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ULLMANNITE, COBALTIAN ULLMANNITE AND WILLYAMITE FROM TUNABERG, BERGSLAGEN, CENTRAL SWEDEN

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ABSTRACT

Ullmannite, cobaltian ullmannite and willyamite from Tunaberg, southeastern Bergslagen, central Sweden, occur in aggregates and in symplectitic intergrowths up to 1 mm across with pyrrhotite, galena, chalcopyrite, breithauptite and nisbite. The symplectitic intergrowths are associated with textures indicating replacement of boulangerite and bournonite by galena and chalcopyrite. The association of sulfides and sulfosalts, including the (Co,Ni)–Sb–S phases, crystallized from hydrothermal solutions of complex polymetallic composition. Ullmannite with Co/(Co + Ni) less than 0.01 is rimmed by cobaltian ullmannite – willyamite solid solution with a Co/(Co + Ni) ratio between 0.31 and 0.87, mainly developed along boundaries of ullmannite and pyrrhotite. The development of zones of cobaltian ullmannite – willyamite solid solution progressively richer in Co around a core of virtually Co-free ullmannite is explained by a crystallization model along the NiSbS–CoSbS pseudobinary join that assumes a miscibility gap between ullmannite and cobaltian ullmannite – willyamite solid solution at low temperatures.

Keywords: ullmannite, cobaltian ullmannite – willyamite solid solution, crystallization model, miscibility gap, Tunaberg, Bergslagen, Sweden.

SOMMAIRE

A Tunaberg, dans l'extrémité sud-est du Bergslagen, en Suède, l'ullmannite, l'ullmannite cobaltifère et la willyamite se trouvent en agrégats et en intercroissances symplectitiques jusqu'à 1 mm de diamètre, en coexistence avec pyrrhotite, galène, chalcopyrite, breithauptite et nisbite. Les intercroissances symplectitiques sont associées à des textures de remplacement de la boulangerite et la bournonite par galène et chalcopyrite. L'association de sulfures et de sulfosels, y comprises les phases (Co–Ni)–Sb–S, a cristallisé à partir de solutions hydrothermales polymétalliques à composition complexe. Les grains d'ullmannite, dont le rapport Co/(Co + Ni) est inférieur à 0.01, sont recouverts par un membre de la solution solide entre ullmannite cobaltifère et willyamite, dont le rapport Co/(Co + Ni) se situe entre 0.31 et 0.87. Ce liseré se développe préférentiellement où l'ullmannite est en contact avec la pyrrhotite. La déposition d'un tel liseré progressivement plus riche en Co sur un grain d'ullmannite sans Co résulterait d'une cristallisation progressive dans le système pseudobinaire NiSbS–CoSbS. Le modèle présuppose une lacune de miscibilité entre ullmannite et la solution solide entre ullmannite cobaltifère et willyamite à faible température.

(Traduit par la Rédaction)

Mots-clés: ullmannite, solution solide entre ullmannite cobaltifère et willyamite, modèle de cristallisation, lacune de miscibilité, Tunaberg, Bergslagen, Suède.

INTRODUCTION

Ullmannite NiSbS, cobaltian ullmannite (Ni,Co)SbS and willyamite (Co,Ni)SbS were discovered in the Hultebo deposit during geological investigations in the Tunaberg area, in the southeastern part of the Precambrian metallogenic province of Bergslagen, central Sweden. The small mine at Hultebo is a Pb–Zn–Ag occurrence in fine-grained dark grey graphite-rich metasedimentary rock. The rocks have attained a metamorphic grade in the upper amphibolite facies.

The (Co,Ni)–Sb–S phases in the Hultebo ores occur in massive sulfide aggregates associated with quartz lenses and chlorite–muscovite streaks in the ore-bearing rock. The main sulfides are pyrrhotite and galena, which are partly replaced by chlorite–muscovite. Minor minerals are arsenopyrite, boulangerite, bournonite, breithauptite, chalcopyrite, freibergite, graphite, gudmundite, marcasite, molybdenite, nisbite, pyrite, sphalerite, ullmannite, willyamite and rutile.

