

Members of the freibergite–argentotennantite series and associated minerals from Silvermines, County Tipperary, Ireland

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Abstract

Ore microscope and electron microprobe investigations on Zn–Pb–Ag ores from B Zone in Silvermines, Ireland, have shown the presence of two As–Sb–Ag phases; a tetrahedrite-group mineral with composition $\text{Cu}_{6.3}\text{Ag}_{3.7}\text{Fe}_{0.9}\text{Zn}_{1.2}\text{As}_{2.2}\text{Sb}_{2.1}\text{S}_{12.7}$ and proustite–pyrargyrite ($\text{Ag}_3\text{As}_{0.5}\text{Sb}_{0.5}\text{S}_3$). It is postulated that both phases inherited their As and Sb from primary geocronite ($\text{Pb}_{14.5}\text{As}_{3.4}\text{Sb}_{2.6}\text{S}_{23}$) and that they are metastable. An enrichment in Ni in the ores is due to very fine to submicroscopic intergrowths of gersdorffite ($\text{Ni}_{0.6}\text{Fe}_{0.4}\text{AsS}$) with geocronite and with galena.

KEYWORDS: freibergite, argentotennantite, tetrahedrite group, Silvermines, Ireland.

Introduction

THE purpose of the investigations reported here is a mineralogical explanation of high Ni and Ag contents in some Pb–Zn ores of the Silvermines mine, County Tipperary, Ireland. This problem was brought to my attention during a short visit to Ireland in May 1979 at the Geological Department at Silvermines, Mogul of Ireland Ltd, which also provided typical specimens from room 4611 in B Zone. This zone is a stratiform orebody in the upper part of the ore-bearing sequence. It contains about 4.6 million tonnes of ore with 2.5 wt. % Pb, 6.5 wt. % Zn and about 30 ppm Ag (Taylor and Andrew, 1978).

Investigated material and methods

Two specimens were investigated in detail by reflected light microscope and electron microprobe. Chemical compositions were determined with a Microscan 9 instrument at 20 kV (25 kV for trace elements in galena), with on-line ZAF matrix corrections. The following standards were used: synthetic PbS (for Pb and for S), PbSe, CdS, Ag, As ($L\alpha$ and $K\beta$), Ni, Bi, and natural chalcopyrite (Cu), troilite (Fe), and stibnite.

The first sample (B4611 A) represents a massive fine-grained sphalerite with a 10 mm thick crust of fractured marcasite, and overgrown by up to 4 mm sized yellowish-white crystals of baryte. Some of the fractures in marcasite are filled by

'ruby silver', Galena occurs in aggregates up to several mm in diameter in the sphalerite. Tetrahedrite, geocronite and gersdorffite were recognized microscopically.

The second sample (B4611 B) represents minerals crystallized in brecciated grey dolomite rock. The minerals recognized macroscopically are (in paragenetical sequence): galena, white dolomite, 'honeyblende' sphalerite, and tetrahedrite as crystals up to 10 mm in size. It is obviously a recrystallized portion of the mineralization.

Mineralogical notes

Textural evidence points to sphalerite and marcasite + pyrite as precipitating first. They occur as colloform crusts (Fig. 1A) or as granular masses (Fig. 1B). Both types are invaded by galena of the first generation that replaced sphalerite. Geocronite and gersdorffite crystallized together with galena (Fig. 2A, B, and C). Tetrahedrite and proustite–pyrargyrite were among the later-forming phases. A second generation of galena, in the form of myrmekitic exsolutions in proustite–pyrargyrite and tetrahedrite (Fig. 2C, D and A), also formed at this stage. Subsequent recrystallization produced the coarse crystals of galena, sphalerite and tetrahedrite interstitial to the breccia fragments.

