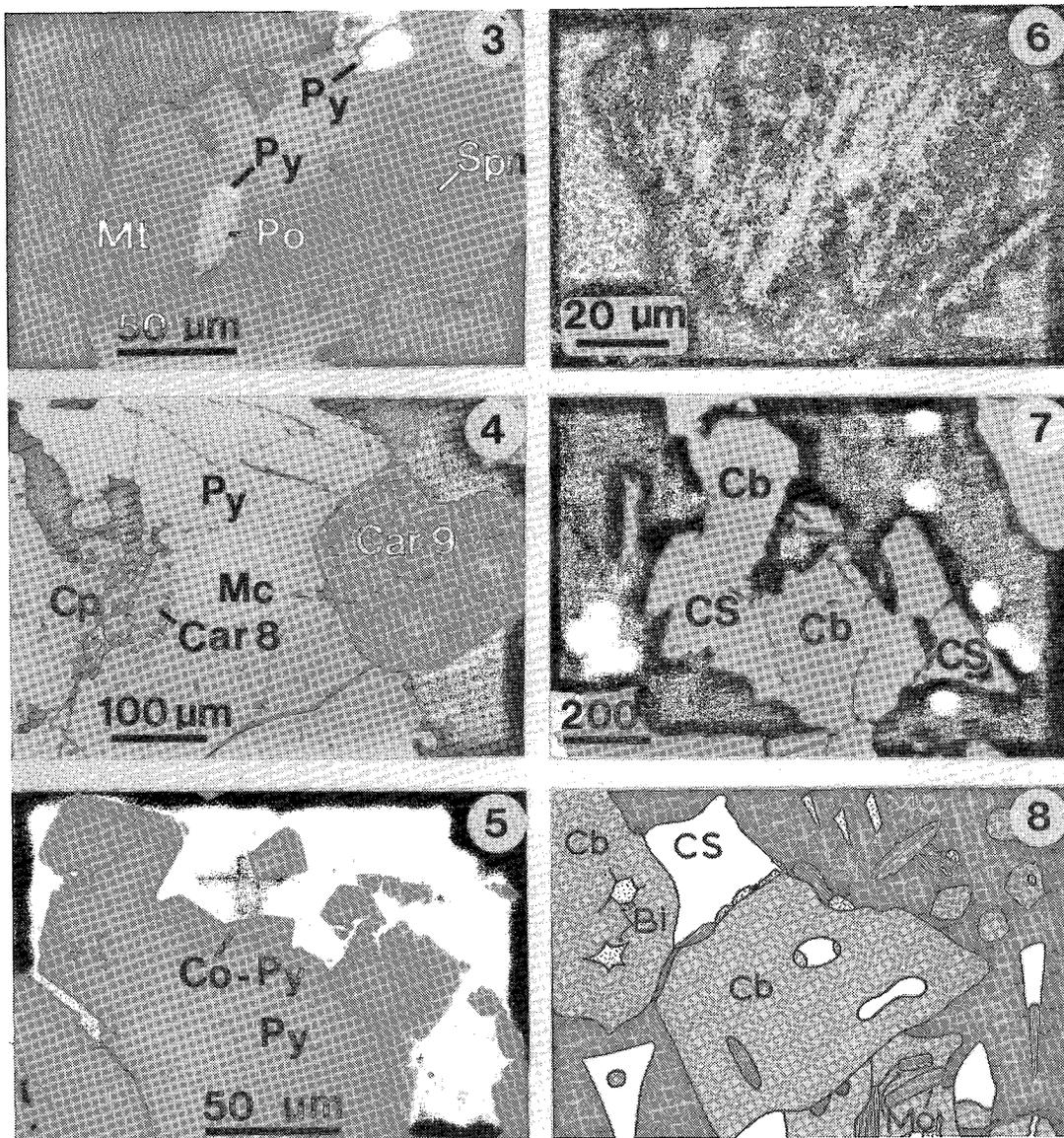


FIG. 3. Pyrrhotite (Po) and pyrite (Py) enclosed in magnetite (Mt) with exsolved spinel (Spn). Pyrite in the upper part is secondary after pyrrhotite.