Electron-microprobe analyses were performed with a Cambridge Instruments Geoscan equipped with a Link energy-dispersion system (EDS) and Microscan 9. Natural and synthetic compounds were used as standards. Apparent concentrations were ZAF-corrected with an on-line program. Compositions of the analyzed minerals are listed in Tables 1 and 2.

A review of the literature on phase relations in the system NiSbS–CoSbS indicates a lack of evidence for the existence of a miscibility gap between ullmannite and willyamite. In this paper, the occurrence in the Hultebo deposit of ullmannite, which has a Co/(Co + Ni) value of less than 0.01, with cobaltian ullmannite – willyamite solid solution having a Co/(Co + Ni) ranging from 0.31 to 0.87, is interpreted as evidence for a miscibility gap at lower-temperature conditions between virtually Co-free ullmannite and cobaltian ullmannite – willyamite solid solution.

TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF MINERALS FROM THE HULTEBO DEPOSIT

		Weight %										Atomic proportions								
Mineral	n	Fe	Ni	Sb	Pb	Cu	Ag	Zn	S	Others	Total	Fe	Ni	Sb	Pb	Cu	Ag	Zn	S	Others
Arsenopyrite	(1)	32.1		0.2					18.8	As 46.5, Co 1.6.	99.2	0.98							1	As 1.06, Co 0.05.
Boulangerite	(4)	-		24.9	56.4	-	-		18.1		99.5			5.30	3.97				11	
Bournonite	(1)	-		24.4	43.5	13.0	-		19.4		100.3			0.99	1.04	1.01			3	
Freibergite*	(2)	5.8		27.2		21.6	22.0	0.6	23.3		100.5	1.89		4.06		6.17	3.71	0.18	13.20	
Freibergite*	(5)	5.9		26.4		16.1	30.5	0.5	21.4		100.7	1.95		4.00		4.69	5.23	0.12	12.36	
Galena**	(4)			0.19			0.16			Bi -.										
Gudmundite	(2)	26.8	-	57.7					15.8	Co -.	100.3	0.98		0.96					1	
Sphalerite	(1)	11.4				-		53.3	34.0	Mn 1.6, Cd 0.4.	100.8	0.20						0.77	1	Mn 0.04.
Breithauptite	(1)	0.8	32.5	67.2					0.1	As 0.4, Co -.	100.6	0.02	1.00	1						
Nisbite	(1)	-	19.0	78.8		0.2			0.1	As 0.4.	98.5		1.00	2						

\- not detected; n number of analyses of minerals in samples RD 653-1 & 653-2.
* two freibergites with a different Ag/Cu ratio in the same sample. Formula based on 16 cations;
** trace elements

TABLE 2. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF (Co,Ni)-Sb-S PHASES

No.	Member ss.	Weight %.						Atomic proportions					Co/Co+Ni
		Co	Ni	Fe	Sb	S	Total	Co	Ni	Fe	Sb	S	
1	Ullmannite*	n.d	27.0	0.2	56.9	15.2	99.7		0.98	0.01	0.99	1	0.00
2		0.3	27.4	0.2	56.6	15.3	100.2	0.01	0.98	0.01	0.98	1	0.01
3	Cobaltian	8.5	18.7	0.9	57.3	15.5	101.3	0.30	0.66	0.03	0.97	1	0.31
4	ullmannite*	11.3	15.6	0.9	56.6	15.1	99.9	0.41	0.57	0.03	0.99	1	0.42
5		11.8	14.5	1.1	56.4	15.0	99.2	0.43	0.53	0.04	0.99	1	0.45
6		12.6	14.0	0.8	56.5	14.7	99.0	0.47	0.52	0.03	1.02	1	0.47
7	Willyamite*	14.3	12.8	1.0	56.6	14.9	99.1	0.52	0.47	0.04	1.00	1	0.53
8		15.2	12.3	1.0	57.1	15.0	101.0	0.55	0.45	0.04	1.00	1	0.55
9		15.3	11.7	0.4	56.8	15.3	99.9	0.55	0.42	0.02	0.98	1	0.57
10		16.3	11.2	1.2	57.0	15.3	101.4	0.58	0.40	0.05	0.98	1	0.59
11		17.7	9.6	1.1	56.2	14.9	99.9	0.64	0.35	0.04	0.99	1	0.65
12		18.3	9.6	0.9	57.4	15.0	101.6	0.66	0.35	0.03	1.01	1	0.66
13		18.4	8.2	1.2	56.9	15.1	100.2	0.66	0.30	0.04	1.00	1	0.69
14		19.0	7.7	1.0	56.3	14.9	99.3	0.70	0.28	0.04	1.00	1	0.72
15		21.7	3.7	1.6	56.9	14.9	99.4	0.79	0.14	0.06	1.01	1	0.84
16		22.5	3.2	1.6	57.3	15.1	100.1	0.81	0.12	0.06	1.00	1	0.87

