Two new occurrences of benleonardite, a rare silver–tellurium sulphosalt, and a possible new occurrence of cervelleite

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Abstract

Benleonardite, ideally $Ag_8(Sb,As)Te_2S_3$, occurs in ore specimens from the Mayflower and Gies epithermal gold–silver telluride deposits in Montana commonly spatially associated with hessite and tetrahedrite. In these deposits, it is Cu-bearing (up to 2.7 wt.%) and exhibits a slight deficiency in Ag+Cu coupled with a slight excess in S. A cervelleite-like mineral coexists with benleonardite at Mayflower and is unusual in composition in that it is Se-bearing suggesting the possibility of solid solution with aguilarite (Ag_4SeS).

KEYWORDS: benleonardite, cervelleite, Mayflower mine, Gies mine, Montana.

Introduction

BENLEONARDITE was identified as a new mineral species by Stanley *et al.* (1986) during studies of ore specimens from the abandoned Bambolla tellurium deposit, Moctezuma, Mexico. In that study it was reported that the species occurred as monomineralic grains up to 40 μm wide or as laths up to 60 μm in length and that it was associated with silver, acanthite, hessite, cervelleite (Ag_4TeS), pyrite and sphalerite. Three incompletely characterized phases mentioned in the literature which may be akin to benleonardite are mineral X of Aksenov *et al.* (1969) from the Zyranov deposit, Russia, mineral C of Karup-Møller and Pauly (1979) from Ivigtut, Greenland, and 'unnamed mineral 2' of Zhang and Spry (1994) from the Gies deposit, Montana.

The present study documents the occurrence of benleonardite in the Mayflower and Gies epithermal gold–silver telluride deposits, Montana. These deposits are two of several gold–silver telluride occurrences in the Great Falls Tectonic Zone (Fig. 1). We also report the presence of a Ag–Te–S mineral at the Mayflower mine that has a composition close to, but not identical with, that of cervelleite, as well as approximate conditions of formation for benleonardite and the cervelleite-like mineral based on mineral assemblages at Gies and Mayflower, and the fluid inclusion studies of Zhang and Spry (1994) for the Gies deposit.

Occurrence and optical properties

The Mayflower deposit is a carbonate-hosted, epithermal gold–silver telluride deposit located in southwestern Montana in the foothills of the Tobacco Root Mountains. Gold–silver tellurides occur as fine-grained disseminations, fracture fillings, replacements and as irregular masses in oolitic, mottled and sandy limestones of the Middle Cambrian Meagher Formation. The Mayflower fault, in the vicinity of the telluride mineralization, abuts Late Cretaceous Elkhorn Mountain Volcanics, the Cambrian Wolsey (primarily limestone), and Flathead Formations (primarily cross-bedded sandstones and arkoses), and conglomerates of the Proterozoic LaHood Formation and is thought to be the major conduit for the hydrothermal fluids. Approximately 6,000 kg of Au have been extracted from the deposit to date but it remains open at depth (Cocker, 1993). Grades of over 30 000 g/ton Au and Ag were encountered in isolated pockets. According to Cocker (1993), mineralization formed during four and possibly six stages. Early stages of mineralization included silicification, pyritization, and dolomitization. Base metal sulphides and gold–silver