FIG. 4. Two textural varieties of carrollite. Grain Car 8, in contact with chalcopyrite (Cp) and secondary marcasite (Mc), corresponds to composition 8 in Table 3. The porous Car 9 (composition 9, Table 3) has been formed from pyrrhotite.

FIG. 5. Cobaltian pyrite (Co-Py) developed on pyrite (Py) along grain borders and cracks. The darker zones are richer in cobalt.

FIG. 6. X-ray scanning photograph for Co of mosaic-like pyrite-cobaltian pyrite intergrowths similar to those of marcasite-pyrite.

FIG. 7. Intergrowths of clinosafflorite (CS) and cobaltite (Cb).

FIG. 8. Schematic representation (not to scale) of intergrowths of clinosafflorite (CS), cobaltite (Cb), native bismuth (Bi) and molybdenite (Mo). Note the freezing cracks around native bismuth in cobaltite (upper left corner). Grey is gangue.

skarn. The presence of magnetite in these nests as inclusions in pyrite, pyrrhotite and chalcopyrite shows it to be the oldest mineral. Magnetite occurring in intimate intergrowths with pyrite and containing marcasite and hematite has been formed at a later stage: small relics of pyrrhotite suggest that the intergrowths have been formed by oxidation of pyrrhotite, possibly during retrograde metamorphism, according to a reaction $6\text{FeS} + 2\text{O}_2 = \text{Fe}_3\text{O}_4 + 3\text{FeS}_2$.

Thiospinel-disulfide assemblage

A reaction of the magnetite-sulfide assemblage with Co-bearing solutions resulted in thiospinels of the carrollite-linnaeite series and Co-bearing disulfides. In the chalcopyrite-bearing sulfide assemblage included in the iron ores, carrollite-linnaeite occurs in two textural varieties (Fig. 4): 1) as isolated grains up to 2 mm across and in intergrowths with pyrite, sometimes with a zone of cobaltian pyrite in between. Relics of pyrite and pyrrhotite are present. This type shows a cleavage in three directions along {100} and takes a poor polish (Fig. 4, Car 9); 2) as grains up to 0.5 mm across accompanying chalcopyrite; the larger grains of this type occur at the contacts with gangue minerals. They are hypidiomorphic, have no visible cleavage and take a good polish; smaller grains are found on the contacts between chalcopyrite and pyrite (Fig. 4, Car 8). The members of the carrollite-linnaeite series have a yellowish white color and are isotropic; their reflectance (Table 2) is somewhat lower than the values given by Craig *et al.* (1979), which reflects the varying contents of Fe and Ni in material from the Nord mine. Compositions 4-10 in Table 3 refer to grains of

TABLE 2. REFLECTANCE* AND VICKERS HARDNESS** OF NORD MINE MINERALS

Wavelength (nm)		R %				VHV ₁₀₀
		470	546	589	650	
Clinosafflorite	R ₁	58.3	55.3	52.8	48.7	724- 933
	R ₂	58.0	57.8	56.2	53.2	
Cobaltite		48.9	52.7	53.6	54.4	1168-1288
Linnaeite-carrollite		39.3	41.5	42.4	44.1	483- 514
Cobaltian pyrite		43.5	46.8	48.0	51.2	1309-1343
Pyrite		45.7	49.3	52.1	53.1	1402-1452

*Measured with a Leitz MPV microscope photometer equipped with Knott 9592A photomultiplier, Veril B-200 continuous band interference filter, objective 16:1, 0.40 N.A., and WC standard.

**Measured with a Leitz Durimet-Pol applying a load of 100 g for 15 s.

this assemblage with the highest contents of Co, Ni, Fe and Cu.