Tetrahedrite-group minerals occur in both primary and recrystallized portions of the mineralization in two textural and chemical varieties. In the recrystallized ore (sample B4611 B) euhedral

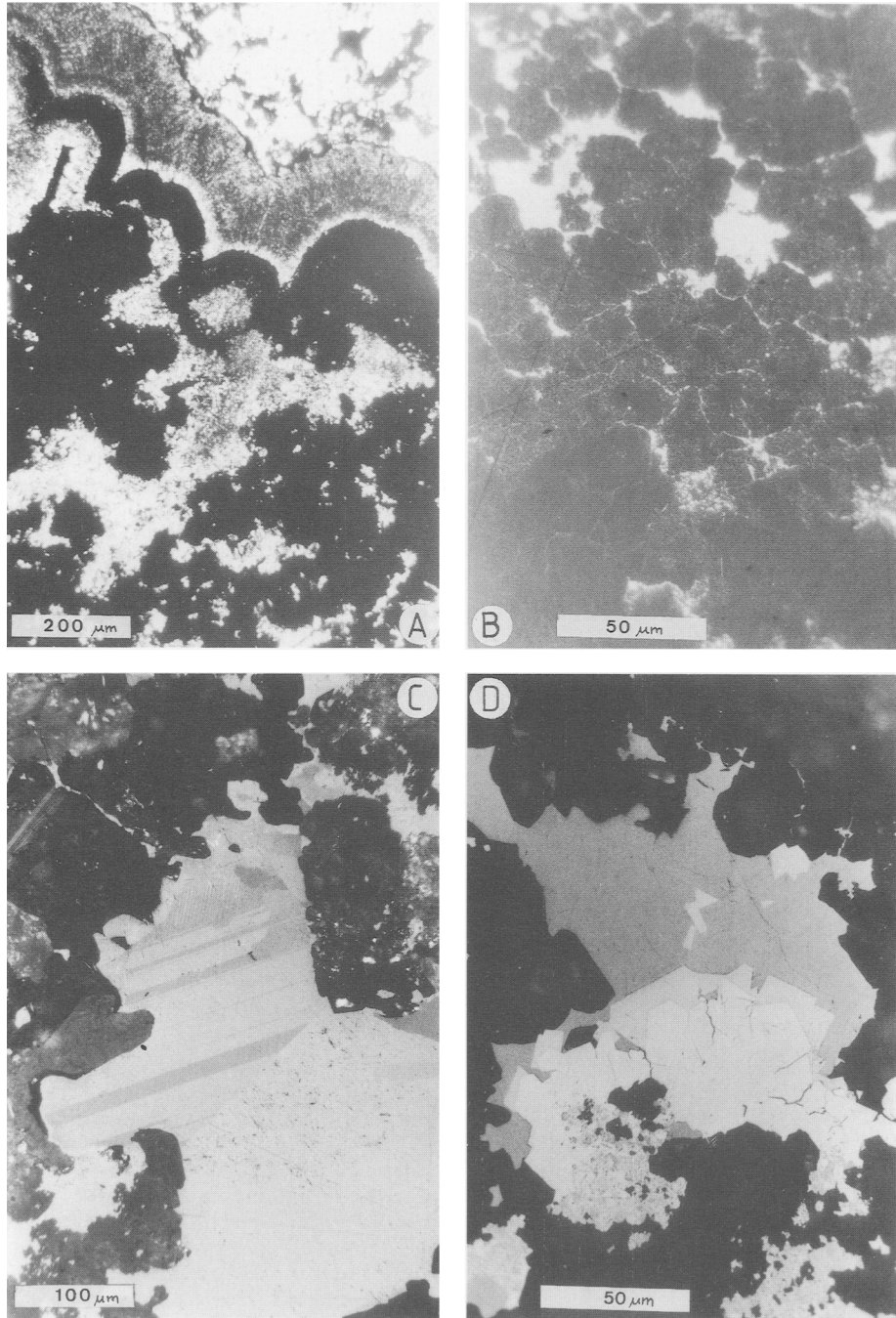


FIG. 1. *A.* Colloform sphaerite with different shades of grey due to the different iron content and pyrite (black). Translucent light. *B.* Granular sphaerite replaced by galena. Reflected light. *C.* Polysynthetic twins of geocronite with sharp contacts with galena. Reflected light, nicols partly crossed. *D.* Overgrowths of gersdorffite (grey) on pyrite (white) and idiomorphic crystals of gersdorffite in galena (dark grey). Reflected light.