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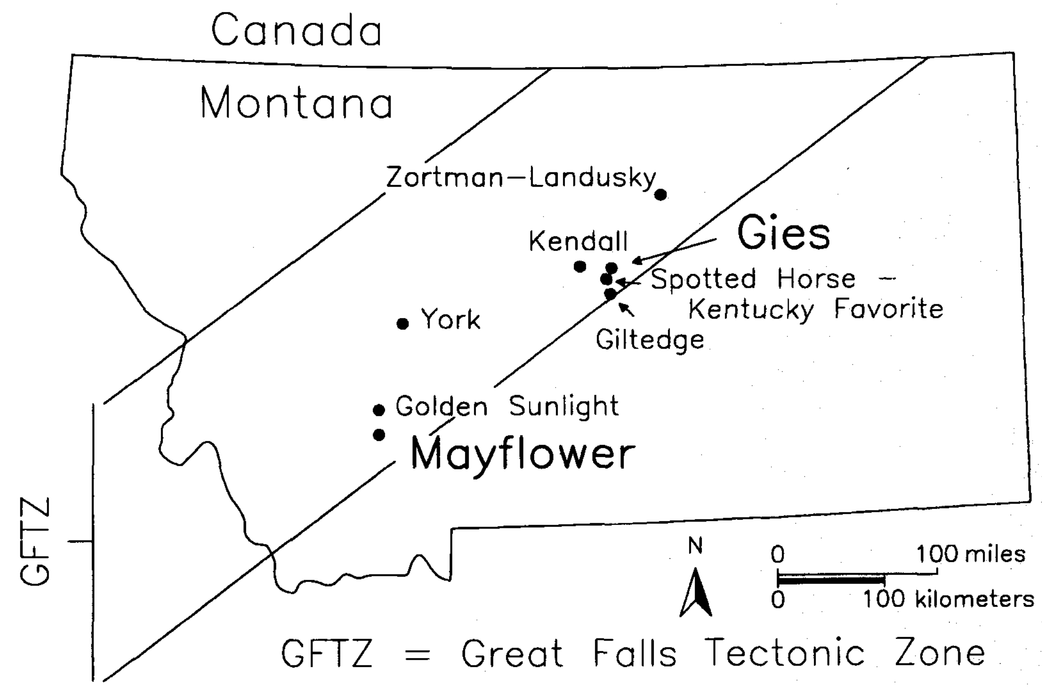

FIG. 1. Location map of the Gies and Mayflower deposits in relation to other gold–silver telluride deposits in the Great Falls Tectonic Zone of Montana.

tellurides cross-cut and, in places, replace earlier stages of mineralization. Mineralogical assemblages documented in the current study indicate the following minerals to be present in at least two gold–silver telluride stages: pyrite, marcasite, freibergite, tetrahedrite, sylvanite, petzite, hessite, stuetzite, calaverite, native gold, coloradoite, altaite, benleonardite, nagyagite, cervelleite (?), native tellurium, galena, low-Fe sphalerite, chalcopyrite, chalcocite, secondary covellite, and possibly acanthite.

Benleonardite is a relatively common constituent of several samples of ore. In one specimen (M95-8) it is the most abundant mineral. It occurs either as monomineralic masses up to 200 μm in diameter intergrown with tetrahedrite, hessite, sphalerite, gold, or rarely cervelleite (?) (Fig. 2*a*), or as laths 5–20 μm by up to 100 μm in hessite (Fig. 2*b*). Optical properties mimic those described for benleonardite by Stanley *et al.* (1986).

As a result of the intimate association of benleonardite with cervelleite at Bambolla (Criddle *et al.*, 1989) and most likely at Zyranov (mineral Z of Aksenov *et al.*, 1969), and Ivigtut (mineral B of Karup-Møller, 1976), particular attention was given to looking for cervelleite in the present study. A pale blue, isotropic mineral that shows no internal reflections occurs as irregular laths and masses (up to 150 μm in length) in contact with benleonardite and hessite in sample 16930A from the Mayflower deposit (Fig. 2*a*).

The Gies deposit is an epithermal vein system that occurs along the contact between Cretaceous-Tertiary alkaline intrusive rocks (syenite, monzonite, and tinguaite) and sedimentary rocks (siltstones, sandstones, and limestones) of Cambrian-Cretaceous age in the Judith Mountains, central Montana (Fig. 1). The average gold grade mined was 13.7 g/t; however, some veins in the deposit contained grades of up to 14 000 g/t where coarse sylvanite was abundant. Zhang and Spry (1991, 1994) have identified at least 36 minerals in four stages of mineralization. Tellurides were identified in stages II and III. Zhang and Spry (1994) described a mineral which they referred to as 'unnamed mineral 2' in two samples of stage III quartz. Two electron microprobe analyses from that investigation closely resemble compositions of benleonardite given by Stanley *et al.* (1986) (Table 1). The samples from Zhang and Spry's (1994) study have been reevaluated here.