The disulfides are members of the pyrite-cattierite series, with compositions ranging from pyrite with only 0.2 wt. % Co to cattierite with 31.8 wt. % Co (Table 3). The highest Co contents commonly are present at the rims of the grains in contact with gangue minerals (Fig. 5) and in bravoite-like zoned crystals. The reflectance and microhardness of members of the pyrite-cattierite series (Table 2) decrease with increasing Co content, and their color gradually changes from yellowish white for pyrite to more distinctly brownish for cattierite. Cobaltian pyrite also occurs in mosaic-like intergrowths with pyrite (Fig. 6); this texture resembles that of secondary marcasite in pyrite and probably formed by replacement of pyrrhotite during retrograde metamorphism.

TABLE 3. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF ARSENIDES AND SULFIDES FROM THE NORD MINE

Sample	Mineral	Weight %						Atomic proportions							Remarks
		Co	Ni	Fe	Cu	As	S	Total	Co	Ni	Fe	Cu	As	S	
1 87 C 2	Clinosafflorite	27.4	0.7	0.4	-	70.1	0.6	99.2	0.98	0.02	0.01		1.96	0.04	As + S = 2.00
2 87 C 2	Clinosafflorite	27.4	0.7	0.3	n.d.	70.7	0.2	99.3	0.98	0.02	0.01		1.99	0.01	As + S = 2.00
3 87 C 2	Cobaltite	35.2	0.3	0.1	n.d.	45.4	19.6	100.6	0.98	0.01	0.00		1.00	1.00	As + S = 2.00
4 87 A 2	Nickelian linnaeite	48.9	4.6	2.3	1.8	n.d.	41.1	98.7	2.59	0.25	0.13	0.09	4.00		lowest Cu
5 87 A 2	Nickelian linnaeite	47.3	6.2	1.0	4.0	n.d.	41.4	99.9	2.49	0.33	0.06	0.19	4.00		highest Ni
6 87 A	Cuprian linnaeite	45.8	2.9	2.5	6.1	n.d.	40.7	98.0	2.45	0.16	0.14	0.30	4.00		
7 87 A	Carrollite	43.5	2.3	1.6	9.9	n.d.	40.0	97.3	2.37	0.13	0.09	0.50	4.00		
8 87 A	Carrollite	43.6	2.1	0.9	12.7	n.d.	41.9	101.2	2.27	0.11	0.05	0.61	4.00		Fig. 4, Car 8
9 87 A	Carrollite	40.8	1.3	2.4	11.7	n.d.	39.0	95.2	2.28	0.17	0.14	0.61	4.00		Fig. 4, Car 9
10 87 A	Ferroan carrollite	41.4	1.3	4.4	10.5	n.d.	41.0	98.6	2.20	0.07	0.25	0.52	4.00		
11 87 TB	Siegenite	41.3	16.5	0.0	0.8	n.d.	42.4	101.0	2.12	0.85	0.00	0.04	4.00		in cobaltite
12 87 TB	Cuprian siegenite	36.4	11.8	2.6	8.4	n.d.	41.2	100.4	1.92	0.62	0.14	0.41	4.00		in cobaltite
13 87 TB	Fe-rich siegenite	20.0	23.2	13.7	-	n.d.	42.4	99.3	1.02	1.20	0.74		4.00		in cobaltite
14 87 A	Cattierite	31.8	-	16.3	-	n.d.	52.2	100.3	0.67		0.36		2.00		
15 87 A	Cobaltian pyrite	21.9	-	25.9	0.1	n.d.	53.7	101.6	0.45		0.55	0.00	2.00		rim around 16
16 87 A	Pyrite	0.3	-	46.2	-	n.d.	53.2	99.7	0.01		0.99		2.00		relic in 7

Analyses 1-3 performed with a Cambridge Microscan, corrected with a program modified after Springer (1967).

Analyses 4-16 performed with a Cambridge Mark 9, corrected with the on-line ZAF program.

Analysts: 1-13 C. Kieft, 14-16 W.J. Lustenhouwer; n.d. not determined, - not detected.