* on average 0.4 wt.% As included (= 0.01 at. prop.). Bi n.d. Samples RD 653-1 & 653-2.

Review of (Co,Ni)–Sb–S Phases

Ullmannite, cobaltian ullmannite and willyamite have a pyrite-type crystal structure (Ramsdell 1925, Pratt & Bayliss 1980, Bayliss 1986). Ullmannite, NiSbS, belongs to the ullmannite subgroup and is cubic, with space group $P2_13$. The substitution of Co for Ni in cobaltian ullmannite, (Ni,Co)SbS, does not distort this cubic structure (Pratt & Bayliss 1980). Willyamite, CoSbS, belongs to the cobaltite subgroup and is pseudocubic, with an orthorhombic space-group $Pca2_1$ (Bayliss 1986). Two other polymorphs with composition CoSbS are costibite and paracostibite, which are orthorhombic with space-groups $Pmn2_1$ and *Pbca*, respectively (Cabri *et al.* 1970a,b). A review of the mineral phases and solid solutions in the NiSbS–CoSbS system is given below and in Figure 1.

Bayliss (1969) synthesized solid solutions in the cubic (Ni,Co)SbS series in the range from NiSbS to $Ni_{0.6}Co_{0.4}SbS$ at 550°C and suggested that the original willyamite, for which the composition $Co_{0.5}Ni_{0.5}SbS$ was reported (Pittmann 1893), is not a valid mineral species but rather a cobaltian ullmannite. A microprobe and X-ray reinvestigation by Cabri *et al.* (1970c) of Pittmann's type specimen of willyamite from Consols mine, Broken Hill, Australia, has re-established the existence of willyamite as pseudocubic (Co,Ni)SbS; it occurs in the type specimen as Co-rich rim zones with composition up to $Co_{0.95}Ni_{0.05}SbS$ around a core of cobaltian ullmannite $Ni_{0.63}Co_{0.37}SbS$, which is characterized by a cubic structure. The findings of Bayliss (1969) and Cabri *et al.* (1970c) suggest the existence of a (Ni,Co)SbS solid-solution series between cubic NiSbS (ullmannite) and pseudocubic CoSbS (willyamite), with the change from cubic to pseudocubic structure occurring near the composition with Co:Ni = 1 (Cabri *et al.* 1970c). Willyamite is defined as pseudocubic (Co,Ni)SbS with Co > Ni (Cabri *et al.* 1970c); as used in this paper, cobaltian ullmannite refers to (Ni,Co)SbS solid solutions with

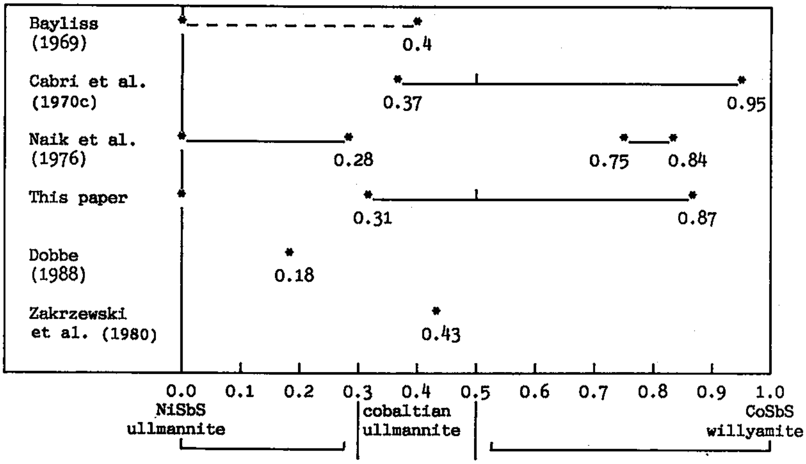

FIG. 1. Nomenclature and reported ranges of solid solutions in the system NiSbS–CoSbS. Broken line refers to synthetic phases; solid lines refer to minerals.