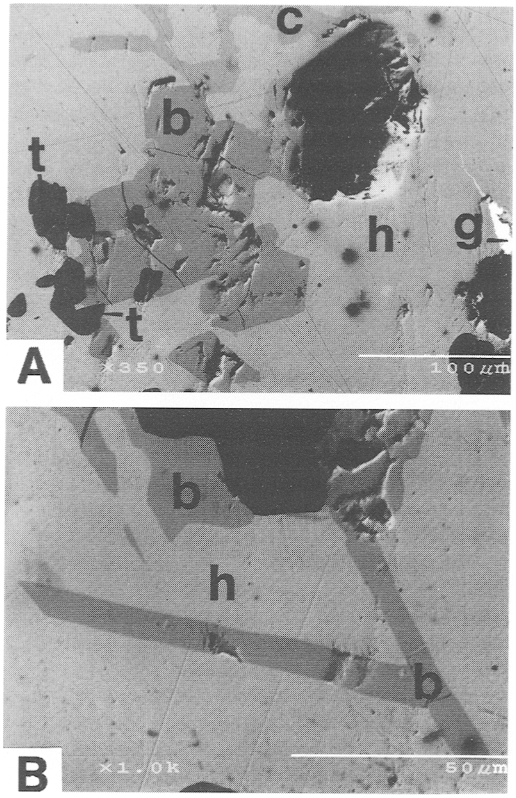

FIG. 2. Back-scattered electron images of (A) Mass of benleonardite (b) intergrown with hessite (h), tetrahedrite (t), and irregular blades of cervelleite (c). Gold (g) also occurs in hessite. (B) A bladed and an irregular mass of benleonardite (b) intergrown with hessite (h).

Benleonardite in the Gies deposit occurs as anhedral grains up to 20 µm in length coexisting with hessite and tetrahedrite. In plane-polarized light, in air, it is gray with a pale blue-brown tint, and non-pleochroic. In immersion oil benleonardite is slightly darker in colour than in air. By comparison with samples from Mayflower it exhibits only weak anisotropism (dark brown to gray-blue).

Electron microprobe analyses

Chemical compositions of benleonardite and one sample of cervelleite (?) were obtained using an ARL-SEMQ electron microprobe. The standards used for the electron microprobe were pure metals (Au, Ag, Te, Se, Sb, and Cu), $AgBiS_2$ and Bi_2S_3 (Bi), Sb_2S_3 (Sb), As_2S_3 (As), ZnS (Zn), HgS (Hg), $Fe_{0.939}S$ (Fe and S), and FeS_2 (Fe and S). Operating conditions for the microprobe included an accelerating voltage of 20 kV and a sample current of 20 nA. The ARL-SEMQ electron microprobe employed the PRSUPR (Donovan *et al.*, 1990) data-reduction procedure.

TABLE 1. Chemical analyses of benleonardite

wt.%	1	2	3	4
Ag	62.52	62.99	60.76	63.07
Cu	1.90	1.65	2.68	0.55
As	1.16	1.70	1.15	1.01
Sb	6.25	5.33	6.94	6.98
Te	19.38	19.06	18.97	18.75
S	8.16	8.33	8.78	8.56
Total	99.37	99.06	99.28	98.92
Based on 14 atoms				
Ag	7.49	7.53	7.17	7.95
Cu	0.39	0.33	0.54	0.11
As	0.20	0.29	0.19	0.18
Sb	0.66	0.56	0.72	0.74
Te	1.96	1.93	1.89	1.91
S	3.29	3.35	3.48	3.47

1. Sample 51-13, Gies deposit (average of 3 analyses)
2. Sample 51-15 Gies deposit (average of 4 analyses)
3. Sample 16930A, Mayflower deposit (average of 4 analyses)
4. Sample M95-8 Mayflower deposit (average of 5 analyses)

Chemical compositions

Electron microprobe analyses of benleonardite from the Mayflower and Gies deposits are summarized in Table 1 whereas those from Bambolla (Stanley *et al.*, 1986), Zyranov (Aksenov *et al.*, 1969), Ivigtut (Karup-Møller and Pauly, 1979), and Gies (Zhang and Spry, 1994) are shown for comparison in Table 2, along with the ideal benleonardite calculated by Stanley *et al.* (1986).