Arsenide-sulfide assemblage

The arsenide-sulfide assemblage is related to the light-colored actinolite-tremolite skarn. Cobaltite usually is the main mineral but, in some places, clinosafflorite prevails. Textural relations between the two minerals are shown in Figure 7 and schematically in Figure 8. Clinosafflorite, in contact with silicates and cobaltite, forms grains as much as 0.5 mm in diameter, and blebs up to 0.03 mm across in cobaltite. Other inclusions in cobaltite consist of bismuth, molybdenite and siegenite. Columns 11-13 in Table 3 give compositions of siegenite from such inclusions. Bismuth and molybdenite also occur as interstitial grains between silicates and opaque minerals (Fig. 8).

Clinosafflorite

Synthetic Co-rich diarsenides in the safflorite-loellingite series containing more than about 80 mole % CoAs_2 are monoclinic (Roseboom 1963, Radcliffe & Berry 1968). Natural clinosafflorite is rare and has only been reported from Cobalt, Ontario (Radcliffe & Berry 1971) and as "safflorite nickelifère" from several Moroccan deposits,

e.g., Bou-Azzer and Aghbar (Picot & Johan 1977).

Under the microscope, clinosafflorite is very similar to safflorite and to nickelian clinosafflorite (Picot & Johan 1977). Zoned crystals, as usually reported for safflorite and also described in "safflorite nickelifère", have not been observed. The reflectance of clinosafflorite has been measured on a grain showing the largest bireflectance (Table 2). The spectral curves for R_1 and R_2 cross at a wavelength of about 480 nm. This phenomenon has also been observed in members of the safflorite-loellingite series, the curves for loellingite FeAs_2 crossing at about 530 nm and the ones for safflorite $(\text{Co,Fe})\text{As}_2$ at about 510 nm (Petruk *et al.* 1971, Picot & Johan 1977). Rammelsbergite NiAs_2 does not show this feature (Petruk *et al.* 1971); it is interesting to note that, in contrast to the low-Ni clinosafflorite, the Ni-bearing Moroccan clinosafflorite does not show this crossing of the spectral curves.

The polishing hardness of clinosafflorite is lower than for cobaltite. Microindentation hardness (VHN) measurements on clinosafflorite (Table 2) yield strongly elongate convex impressions, the result of a considerable hardness anisotropy also known to exist in safflorite. The mineral is very brittle.

Microprobe analyses of the Nord mine clinosafflorite (Table 3) indicate a composition close to CoAs_2 , with only minor amounts of Fe, Ni and S. X-ray-diffraction data for clinosafflorite have been obtained on powder drilled out under the microscope and taken into a rubber solution. The powder pattern and the unit-cell data are given in Table 4 along with the pattern of synthetic CoAs_2 (PDF 14-412) and that of clinosafflorite from Cobalt (Radcliffe & Berry 1971).

GENETIC CONSIDERATIONS

The mineral assemblages (Table 1) and their textural relations indicate that pyrite, pyrrhotite and chalcopyrite included in the iron ores reacted with Co-bearing solutions to form the thiospinel-disulfide assemblage. The thiospinel associated with the iron sulfides is carrollite-linnaeite, whereas it is siegenite in the Co assemblage (Table 3). The compositions of the disulfides adjacent to or intergrown with different thiospinel grains in the presence of chalcopyrite are in accordance with the phase relations in the Cu-Co-Fe-S system as proposed by Craig *et al.* (1979). It is assumed that the two textural varieties of carrollite-linnaeite occurring with

TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR CLINOSAFFLORITE AND SYNTHETIC CoAs_2