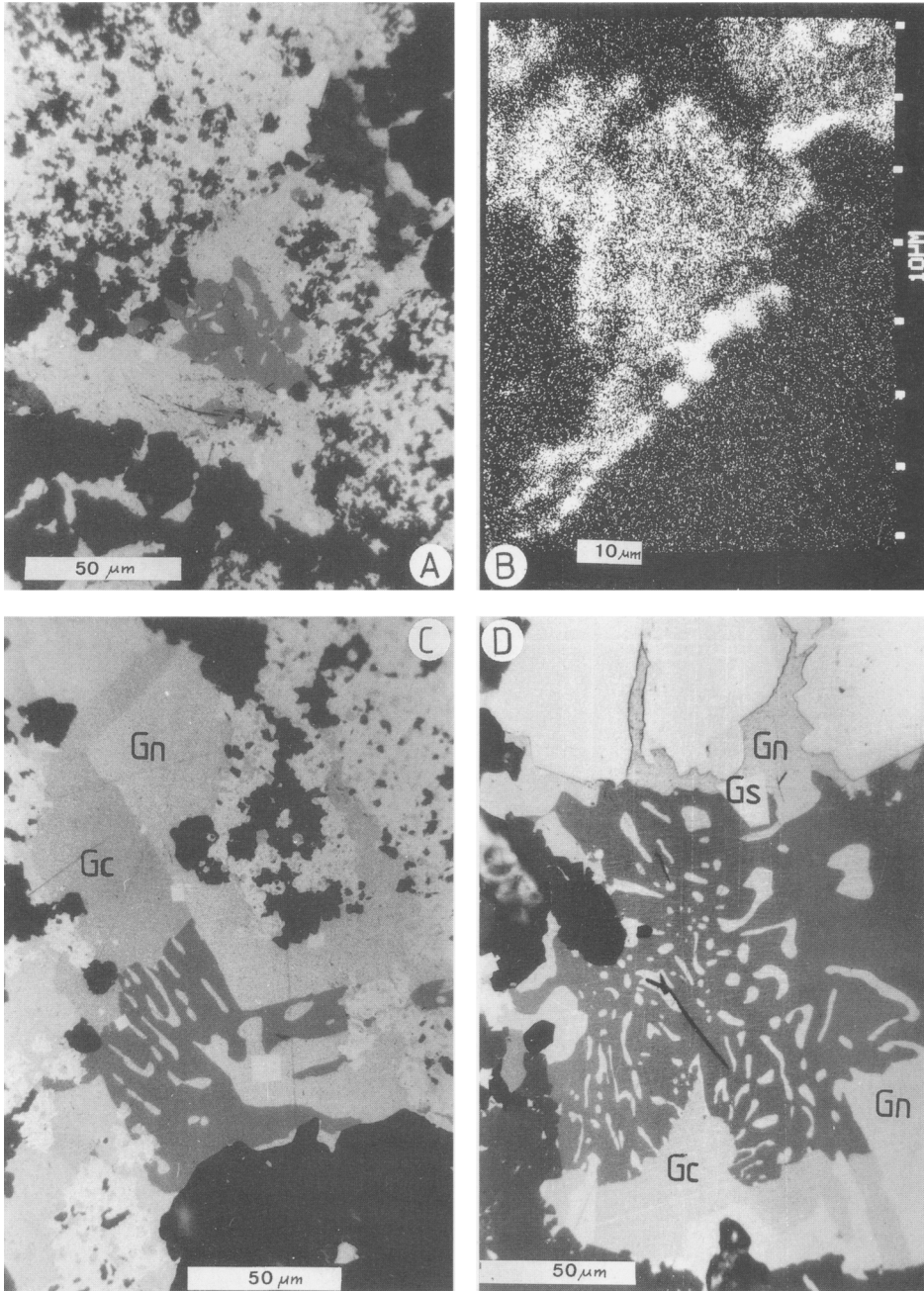


FIG. 2. *A.* Myrmekite-like intergrowths of freibergite—argentotennantite with galena (dark in centre) surrounded by intimate intergrowths of galena and gersdorffite. Reflected light. *B.* X-ray image for Ni- $K\alpha$ showing the contacts between galena and a mixture of galena and gersdorffite (compare anal. 23 in Table 1). *C.* Replacement of geocronite (Gc) by proustite—pyrargyrite/galena (second generation) myrmekite. Gersdorffite occurs as euhedral crystals and as intergrowths with galena of the first generation. Reflected light. *D.* Galena of the first generation (Gn) intergrown with geocronite (Gc) which is partly replaced by myrmekite of proustite—pyrargyrite and galena of the second generation. Single crystal of gersdorffite (Gs). Reflected light.