Benleonardite from the Mayflower and Gies deposits is almost identical in composition to that from the Bambolla mine. The concentrations of Se, Hg, Bi, Fe and Zn in samples from these deposits were below detection limits. One significant difference between Bambolla benleonardites and those from Mayflower and Gies is the presence of Cu in all specimens of benleonardite from the Mayflower (up to 3.3 wt.% Cu) and Gies (up to 2.1 wt.% Cu) deposits. The presence of Cu in benleonardite grains occurred regardless of whether the mineral was surrounded by tetrahedrite (i.e. Cu-bearing) or hessite (i.e. Cu-free). The measured

TABLE 2. Chemical analyses of benleonardite and benleonardite-like minerals

wt.%	1	2	3	4	5	6	7
Ag	64.5	64.6	60.0	58.0	61.7	62.7	63.4
Cu	0.1	–	1.5	–	–	1.9	2.1
Sb	7.3	9.1	8.0	11.0	7.1	6.7	4.4
As	1.4	–	–	–	–	0.9	2.6
Te	18.7	19.1	20.0	18.0	17.0	19.6	18.8
S	8.0	7.2	10.0	13.0	8.8	8.4	8.6
Total	100.0	100.0	99.5	100.0	94.6	100.2	99.9
Based on 14 atoms							
Ag	7.80	8.00	6.99	6.41	7.71	7.44	7.43
Cu	0.02	–	0.30	–	–	0.38	0.42
Sb	0.78	1.00	0.83	1.08	0.79	0.70	0.46
As	0.24	–	–	–	–	0.15	0.44
Te	1.90	2.00	1.97	1.68	1.80	1.97	1.86
S	3.23	3.00	3.92	4.82	3.70	3.35	3.39

1. Benleonardite, Bambolla deposit (Stanley *et al.*, 1986)
2. Theoretical benleonardite ($Ag_8SbTe_2S_3$) (Stanley *et al.*, 1986)
3. and 4. Mineral X, Zyranov deposit (Aksenov *et al.*, 1969)
5. Mineral C, Ivigtut (Karup-Møller and Pauly, 1979)
6. and 7. Unnamed mineral 2, Gies deposit (Zhang and Spry, 1994)

concentrations of Cu, therefore, are not the results of secondary electron emission of Cu from surrounding minerals. A maximum of 0.1 wt.% Cu was reported by Stanley *et al.* (1986) for samples from Bambolla. It should be noted that up to 1.5 wt.% Cu occurs in 'mineral X' from the Zyranov deposit (Table 2, analysis 3). Copper appears to substitute for Ag in the Mayflower and Gies samples.

Stanley *et al.* (1986) reported that benleonardite samples from the Bambolla deposit appeared to contain excess sulphur. When calculated on the basis of 14 atoms, ideal benleonardite should contain 3 S atoms. However, an average of 3.3 S atoms was reported by Stanley *et al* (1986) regardless of the choice of standard used in their analyses. A sulphur excess is also characteristic of benleonardites from the Gies (3.3 S atoms) and Mayflower (3.5 S atoms) deposits when calculated on the basis of 14 atoms. This S excess is maintained regardless of whether troilite or pyrite is used as a standard for sulphur. In order to ensure the reliability of the Ag and Te concentrations determined, the two most common elements in benleonardite, the composition of coexisting hessite was also obtained. A stoichiometry of two Ag atoms and one Te atom in hessite supports the veracity of the quality of the standards and supports the concept that the excess sulphur in benleonardite is real and is not an artifact of erroneous ZAF corrections or poor standards.

Acceptable electron microprobe analyses of cervelleite (?) were difficult to obtain due to very easy breakdown of the mineral grains by the electron beam. Attempts were made to defocus the beam or to move the beam every two to three seconds; however, beam damage persisted. The analyses of two grains are given in Table 3, along with cervelleite and cervelleite-like minerals reported in the literature. The following formula is suggested for the Mayflower sample: $(Ag, Cu, As)_{3.88}(Te,Se)_{1.33}S_{0.79}$. This mineral contains approximately 6 wt.% Ag and 2 wt.% S less, and 2 wt.% Te more than cervelleite from Bambolla mine (Stanley *et al.*, 1986). It also contains up to 1 wt.% Cu, 3 wt.% Se, and 1 wt.% As. Although the Au–Te–S mineral from Mayflower is deficient in Ag (3.75 atoms) relative to stoichiometric cervelleite, which contains four atoms, it should be stressed here that all other cervelleite-like minerals reported in the literature (Table 3) are also deficient in Ag and range from 3.63 to 3.70 atoms (on the basis of 6 atoms for cervelleite). The cervelleite-like mineral from Mayflower bears a closer compositional resemblance to 'mineral B' from Ivigtut (Karup-Møller, 1976) than cervelleite from the Bambolla mine. Criddle *et al.* (1989) reported that cervelleite from Bambolla was altered by light in a photo-chemical reaction with acanthite and hessite, and that it was not sensitive to electron beam