Synthetic CoAs_2 PDF 14-412			Clinosafflorite* Cobalt, Ont.		Clinosafflorite** Nord mine, Sweden		
hkl	d _{obs.}	I/I ₁₀₀	d _{obs.}	I/I ₁₀₀	d _{obs.}	d _{calc.}	I/I ₁₀
111	3.83	8			3.824	3.823	2
020	2.936	12	2.932	10	2.929	2.931	2
111	2.758	18			2.768	2.764	2
002	2.666	45	2.671	40	2.669	2.673	3
200	2.648	45	2.657	40	2.652	2.651	3
121	2.536	100	2.531	100	2.533	2.534	10
012	2.429	60	2.427	80	2.432	2.432	4
210	2.413	50	2.422	80	2.419	2.416	4
212	2.319	25	2.313	20	2.312	2.316	3
221	2.083	4			2.054	{2.080	1
102	2.045	6				{2.050	
022	1.974	6				{1.975	
220	1.966	4			1.972	{1.973	2B
222	1.913	10			1.911	1.911	2
113	1.870	30	1.865	30	1.869	1.870	4
311	1.856	30	1.861	30	1.855	1.855	4
213	1.829	16			1.822	{1.829	
131	1.825	25				{1.822	4
013	1.702	2					
131	1.658	35	1.656	30	1.658	1.658	6
123	1.6370	14	1.636	10	1.638	1.637	1
321	1.6274	18	1.631	10	1.626	1.627	1
313	1.6176	18					
032	1.5777	10	1.576	5		{1.577	
230	1.5744	14	1.570	5	1.572	{1.572	3B
202	1.5637	16				{1.567	

a = 5.916 Å
b = 5.872
c = 5.960
β = 116°27'

a = 5.914 ± 0.003 Å
b = 5.862 ± 0.003
c = 5.962 ± 0.003
β = 116°16' ± 04'

*Data from Radcliffe & Berry (1971).

**Straumanns-type 114.57 mm Debye-Scherrer camera, Mn-filtered $\text{FeK}\alpha$ radiation.

the sulfides (Fig. 4) are replacement products of pyrrhotite and chalcopyrite, respectively. In the absence of chalcopyrite, disulfide crystals with zones of different Co contents have been formed.

Complete solid solution between FeS_2 and CoS_2 exists only above 600°C (Klemm 1965); solid solution in the carrollite-linnaite series extends at 700°C from 16.5 to 2 wt. % Cu, and at 600°C from 18 to 0 wt. % Cu (Craig *et al.* 1979). This temperature range is also suitable for coexisting cobaltite and clinosafflorite (Maurel & Picot 1974), and is in agreement with conditions of amphibole- and pyroxene-hornfels facies deduced from Magnusson's (1929) descriptions of the skarns related to the intrusion of the Gothian postorogenic granite.

The theories of Magnusson (1929) concerning the "invasion of sulfides" cannot be upheld any longer. As the Nordmark mine is located close to a late-orogenic granite (1841 Ma) and the Nord mine close to a postorogenic granite (1665 Ma), it is unlikely that the granites supplied the metals. The almost identical association of elements in both mines points to a common source for both cases of mineralization. The granites can only have served as a motor of mobilization of elements and recrystallization of minerals already present in the older volcano-sedimentary complex of supracrustal rocks.

The different types of iron ores and associated base metals are believed to have separated from a common volcanogenic source by geochemical differentiation (Zakrzewski 1982). Two associations of elements have been recognized in Bergslagen province: the Sikfors type, with Cu-Bi-Co-Mo-Au-Se-Te-W-Ce-As, and the Hällefors type, with Pb-Zn-Ag-Sb-Sn-Hg-Mn-As; the Cu-Bi-Co-Mo-bearing examples of mineralization of the Nord and Nordmark mines would thus represent the Sikfors type. In western Bergslagen, this group is related to iron ores interpreted to be chemical sediments formed under conditions of the iron silicate geochemical facies (Zakrzewski 1982). This is supported by the presence of 0.06-0.07 wt. % P in the iron ores of the Nord mine (Magnusson 1929), an order of magnitude higher than in other skarn iron ores.

The occurrence of a cobalt mineralization in the Nord mine in skarn outside the iron ores probably reflects a premetamorphic spatial relation in which cobalt minerals and associated phases formed an outer zone around the sediments that were the progenitors of the iron ores. The iron ores were also enriched in Co as manifested by the presence of 0.012 wt. % Co in the nearby Ång mine (Magnusson 1929). The

association of elements of the Nordmark and Nord mines points to a possible proximal character in relation to an exhalative centre; the Pb-Zn-Ag mineralization west of Nordmark (Magnusson 1929) and the mineralization in carbonate beds east of Filipstad (Magnusson 1925) would then represent the distal ores in the carbonate facies.

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