Co/(Co + Ni) from 0.3 to 0.5, whereas ullmannite refers to cubic (Ni,Co)SbS with a Co/(Co + Ni) value of less than 0.3 (Fig. 1).

The phase relations in the system NiSbS–CoSbS may be considered as essentially analogous to those in the NiAsS (gersdorffite) - CoAsS (cobaltite) system, which shows complete miscibility at higher temperatures (above 550°C in NiAsS–CoAsS system; Klemm 1965) and a miscibility gap at lower temperatures. Thus, although the solid-solution ranges in the (Ni,Co)SbS series as reported by various authors overlap and suggest a complete solid-solution series (Fig. 1), the possibility of occurrence of a miscibility gap in the (Ni,Co)SbS series at lower temperatures, presumably below 550°C (Bayliss 1969), cannot be precluded. This paper presents paragenetic evidence from the Hultebo deposit for the existence of such a miscibility gap.

Willyamite solid solution with Co/(Co + Ni) between 0.75 and 0.84 and ullmannite - cobaltian ullmannite solid solution with Co/(Co + Ni) between 0 and 0.28 have been reported to occur as inclusions in galena from Espeland, Norway (Naik *et al.* 1976).

Cobaltian ullmannite with a Co/(Co + Ni) of 0.43, costibite, paracostibite and nisbite have been described from Getön, western Bergslagen, Sweden (Zakrzewski *et al.* 1980). In the Pb–Zn ores of the Klenbystugan deposit in the Tunaberg area, ullmannite [Co/(Co + Ni) = 0.18], (para)costibite and nisbite have been identified (Dobbe 1988).

DESCRIPTION OF ORE MINERALS

(Ni,Co)-Sb-S phases

Co-free ullmannite and cobaltian ullmannite -

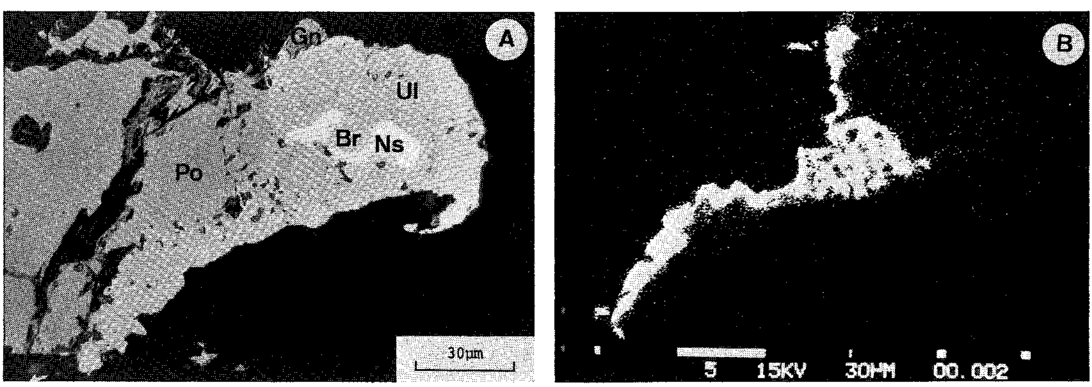

FIG. 2. A. Ullmannite (Ul) with inclusions of nisbite (Ns) and breithauptite (Br) is separated from pyrrhotite (Po) by a rim of willyamite (not visible, but see Fig. 2B). Black areas are gangue minerals. B. Electron microprobe Co*K*α X-ray scanning micrograph of same area shown in Fig. 2A.

