Silver sulphosalts in galena from Espeland, Norway

M. S. NAIK

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The silver-bearing phases in galena from Espeland are freibergite, unknown 'phase C' ($Pb_{11}Ag_2Sb_{10}S_{27}$), pyrargyrite, stephanite and hessite. The compositions of these phases were determined by electron microprobe. Freibergite is homogeneous in composition with an average 35 percent silver. The average calculated atomic proportions $(Cu,Ag,Fe)_{12.2}Sb_4S_{12.4}$, deviate from the stoichiometric composition $(Cu,Ag,Fe,Zn)_{12}(SbAs)_4S_{13}$ of tetrahedrite. It has been found that most of the silver present in the ore occurs in the silver phases and not in structural positions in the galena lattice.

M. S. Naik, Mineralogisk-geologisk museum, Sars gate 1, Oslo 5, Norway. Present address: Indian School of Mines, Dhanbad, Bihar, India.

Galenas with high contents of bismuth and silver have been described from Espeland and other localities in Norway by Oftedal (1942). He proposed that Bi atoms enter into the PbS lattice without causing any distortion, if an equal number of Ag atoms enter simultaneously. The excess of Bi over (BiAg) was considered to be responsible for the octahedral parting in some of these galenas.

In the present study of the silver bearing galena from Espeland it has been found that the galena contains inclusions of several silver-bearing phases, as well as native bismuth, while the galena itself contains only normal amounts of Ag and essentially no Bi.

Geology of the Espeland deposit

The Espeland deposit is located SW of Vegårshei church, between the farms Myre and Espeland in Aust-Agder fylke, southern Norway. It lies in schistose amphibolite only 60–80 meters from the contact of the Telemark granites. Sulphide mineralization is largely confined to irregular veins of granitic aplite; lesser amounts are found in pegmatite and quartz veins, and as impregnations in the adjoining wallrocks. The major sulphides are galena, pyrrhotite and sphalerite, with minor chalcopyrite and arsenopyrite. The mine was in operation in two periods (1879–84, 1890–91) and produced less than 500 tons of galena concentrate. This concentrate, however, ran 0.3–0.6 % Ag. The mine workings are now inaccessible. The samples were collected from the dumps and surface exposures of the wallrocks.

Mineral descriptions

The occurrence and associations of the silver sulphosalts in the galena are summarized in Table 1. The other inclusion phases will be the subject of a separate report.

Freibergite occurs as rods (up to 0.5 × 0.1 mm) and fine lamellae (up to 1.0 × 0.2 mm). The mineral is grey to greenish grey in colour and isotropic.

Phase C is found as blebs (up to 0.7 × 0.2 mm) and shows distinct bireflection from olive green to bright yellowish green. Reflectivity is equal to that of galena, while polishing hardness is lower.

Pyrargyrite is present as irregularly shaped grains up to 0.5 mm long and 0.2 mm thick. It is bluish green in colour and shows red internal reflection.

Euhedral grains of *stephanite* from 0.2 × 0.2 mm to 0.3 × 0.3 mm in size are pale green in colour, with weak bireflection.

In reflected light the mineral *hessite* (up to 0.3 × 0.2 mm in size) is yellow in colour with a distinct green tint and shows high reflectivity.

Bismuth occurs as equidimensional grains from 0.2 mm to 0.3 mm in diameter. The mineral is bright yellow in colour.

All the silver phases in galena are found as isolated grains and no textural relationships between them, or with the associated minerals, have been observed.

Chemistry

The silver phases were analysed using the ARL-EMX microprobe housed in the Central Institute for Industrial Research, Oslo. The standards used were Elba pyrite for Fe and S, galena for Pb, chalcopyrite for Cu, arsenopyrite for As, sphalerite for Zn and the pure metals for Ag and Sb. Accelerating voltage was 20 KV, sample current 0.2×10^{-6} amperes. Raw data were reduced using the Springer correction program.

Table 1. Occurrence and associations of silver sulphosalts in the galena.

Mineral	Occurrence	Association	Other inclusions
Phase C ($Pb_{11}Ag_2Sb_{10}S_{27}$)	wall rock	–	Freibergite Phase A (Ni,Co) SbS
Freibergite	wall rock and ore body	–	Phase C + Phase A
Pyrargyrite Stephanite Hessite	ore body	Pyrrhotite + Bismuth + Breithauptite	Ullmannite Gudmundite Phase B (Co,Ni) SbS

Table 2. Chemical compositions and atomic proportions of freibergite.