Table 1. Results of electron-microprobe analyses of some ore minerals from Silvermines, Ireland*

| | Cu | Ag | Fe | Zn | As | Sb | Pb | Ni | S | Total | Remarks |
|------------------|------|-------------|------|------|------|------|------|-------------|------|--------|---------------|
| 1. Tetrahedrite | 23.3 | 20.6 | 3.54 | 4.04 | 9.2 | 14.9 | | | 23.1 | 98.68 | Max. Fe |
| 2. | 22.9 | 22.0 | 3.02 | 5.57 | 8.6 | 14.6 | | | 23.3 | 99.99 | max. Zn |
| 3. | 23.9 | 21.1 | 2.88 | 4.79 | 8.3 | 14.9 | | | 23.3 | 99.43 | incl. 0.26 Bi |
| 4. | 22.1 | 23.9 | 3.01 | 5.05 | 8.3 | 14.7 | | | 22.7 | 99.76 | max. Ag |
| 5. | 22.6 | 22.5 | 2.83 | 4.22 | 9.1 | 14.7 | | | 22.9 | 99.85 | |
| 6. | 37.5 | 2.9 | 2.43 | 5.00 | 4.9 | 22.4 | | | 24.4 | 99.53 | aver. of 4 |
| 7. | 40.0 | 1.7 | 2.87 | 4.93 | 11.2 | 13.3 | | | 26.8 | 100.80 | |
| 8. Geocronite | | | | | 5.5 | 7.7 | 69.4 | | 17.2 | 99.8 | |
| 9. | | 0.04 | | | 6.0 | 6.9 | 70.5 | | 17.2 | 100.74 | incl. 0.10 Bi |
| 10. | | - | | | 5.9 | 6.7 | 70.2 | | 17.3 | 100.26 | incl. 0.16 Bi |
| 11. Proustite | | 61.1 | | | 7.8 | 11.0 | | | 18.3 | 98.2 | |
| 12. | | 61.5 | | | 8.1 | 10.9 | | | 18.5 | 99.0 | |
| 13. | | 61.4 | | 0.09 | 8.2 | 11.2 | | | 18.6 | 99.49 | |
| 14. Gersdorffite | | | 14.3 | | 43.5 | | | 19.5 | 20.2 | 97.5 | max. Fe |
| 15. | | | 8.6 | | 45.6 | | | 25.9 | 19.5 | 99.6 | max. Ni |
| 16. | | | 12.6 | | 43.5 | | | 21.7 | 19.9 | 97.6 | aver. of 6 |
| 17. Marcasite | | 0.20 | 46.2 | | 0.42 | 0.09 | | 0.09 | 52.6 | 99.60 | crystals |
| 18. | | - | 46.7 | | 0.14 | - | | - | 53.0 | 99.84 | colloform |
| 19. Sphalerite | 0.05 | - | 0.23 | 65.5 | | | | | 32.6 | 98.74 | incl. 0.36 Cd |
| 20. | 0.09 | 0.17 | 0.19 | 65.6 | | | | | 32.6 | 99.02 | incl. 0.37 Cd |
| 21. Galena | | 0.05 ± 0.01 | | | 11.6 | 6.3 | 60.4 | 0.04 ± 0.01 | 16.9 | 99.55 | neg. Bi, Se |
| 22. Mixture I | | - | 1.35 | | 11.6 | 6.3 | 60.4 | 3.0 | 16.9 | 99.55 | |
| 23. Mixture II | | 0.05 | 1.89 | 0.59 | 9.5 | 0.2 | 68.8 | 5.0 | 14.1 | 100.13 | |