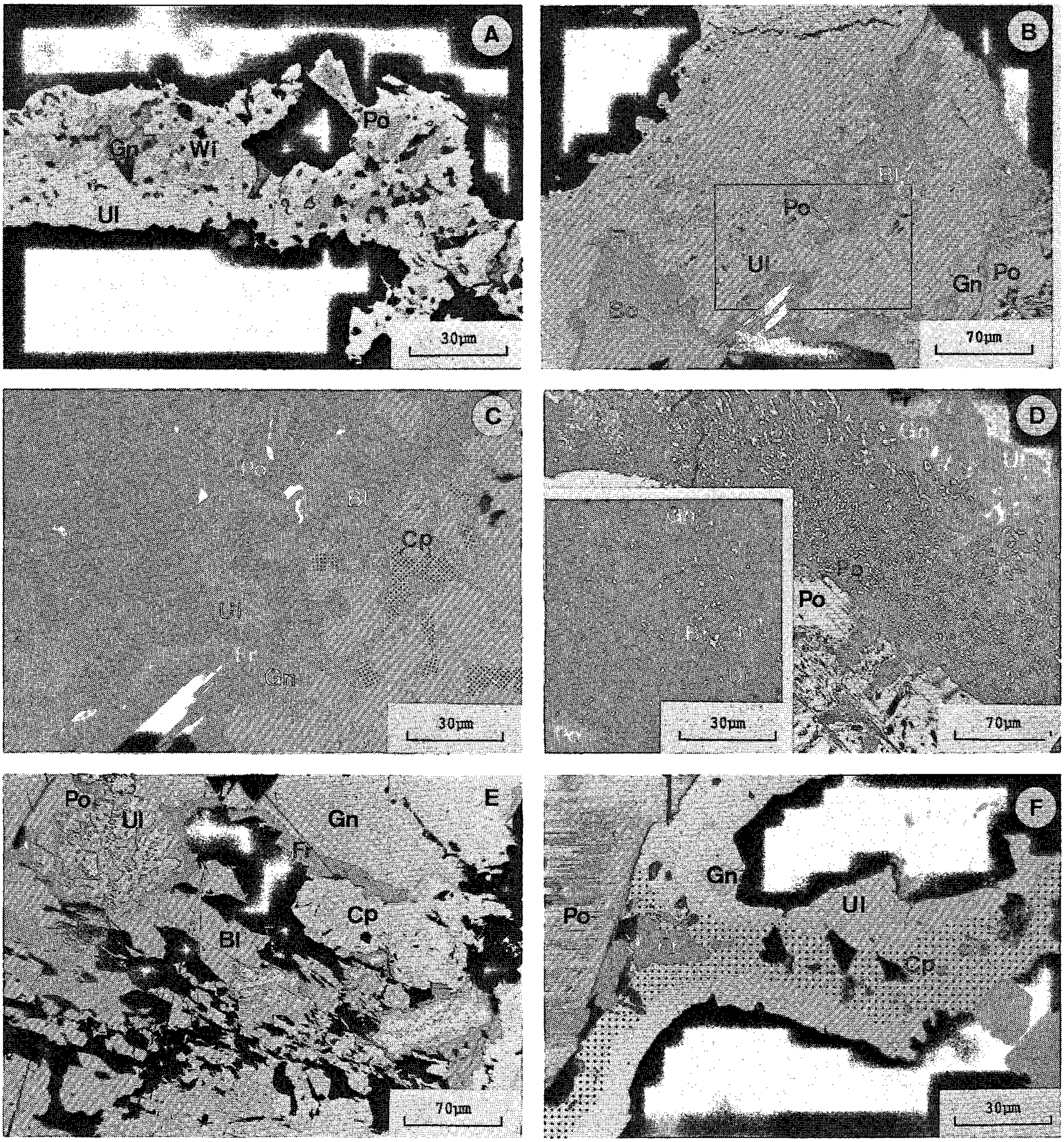

FIG. 3. A. Co-free ullmannite (Ul) rimmed by willyamite (Wi) containing inclusions of pyrrhotite (Po), galena (Gn) and gangue minerals. B. Symplectitic intergrowths of ullmannite (Ul), pyrrhotite (Po), galena (Gn) and chalcopyrite. Boulangerite (Bl) and bournonite (Bo) are replaced by galena and the intergrowths with ullmannite. Freibergite (Fr) occurs as rims along bournonite grain boundaries. Cobaltian ullmannite occurs as rims and edges around ullmannite in the symplectitic intergrowth with pyrrhotite, galena and chalcopyrite. Left of boulangerite: ullmannite–pyrrhotite–galena symplectite with chalcopyrite-bearing domains (not visible); right of boulangerite: ullmannite–chalcopyrite–galena symplectite (see text and Fig. 3C). C. Enlargement of Fig. 3B. Upper left-hand side of picture shows fine-grained vermicular ullmannite–pyrrhotite–galena symplectite coarsening toward the sulfosalts. Right-hand side of picture shows coarse and more blocky ullmannite–chalcopyrite–galena symplectite. Chalcopyrite (Cp) grains are stippled. D. Rim of vermicular ullmannite (Ul) – pyrrhotite (Po) – galena (Gn) symplectite between large pyrrhotite and galena grains (upper right-hand side) with sulfosalts. Pyrrhotite flakes in symplectites have the same orientation as in the large pyrrhotite grains. Nicols partly crossed. Insert: Small oriented breithauptite (Br) inclusions in same type of ullmannite–pyrrhotite–galena symplectite as shown in Fig. 3D. Nicols partly crossed. E. Oriented boulangerite (Bl) replacement relics in galena (Gn) and chalcopyrite (Cp). These textures are associated with ullmannite (Ul) in symplectitic intergrowths. F. Freibergite (Fr) with chalcopyrite (Cp) and ullmannite (Ul) as fracture fillings between gan-

willyamite solid solution have virtually identical optical properties. They are isotropic and have a white color with a faint greenish tint, in contrast to pyrrhotite. Ullmannite and cobaltian ullmannite - willyamite solid solution occur in different textural varieties. Ullmannite, in contrast with cobaltian ullmannite - willyamite solid solution, forms larger and clean grains without inclusions of sulfides, whereas the cobaltian ullmannite - willyamite solid solution has a "dirty" look, with inclusions of gangue minerals, pyrrhotite and galena (Figs. 2A,2B,3A). Definite identification of the two minerals can only be obtained with the microprobe results.

