Contribution to the mineralogy of Norway, No. 62.

(Co,Ni)SbS phases and argentian boulangerite in galena from Espeland, Norway

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Naik, M. S., Griffin, W. L. & Cabri, L. J.: (Co,Ni)SbS phases and argentian boulangerite in galena from Espeland,Norway. Contribution to the mineralogy of Norway, No. 62. *Norsk Geologisk Tidsskrift,* Vol. 56, pp. 449–454. Oslo 1976.

Ullmannite, cobaltian ullmannite and willyamite occur as blebs and laths in galena from Espeland, Aust-Agder, Norway. There is continuous solid solution from $Co/Co+Ni=0$ to $Co/Co+Ni=0.28$, and from $Co/Co+Ni=0.75$ to $Co/Co+Ni=0.84$. Among the numerous other inclusions in the galena are native Bi and several Ag-bearing sulfosalts, including boulangerite with up to 4.9 wt. % Ag.

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The Espeland mine is a small galena deposit located SW of Vegårshei church in Aust-Agder fylke, southern Norway. The mineralization occurs where small aplite veins cut a schistose amphibolite; a galena-rich ore zone about one meter wide is surrounded by an irregular zone of sulfide impregnation in the amphibolitic wall rock. The major sulfides are galena, pyrrhotite, and sphalerite; chalcopyrite and arsenopyrite also occur locally. Moorbath & Vokes (1963) reported a model Pb-isotope age of 1516 ± 60 m.y. for the galena.

Oftedal (1942) included material from Espeland in his study of Bi- and Ag-rich galenas. He described probable exsolution bodies in the galena; these included native Bi, pyrargyrite, schapbachite (matildite), and several unidentified phases. Naik (1975), using a combination of ore microscopy and microprobe studies, distinguished and analyzed 12 different mineral inclusions in the galena (Table 1). Three of these were designated as phases A, B, and C pending further work. These have now been identified as, respectively, cobaltian ullmannite, willyamite, and argentian boulangerite.

Description

The occurrence and associations of the various included minerals are summarized in Table 1.

Ullmannite occurs as isolated irregular laths up to 100 μm long. *Cobaltian ullmannite* (phase A of Naik (1975)) occurs as elongated, irregularly shaped

Table 1. Occurrence of phases included in galena.

Zone	Phases in galena	Observed intergrowths
Wall rocks	pyrrhotite $Fe_{1-x}S$	Co-ullm.+pyrrh.±sphalerite
	sphalerite ZnS	
	Co-ullmannite (Ni,Co)SbS	
	Ag-boulangerite $(Pb,Ag)_5Sb_4S_{11}$	
	freibergite $(Cu,Ag,Fe)_{12}Sb_4S_{13}$	
Ore zone	bismuth Bi	
	pyrrhotite $Fe_{1-x}S$	willyamite + pyrrhotite ± breithauptite
	sphalerite ZnS	
	breithauptite NiSb	breithauptite + pyrrhotite
	gudmundite FeSbS	stephanite + pyrrhotite
	ullmannite NiSbS	
	Co-ullmannite (Ni,Co)SbS	
	willyamite (Co,Ni)SbS	
	freibergite $(Cu,Ag,Fe)_{12}Sb_4S_{11}$	
	pyrargyrite Ag_3SbS_3	
	stephanite Ag_5SbS_4	
	heesite Ag_2Te	

grains, commonly intergrown with pyrrhotite along its margins (Fig. 1). The grains are so small and scattered that no obvious preferred orientation could be established. A grain 33×55 μm in size was removed from specimen E 38 (wall zone) for X-ray on the Gandolfi camera. The pattern contained many