Formula calculated for:

| | | | | |
|----------|----|---|---|--------------------|
| 29 atoms | 1 | (Cu _{6.44} Ag _{3.35} Fe _{1.12} Zn _{1.09}) _Σ 12.00 | (As _{2.16} Sb _{2.16}) _Σ 4.32 | S _{12.68} |
| | 2 | (Cu _{6.28} Ag _{3.56} Fe _{0.94} Zn _{1.49}) _Σ 12.27 | (As _{1.99} Sb _{2.10}) _Σ 4.09 | S _{12.64} |
| | 3 | (Cu _{6.59} Ag _{3.43} Fe _{0.90} Zn _{1.28}) _Σ 12.20 | (As _{1.93} Sb _{2.14} Bi _{0.02}) _Σ 4.09 | S _{12.70} |
| | 4 | (Cu _{6.16} Ag _{3.92} Fe _{0.95} Zn _{1.37}) _Σ 12.40 | (As _{1.96} Sb _{2.13}) _Σ 4.09 | S _{12.51} |
| | 5 | (Cu _{6.32} Ag _{3.70} Fe _{0.90} Zn _{1.15}) _Σ 12.07 | (As _{2.15} Sb _{2.13}) _Σ 4.28 | S _{12.66} |
| | 6 | (Cu _{9.79} Ag _{0.45} Fe _{0.72} Zn _{1.27}) _Σ 12.23 | (As _{1.09} Sb _{3.05}) _Σ 4.14 | S _{12.63} |
| | 7 | (Cu _{9.78} Ag _{0.25} Fe _{0.80} Zn _{1.17}) _Σ 12.00 | (As _{2.32} Sb _{1.70}) _Σ 4.02 | S _{12.99} |
| 23 S | 8 | Pb _{14.36} As _{3.15} Sb _{2.71} S ₂₃ | | |
| | 9 | Pb _{14.59} Ag _{0.02} As _{3.43} Sb _{2.43} Bi _{0.02} S ₂₃ | | |
| | 10 | Pb _{14.44} As _{3.35} Sb _{2.34} Bi _{0.02} S ₂₃ | | |
| 3 S | 11 | Ag _{2.98} As _{0.55} Sb _{0.48} S ₃ | | |
| | 12 | Ag _{2.96} As _{0.56} Sb _{0.47} S ₃ | | |
| | 13 | Ag _{2.94} As _{0.57} Sb _{0.48} S ₃ | | |
| As+S=2 | 14 | Ni _{0.55} Fe _{0.42} As _{0.96} S _{1.04} | | |
| | 15 | Ni _{0.72} Fe _{0.25} As _{1.00} S _{1.00} | | |
| | 16 | Ni _{0.62} Fe _{0.38} As _{0.97} S _{1.03} | | |
| | 22 | Mixture of ca. 10% gersdorffite and 90% geocronite | | |
| | 23 | Mixture of ca. 20% gersdorffite and 80% galena | | |

*analyst W.J. Lustenhouwer, no 6&7 C. Kieft.

crystals may reach up to 10 mm. Their chemistry is characterized by relatively low Ag content (Table 1, anal. 6 and 7). The antipathetic relationship between Ag and As is in accordance with the general rule of a low mutual tolerance of these metals in the tetrahedrite structure (Johnson *et al.*, 1986). No other silver-bearing phases were observed in this specimen.

In the specimen B4611 A, the tetrahedrite-group minerals occur as anhedral grains up to 50 μm in diameter, intergrown with geocronite, proustite-pyrargyrite and galena. They appear to replace geocronite and may be replaced by proustite-pyrargyrite. Myrmekite-like inclusions of galena in tetrahedrite were also observed (Fig. 2. A). The chemical compositions of the tetrahedrite-group minerals are given in Table 1 (anal. 1-5). An unusually high Ag and As content is characteristic. On the basis of their As/Sb ratios they are intermediate members of the tetrahedrite-tennantite series. For Ag-rich mem-

bers freibergite and argentotennantite are the established names, but their compositional limits are not clearly defined. Riley (1974) proposed the name freibergite for compositions with more than 1/3 of Cu sites being occupied by Ag. The results of structural investigations of Peterson and Miller (1986) suggest that freibergite should be defined as a member of the tetrahedrite group with Sb > As and the trigonal-12(e) site predominantly occupied by Ag. Argentotennantite has been established for phases with As > Sb and Ag > Cu (Spiridonov *et al.*, 1986); however, by analogy with freibergite, argentotennantite could be defined as a member of tetrahedrite group with As > Sb and with Ag predominant in the 12(e) structural site (E. H. Nickel, written comm.).