Ullmannite occurs rarely as small isolated inclusions in galena. Irregularly shaped grains up to 200 μm across adjacent to pyrrhotite consist of ullmannite that is always separated from the pyrrhotite by a thin rim of cobaltian ullmannite - willyamite solid solution (Figs. 2A,B). These rims of cobaltian ullmannite - willyamite solid solution are less well developed along boundaries of 1) ullmannite and gangue minerals, 2) pyrrhotite and gangue minerals, and 3) ullmannite and chalcopyrite. Pyrrhotite and galena are generally replaced by the (Ni,Co)-Sb-S phases. Complex symplectitic intergrowths of ullmannite and cobaltian ullmannite - willyamite solid solution with pyrrhotite, galena and chalcopyrite are found between the gangue minerals and as aggregates up to 1 mm in galena along the contact with pyrrhotite (Fig. 3B). The symplectite mainly consists of fine-grained vermicular to lamellar ullmannite-pyrrhotite-galena intergrowths (Figs. 3C,D), which become more coarse grained and blocky near contacts with the sulfosalts and gangue minerals (Figs. 3B,E). The vermicular intergrowths may contain more coarse-grained and blocky domains with minor or no pyrrhotite; chalcopyrite is a constituent of such intergrowths. These chalcopyrite-dominant intergrowths also are observed as separate areas of symplectite between pyrrhotite and sulfosalts (Figs. 3B,C). The (Ni,Co)-Sb-S phases in the intergrowths show the usual textural development, with homogeneous Co-free ullmannite surrounded by rims and irregular edges of cobaltian ullmannite - willyamite solid solution along the contacts with the intergrown sulfides. The pyrrhotite and galena in the intergrowths display the same orientation as in adjacent large grains (Fig. 3D). The formation of the symplectites is interpreted as a late-stage replacement of the earlier sulfides by ullmannite and still later by cobaltian ullmannite - willyamite solid solution.

Breithauptite occurs as small grains with one dominant orientation, crystallographically intergrown with pyrrhotite in the ullmannite-pyrrhotite-galena symplectite (Fig. 3D, insert). Breithauptite also occurs as round or elongate grains (smaller than 50 μm) in pyrrhotite along contacts with galena. Small round inclusions of breithauptite and elongate grains of nisbite are commonly found in ullmannite (Fig. 2A) and occasionally also in contact with cobaltian ullmannite - willyamite solid solution. Furthermore, nisbite is observed as idiomorphic inclusions in galena and between pyrrhotite and galena grains. The mineral is white in comparison with ullmannite, and displays a more yellowish tint where enclosed in galena.