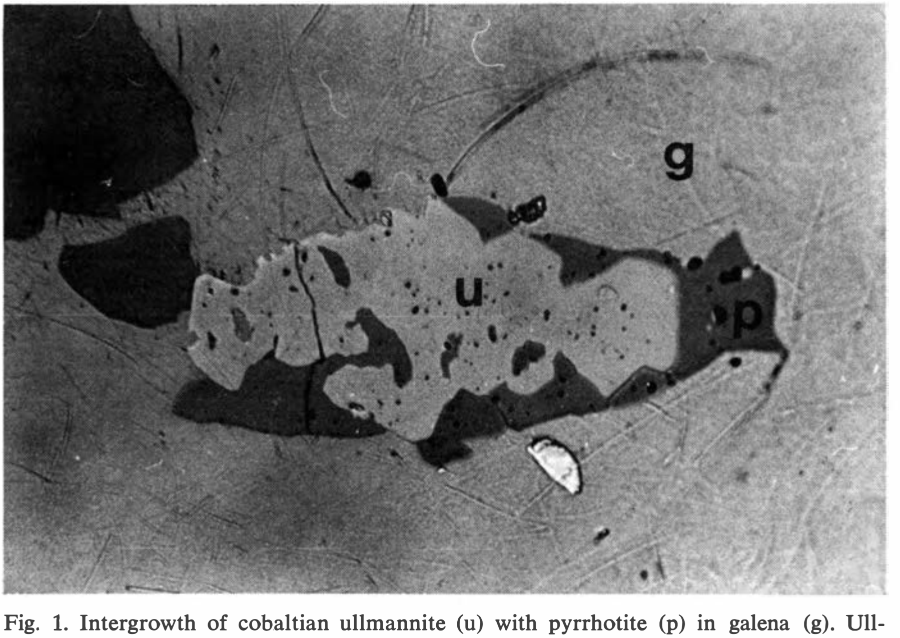

Fig. 1. Intergrowth of cobaltian ullmannite (u) with pyrrhotite (p) in galena (g). Ullmannite grain is ca. 100 μm long. Bright grain is native bismuth (Bi). Sample E38.

Table 2. Chemical analyses of Ni-Co phases.

	Ullmannite		Co-ullmannite							Willyamite			
	1	2	3	4	5	6	7	8	range	9	10	11	range
Co	tr	tr	2.7	4.1	4.7	5.0	5.5	5.7	0.93–7.7	21.2	22.8	23.3	20.5–23.3
Fe	tr	tr	0.37	0.30	0.45	0.41	0.81	0.35	0.26–0.90	0.44	tr	tr	0.0–0.61
Ni	28.0	29.0	25.0	23.3	22.9	22.9	22.8	22.3	20.0–26.8	6.1	4.5	4.7	4.5–6.7
Sb	57.3	56.7	55.9	57.1	56.1	56.7	55.3	57.1	55.7–57.2	57.5	57.4	57.2	57.2–57.8
S	14.9	15.0	14.7	15.4	14.9	15.2	15.4	14.4	14.7–15.5	15.2	15.4	15.0	14.8–15.5
Σ	100.2	99.7	98.67	100.20	99.05	100.21	99.81	99.85	– –	100.44	100.1	100.2	– –
Atomic proportions, 3 atoms:													
Co	–	–	0.098	0.147	0.171	0.179	0.196	0.207	– –	0.761	0.820	0.839	
Fe	–	–	0.014	0.011	0.013	0.015	0.030	0.013	– –	0.017	–	–	
Ni	1.013	1.013	0.915	0.838	0.834	0.823	0.814	0.813	– –	0.220	0.162	0.170	
Sb	1.000	0.990	0.987	0.990	0.987	0.983	0.952	1.004	– –	0.999	0.999	0.997	
S	0.997	0.997	0.985	1.014	0.994	1.000	1.007	0.962	– –	1.003	1.018	0.993	
Co/Co+Ni	0	0	0.10	0.15	0.17	0.18	0.19	0.20	0.03–0.28	0.78	0.84	0.83	0.84–0.75

Comments: Analyses 3, 5 and 9 done in Ottawa (anal. J. H. G. Laflamme); others done in Oslo (anal. W. L. Griffin). Grains 3–8 are from wall rock (samples E 38, E 10); others are from ore zone (sample E 37).