TABLE 3. Chemical analyses of cervelleite and cervelleite-like minerals

wt.%	1	2	3	4	5	6	7
Ag	67.35	67.30	73.00	68.00	68.50	65.50	68.12
Cu	0.94	0.80	0.10	–	2.50	1.50	3.36
Bi	0.00	0.00	–	–	0.30	1.00	–
Pb	0.00	0.00	–	–	0.80	1.50	–
As	1.25	0.00	–	–	–	–	–
Sb	0.00	0.06	–	–	–	–	–
Te	25.49	23.52	22.20	22.00	23.00	25.40	22.54
Se	2.79	1.83	–	–	–	–	0.10
S	3.54	4.84	5.30	7.00	5.80	5.20	5.62
Total	101.36	98.35	100.60	97.00	101.00	100.10	99.74
Based on 6 atoms							
Ag	3.74	3.76	3.99	3.70	3.66	3.63	3.65
Cu	0.09	0.08	0.01	–	0.23	0.14	0.31
Bi	0.00	0.00	–	–	0.01	0.03	–
Pb	0.00	0.00	–	–	0.02	0.04	–
As	0.10	0.00	–	–	–	–	–
Sb	0.00	0.00	–	–	–	–	–
Te	1.20	1.11	1.03	1.01	1.04	1.19	1.02
Se	0.21	0.14	–	–	–	–	0.01
S	0.66	0.91	0.97	1.28	1.04	0.97	1.01

1. and 2. Cervelleite-like mineral Mayflower deposit (this study)
3. Cervelleite, Bambolla deposit (Criddle *et al.*, 1989)
4. Mineral Z, Zyranov deposit (Aksenov *et al.*, 1969)
5. and 6. Mineral B, Ivigtut (Karup-Møller, 1976)
7. Unnamed phase, Shadiitsa deposit (Gadzheva, 1985)

damage during electron microprobe analyses. The cervelleite-like minerals from Ivigtut (Karup-Møller, 1976) and Mayflower both breakdown due to electron beam damage and are both apparently unaltered when exposed to light.

Discussion

Optical properties and chemical analyses suggest the presence of benleonardite and a cervelleite-like mineral in gold–silver ores in Montana. The compositions obtained herein are close to the formula for benleonardite ($Ag_8(Sb,As)Te_2S_3$) as proposed by Stanley *et al.* (1986). However, there appears to be a slight deficiency in Ag+Cu coupled with a slight excess in S. Such an excess in S was also recognized by Stanley *et al.* (1986). Whether these observations require a modification in the formula for benleonardite is unclear because there may be sub-microscopic intergrowths, typical of that found in other homologous series minerals. Considerably more compositional and structural data are required to support this proposal since available data are limited in number. The cervelleite-like mineral at Mayflower is unusual in composition in that it contains Se. This indicates the possibility of a solid solution, or at least a limited solid solution, between cervelleite and the Se equivalent of cervelleite, aguilarite (Ag_4SeS).

No fluid inclusion data are available from the Mayflower mine. However, the presence of coexisting sylvanite and petzite in veins that contain benleonardite implies, on the basis of the experimental data of Cabri (1965), a maximum temperature of formation of these tellurides and associated benleonardite of 170°C. Fluid inclusion data on stage III quartz that contains benleonardite at the Gies deposit by Zhang and Spry (1994) suggests benleonardite and the cervelleite-like mineral formed between 195 and 250°C. Note that mineral assemblages associated with mineral B (cervelleite) at Ivigtut suggested to Karup-Møller (1976) that it formed at <230°C. This overlaps the fluid inclusion temperature range observed by Zhang and Spry (1994) at Gies and the proposed range of stability of the cervelleite-like mineral.

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