Results of electron-microprobe analyses of (Ni,Co)-Sb-S phases are listed in Table 2. The presence of complex intergrowths of the cobaltian ullmannite - willyamite solid solution with sulfides has influenced the selection of points for analysis. The preferred points for analysis are in more or less homogeneous parts of grains, which generally seem to show highest Co-contents within the grain. This selection procedure resulted in an abundance of data for willyamite over cobaltian ullmannite. Cobaltian ullmannite with a Co/(Co + Ni) of 0.31 (anal. 5) rims ullmannite in a symplectitic intergrowth. The other analyses of cobaltian ullmannite - willyamite solid solution pertain to rims along the boundary of ullmannite and other minerals described above. The analyses suggest a continuous range of composition for the cobaltian ullmannite - willyamite solid solution, from a Co/(Co + Ni) of 0.31 (anal. 3) to 0.87 (anal. 16); the two small discontinuities between a Co/(Co + Ni) of 0.31 and 0.42 (anal. 3,4), and between 0.72 and 0.84 (anal. 14,15) are considered as accidental. No Co was detected in breithauptite and nisbite (Table 1).

Sulfosalts

Boulangerite occurs as tabular crystals up to 800 μm across in galena; the mineral is commonly rimmed and presumably replaced by bournonite and freibergite. Boulangerite inclusions in chalcopyrite and galena with the same orientation as in adjoining crystals of boulangerite are interpreted as replacement relics of boulangerite in chalcopyrite and galena. These replacement textures are nearly always associated with the formation of the symplectitic texture described above (Figs. 3B,E). Bournonite also is rimmed and replaced by freibergite and chalcopyrite (Fig. 3B). Two varieties of freibergite are observed in the Hultebo deposit (Table 1). Inclusions of freibergite with 22 wt.% Ag is found in galena

gue minerals and pyrrhotite (Po). A thin rim of willyamite between chalcopyrite (stippled) and ullmannite is indicated by the microprobe.

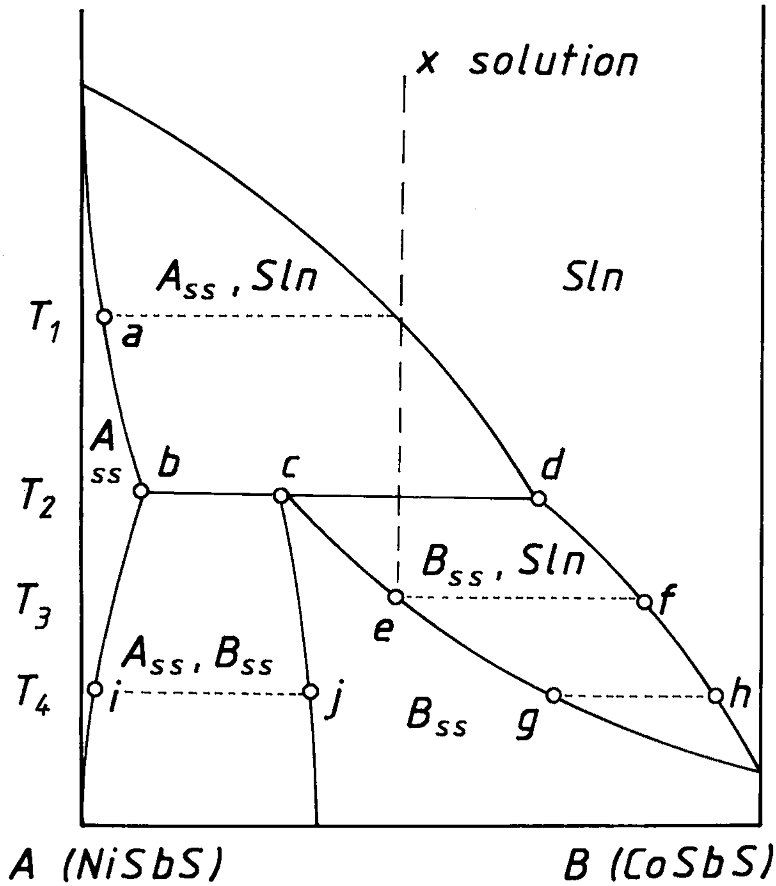

FIG. 4. Hypothetical phase-relations depicting crystallization along the pseudobinary join NiSbS–CoSbS in a system of Ni–Co–Sb–S-bearing hydrothermal fluid. Sln refers to solution.