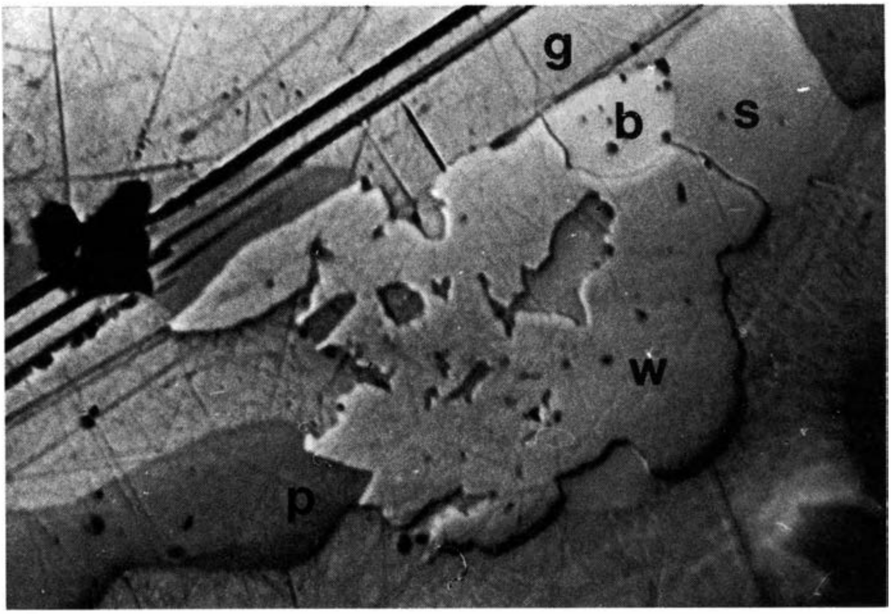

Fig. 2. Intergrowth of willyamite (w) with galena (g), sphalerite (s), breithauptite (b), and pyrrhotite (p). Willyamite grain is ca. 40×55 μm. Sample E37.

lines of galena, sphalerite, and pyrrhotite. Only the (112) reflection of ullmannite at 2.41Å could be distinguished, because of overlap with the other minerals; this was measured and calculated to a cell edge of 5.91 Å. This would indicate a Co/Co+Ni of about 0.20 using the curve of Bayliss (1969), which lies within the range of the analyzed grains from this sample (Table 2).

Willyamite (phase B of Naik (1975)) occurs as equidimensional grains up to about 60 μm across, with irregular outlines. It is commonly complexly intergrown with pyrrhotite and breithauptite (Fig. 2).

These three phases are nearly identical in their optical properties. All are white in color, sometimes with a faint creamish tint. They are optically isotropic, and have higher reflectivity and greater polishing hardness than galena. The various phases were distinguished during the microscopic studies by the textural differences among them. This proved, as might be expected, to be a fallible guide. Naik (1975) reported cobaltian ullmannite only from the wall rock; further microprobe studies have revealed this phase, as well as ullmannite and willyamite, in grains of galena from the ore zone.

Argentian boulangerite (phase C of Naik (1975)) is found as irregular blebs up to 70×200 μm, and shows distinct bireflectance from olive-green to bright yellow-green. Its polishing hardness is lower than that of galena, while its reflectivity is about the same as galena's. A 40×55 μm grain was removed for X-ray with the Gandolfi camera and gave a mixed pattern of boulangerite and galena. Silver-free boulangerite was also found in the same sample (Table 3, anal. 4).

Table 3. Analyses of boulangerite inclusions in galena.