All analyses of the Ag-As-rich tetrahedrites from Silvermines have more than 3 Ag atoms per formula unit and could be classified as members of the freibergite-argentotennantite series; analyses 1 and 5 (Table 1), give As/(As + Sb) ratios

of 0.501 and 0.502 and therefore could be characterized as stibioan argentotennantite; analyses 2, 3 and 4 as arsenoan freibergite.

Geocronite is always associated with galena. It occurs as grains up to 200 μm , often polysynthetically twinned (Fig. 1C). Unusual intergrowths of geocronite with gersdorffite are discussed below. Chemical analyses (Table 1) show that geocronite is As-rich with an average As/(As + Sb) ratio of 0.57. It shows a small deficiency of As + Sb and some surplus of Pb compared the ideal formula of $\text{Pb}_{28}\text{As}_{4+x}\text{Sb}_{8-x}\text{S}_{46}$ with $0 < x < 8$.

Gersdorffite occurs as idiomorphic crystals up to 20 μm associated with myrmekitic intergrowths of proustite-pyrargyrite and galena (Fig. 2C, D), and as overgrowths on pyrite (Fig. 1D), but in most cases as dense fine-grained, homogeneously distributed, intergrowths with geocronite and with galena (Fig. 2A, B, C). Individual grains of gersdorffite show considerable variations of the Ni/Fe ratios (Table 1), but they are too small to observe any zonation. The contents of Co and Sb are lower than the detection limits of microprobe (0.05 and 0.03 wt. % respectively).

Proustite-pyrargyrite forms less than 1 vol % of the investigated specimens but it is the main silver carrier, because of its high Ag content. It occurs as veinlets and nestlets between other minerals. Myrmekitic intergrowths with galena are common (Fig. 2C, D). Chemical analyses revealed composition intermediate between proustite and pyrargyrite with an As/(As + Sb) ratio between 0.535 and 0.547 (Table 1).

Discussion

According to the data of Klemm (1965), the ferroan gersdorffite from Silvermines was formed around 500°C. The only speculative indication that could support such a high temperature of formation are the homogeneous intergrowths of gersdorffite with geocronite and with galena. These textures could result from a break-down of a hypothetical Pb–Ni–As–Sb–S (probably high-temperature) phase. Its composition could be close to the analysed mixtures (Table 1 anal. 22, 23). However, there are more indications supporting the low-temperature concept of formation of the deposit and the subsequent recrystallization (e.g. fluid inclusion data of Samson and Russell (1987) give homogenization temperatures between 50° and 260°C). Similar contradictions in the composition of sulphoarsenides from northern England were observed by Ixer *et al.* (1979), and interpreted as a result of metastability of the assemblage.

Metastability of the assemblage could also be

a plausible explanation of the composition of gersdorffite from Silvermines, as well as of the other unusual minerals: freibergite–argentotennantite and proustite–pyrargyrite. Textural evidence shows that both formed by replacement of geocronite, and their As/Sb ratios strongly suggest that these elements were inherited from geocronite. A replacement of geocronite by proustite–pyrargyrite/galena myrmekite and freibergite–argentotennantite/galena intergrowths could be caused by supply of Ag during remobilization. The relatively high content of silver in galena and sphalerite (Table 1, anal. 20 and 21) suggest that Ag is released from the pre-existing sulphides and after a migration on some (probably short) distance, fixed again in the metastable Ag-bearing phases. A possible reaction to form proustite–pyrargyrite: $\text{Pb}_{28}\text{As}_7\text{Sb}_5\text{S}_{46}$ (geocronite) + $18\text{Ag}_2\text{S} \rightarrow 12\text{Ag}_3(\text{As}, \text{Sb})\text{S}_3 + 28\text{PbS}$. The formation of tetrahedrite was probably triggered by the presence of traces of Cu. However, the general paucity of Cu in the ores from Silvermines may explain the origin of the unusual members of the tetrahedrite group minerals.

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