along its contacts with sphalerite. Freibergite with 30 wt.% Ag is found in gangue accompanied by galena, chalcopyrite and ullmannite (Fig. 3F), and in galena associated with boulangerite, bournonite, chalcopyrite and ullmannite (Fig. 3B).

DISCUSSION

In the Hultebo deposit, the paragenesis of sulfides and sulfosalts, including the (Co,Ni)–Sb–S phases, is generally interpreted to have originated from metamorphogenic or postmetamorphic hydrothermal solutions that have remobilized Co, Ni and other metals during their percolation through the rocks.

The replacement relations and intergrowth textures in the Hultebo deposit indicate an overlapping paragenetic sequence of: (1) the sulfides galena, pyrrhotite, chalcopyrite (and Co-free ullmannite); (2) the Pb–Sb sulfosalts boulangerite and bournonite; (3) symplectitic intergrowths of ullmannite and sulfides, breithauptite and nisbite, rims and interstitial fillings of freibergite and cobaltian ullmannite – willyamite solid solution. The crystallization of ullmannite followed by cobaltian ullmannite – willyamite solid solution from a cooling hydrothermal solution of complex composition can be explained by the model illustrated in Figure 4.

Figure 4 shows the hypothetical phase-relations along the pseudobinary join NiSbS–CoSbS, in a system of Ni–Co–Sb–S-bearing hydrothermal fluid. A miscibility gap at lower temperatures is assumed in analogy to the system NiAsS (gersdorffite) – CoAsS (cobaltite), which shows a miscibility gap below 550°C (Klemm 1965). In Figure 4, crystallization from a cooling hydrothermal fluid of composition x will start at temperature T_1 with precipitation of Co-poor ullmannite of composition a. During cooling from T_1 to T_2, reactions between solid and fluid phases will cause the composition of the ullmannite to change toward b, while the composition of the fluid phase shifts toward *d*. At temperature T_2, the peritectic-type reaction ullmannite *b* + fluid *d* = cobaltian ullmannite *c* will take place. Rims of *c* around *b* are the result of incomplete reaction. During further cooling below temperature T_2, the composition of the fluid will change along *d–f*, while cobaltian ullmannite - willyamite solid solution of composition *c–e* crystallizes. In case of non-equilibrium crystallization, a rest-fluid *f* remains at T_3, and continued crystallization down to T_4 will result, with crystals *e–g* precipitating from fluids *f–h*. During the cooling from T_2 to T_4, the relict crystals *b* will tend to establish a new equilibrium: the composition of crystals *b* changes to that of crystals *i* as a result of segregation of small amounts of cobaltian ullmannite *j*. The result at temperature T_4 consists then of virtually Co-free ullmannite *i* surrounded by a rim of cobaltian ullmannite - willyamite solid solution *j* and *c–g*.

The zoned crystals described from the Consols mine, which have a core of cobaltian ullmannite and a rim of almost pure willyamite (Cabri *et al.* 1970c), may have crystallized, according to this model, from a cooling hydrothermal solution richer in Co than *d*. The ullmannite - cobaltian ullmannite and willyamite solid solutions described by Naik *et al.* (1976) were apparently not formed by crystallization from hydrothermal solutions, but by solid-state exsolution from a complex solid-solution with galena at temperatures below the ullmannite - willyamite solvus. The different ranges of ullmannite and willyamite solid solutions found by Cabri *et al.* (1970c), Naik *et al.* (1976), and in the present paper, suggest that the solvus boundaries depend strongly on composition, temperature, and other physicochemical conditions of crystallization in complex natural systems. Therefore, slightly different conditions of crystallization in different deposits may result in overlapping ranges of the solid-solution series, and thus create the false impression that a complete range of solid solution does exist between ullmannite and willyamite at low temperatures.

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