	1	2	3a	3b	4
Pb	49.3	50.3	49.6	50.4	55.8
Ag	4.7	4.9	3.2	3.5	0.0
Cu	0.52	0.26	0.2	0.2	0.1
Sb	26.6	26.6	26.4	26.9	24.5
S	19.1	18.8	18.6	18.9	18.9
Σ	100.22	100.86	98.0	99.9	99.3
Formula, 20 atoms					
Pb	4.311	4.426	4.471	4.467	5.071
Ag	0.789 } 5.25	0.828 } 5.33	0.561 } 5.09	0.558 } 5.11	– } 5.11
Cu	0.148	0.076	0.056	0.055	0.038
Sb	3.958	3.983	4.060	4.063	3.789
S	10.792	10.689	10.851	10.827	11.103

Comments: Analyses 1+2 done in Oslo (Naik 1975); others in Ottawa (anal. T. T. Chen). Analyses 3a and 3b from one grain.

Chemistry

Microprobe analyses were carried out in Oslo using an ARL-EMX microprobe at 20KV accelerating voltage and 0.2×10^{-6} amperes sample current. Probe analyses done in Ottawa used a MAC 400 instrument at 25KV accelerating voltage and 0.03×10^{-6} amperes. Standards in both cases were natural sulfides, synthetic sulfides, and pure metals. Oslo data were reduced using the Springer program, Ottawa data using the ERPMAG program, modified from EMPADR VII (Rucklidge & Gasparini 1969) and MAGIC IV (Colby 1971). X-ray studies were carried out in Ottawa.

Analyses of the three (Co,Ni) phases are presented in Table 2. Each analysis represents an average of 2–5 spots on a single grain. The individual grains of cobaltian ullmannite and willyamite are typically very irregularly inhomogeneous; there is in some cases nearly as much variation within a single grain as among the averages of several grains. The analyses demonstrate that a complete range of compositions is present from pure ullmannite (Co/Co+Ni=O) to cobaltian ullmannite with Co/Co+Ni=0.28. Willyamite ranges in composition from Co/Co+Ni=0.84 to Co/Co+Ni=0.75. Although no exhaustive search has been made to find the extreme compositions in each series, the compositional gap between the two series is large and appears to be real.

Analyses of boulangerite and argentian boulangerite are presented in Table 3. Naik (1975) suggested a formula of $Pb_{11}Ag_2Sb_{10}S_{27}$ for 'Phase C'. The analyses (especially the Ottawa analyses) may also be recalculated to a boulangerite formula $(Pb,Ag)_5Sb_4S_{11}$, in agreement with the X-ray data. This is the only occurrence of an argentian boulangerite known to the authors.

Discussion

Cabri et al. (1970a) demonstrated that the original definition of willyamite as $Co_{0.5}Ni_{0.5}SbS$ (Pittman 1893) was based on analysis of strongly zoned material. They redefined willyamite as that part of the pseudocubic (Co,Ni) SbS series with $Co/Co+Ni>0.5$, and designated the part of the series with $Co/Co+Ni<0.50$ as cobaltian ullmannite. Two orthorhombic CoSbS phases have also been described; these are costibite (Cabri et al. 1970b) and paracostibite (Cabri et al. 1970c). The material studied here represents the second known occurrence of willyamite.

While ullmannite is cubic, willyamite is pseudocubic. The change in crystal structure may take place near $Co/Co+Ni=0.5$ (Cabri et al. 1970a); the synthesis experiments of Bayliss (1969) suggest that the maximum Co substitution possible in ullmannite is $Co/Co+Ni=0.40$. If so, this could explain the observed gap in composition between willyamite and cobaltian ullmannite grains in the Espeland galenas. However, if the analysed inclusions formed by exsolution from the galena, they may represent widely different temperatures of exsolution. In this case the observed compositions may simply reflect different rates of exsolution for Ni and Co. A similar interpretation may be applied to the occurrence of argentian boulangerite and silver-free boulangerite in the same sample. At present too little is known about the genesis of this deposit to allow reliable estimates of crystallization temperatures or cooling history.

Acknowledgements: T. T. Chen and J. H. G. Laflamme carried out probe analyses in Ottawa; J. M. Stewart helped with the X-ray diffraction analyses. F. S. Nordrum contributed valuable help with the microscopy and several useful criticisms.

June 1975

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