	Cu	Ag	Fe	Sb	S	Total
	Chemical compositions (weight percent)					
1	13.81	34.10	5.27	25.75	20.94	99.87
2	13.69	34.13	5.57	25.76	21.37	100.48
3	12.96	35.08	5.61	26.04	20.35	100.24
4	12.22	37.86	6.05	24.27	20.17	100.57
	Atomic proportions					
	14.54	21.15	6.32	14.15	43.71	
	14.35	21.25	6.65	14.09	44.30	
	13.77	21.96	6.79	14.44	43.29	
	13.07	23.85	7.36	13.55	42.75	
Av.	13.93	22.05	6.78	14.05	43.51	

Zn and As were looked for but not detected.

Table 3. Analyses of phase 'C'.

	Pb	Ag	Cu	Sb	S	Total
	Chemical composition (weight percent)					
1	49.26	4.73	0.52	26.62	19.09	100.22
2	50.32	4.89	0.26	26.56	18.78	100.81
	Atomic proportions					
	21.54	3.97	0.73	19.80	53.94	
	22.15	4.13	0.36	19.90	53.44	

Table 4. Analyses of pyrargyrite and stephanite.

	Ag	Sb	S	Total		Ag	Sb	S	Total
1	58.62	21.78	17.97	98.37		68.65	15.63	16.42	100.70
2	60.11	22.20	18.09	100.70		69.85	15.00	17.06	101.91
3	59.66	21.78	17.97	99.41		68.12	15.49	16.53	100.14
4	61.63	22.21	18.09	100.93		69.31	15.22	16.05	100.58
Ag_3SbS_3 theoretical	59.80	22.50	17.70	100.00	Ag_5SbS_4 theoretical	68.30	15.40	16.60	100.00

As, Cu, Co and Ni were looked for but not detected.

The chemical analyses of four different grains of freibergite are given in Table 2, and the chemical analyses of phase 'C' are shown in Table 3.

Electron microprobe analyses of pyrargyrite and stephanite are presented in Table 4.

Qualitative microprobe examination of hessite showed the presence of silver and tellurium.

Microprobe analyses of the galena from the ore body showed that it contains 0.3 wt. percent silver; the bismuth content is < 0.1 percent.

Discussion

The name freibergite is used for tetrahedrites with more than 20 wt. percent silver. The analyses of freibergite from Espeland (Table 2) show that it is rather homogeneous in chemical composition with an average 35 percent silver. The formula based on the average of 4 analyses, $(Cu,Ag,Fe)_{12.2}Sb_4S_{12.4}$, deviates from the stoichiometric composition of tetrahedrite, $(Cu,Ag,Fe,Zn)_{12}(SbAs)_4S_{13}$. X-ray work to study the variation of cell size with silver content was not possible due to difficulties in extracting the small grains. Staples & Warrens (1946) state that silver may substitute for copper in the tetrahedrite structure up to 25 wt. percent or more. The high silver content in the freibergite from Espeland extends the silver content in freibergite to 35 percent.

The chemical analyses of the unknown 'phase C' (Table 3) give average atomic proportions for $Pb_{21.84}$, Ag 4.05, Cu 0.54, Sb 19.85 and S 53.69 percent, equivalent to $Pb_{11}Ag_2Sb_{10}S_{27}$. No x-ray work was possible, since material could not be separated.

Pyrargyrite, stephanite and hessite have conspicuous properties which are generally known. The chemical analyses (Table 4) agree with their known compositions.

This study demonstrates that most of the silver present in the ores from Espeland occurs as inclusions in galena, and that Bi is not as a substituent in galena. The octahedral parting in galena from Espeland described by Oftedal (1942) does not seem to be due to excess of Bi over (Bi,Ag) in galena after the substitution of Bi and Ag atoms into the PbS lattice.

All five silver phases in galena are found as isolated small grains and no textural relationships between them and with the associated minerals have been observed that could cast light on their paragenesis.

The depositional conditions of these silver phases can be interpreted by correlating mineral data with data on synthetic material. The synthetic system $(Cu\text{-}Ag)_{12}Sb_4S_{13}$ has not been investigated so far. The pseudobinary phase-equilibrium diagrams for the Ag_2S-Sb_2S_3 system (Kneighin & Honea 1969) indicate that stephanite is stable only below 197°C and that it may co-exist with any of pyrargyrite, argenite, acanthite or pyrostilpnite. This suggests that the mineral pair stephnite-pyrargyrite in the galena at Espeland deposit was formed at temperatures below 197°C.

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