

## Silver sulfotellurides from volcanic-hosted massive sulfide deposits in the Southern Urals

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### Summary

This paper addresses Ag-sulfotellurides occurring in volcanic-hosted massive sulfide deposits of the Southern Urals. Cervelleite-like minerals were identified in ores from the Gayskoe, Yaman-Kasy, Severo-Uvaryazhskoe, Tash-Tau, and Babaryk deposits, where they occur in ores containing chalcopyrite, galena, sphalerite, tennantite ± bornite. Other Ag- and Te-bearing minerals (electrum, hessite, stromeyerite and Ag-bearing chalcocite) are present in the association. A benleonardite-like mineral associated with sylvanite and native tellurium was found as a metastable phase in paleohydrothermal tubes relics from the Yaman-Kasy deposit. Formation of the sulfotellurides indicates relative low  $f_{\text{Te}_2}$  in the hydrothermal systems, insufficient for formation of most S-free tellurides. The significant Cu enrichment in cervelleite relates to the association with bornite. Broad variations in composition and physical properties of cervelleite-like sulfotellurides allow the supposition of the presence of several, as yet unnamed mineral species, which can be distinguished by Cu contents, Te/S ratios, and presumably by crystal structure.

### Introduction

Natural compounds of silver containing both sulfur and tellurium are inadequately studied at present. Based on composition, there are two main groups: benleonardite-like sulfosalts; and cervelleite-like compounds. Benleonardite,  $\text{Ag}_8(\text{Sb,As})\text{Te}_2\text{S}_3$ , was described as a new mineral species from the Bambolla Au–Te Mine, Mexico (Stanley et al., 1986). Prior to acceptance of benleonardite as a mineral, Sb-bearing Ag-sulfotellurides had been determined as phases *x* (60 wt.% Ag, 8 wt.% Sb, 20 wt.% Te, 10 wt.% S, 1.5 wt.% Cu) and *u* (66 wt.% Ag, 16 wt.% Sb, 8 wt.% Te, 10 wt.% S) by Aksenov et al. (1969) from the Zyranovskoe volcanic-hosted massive

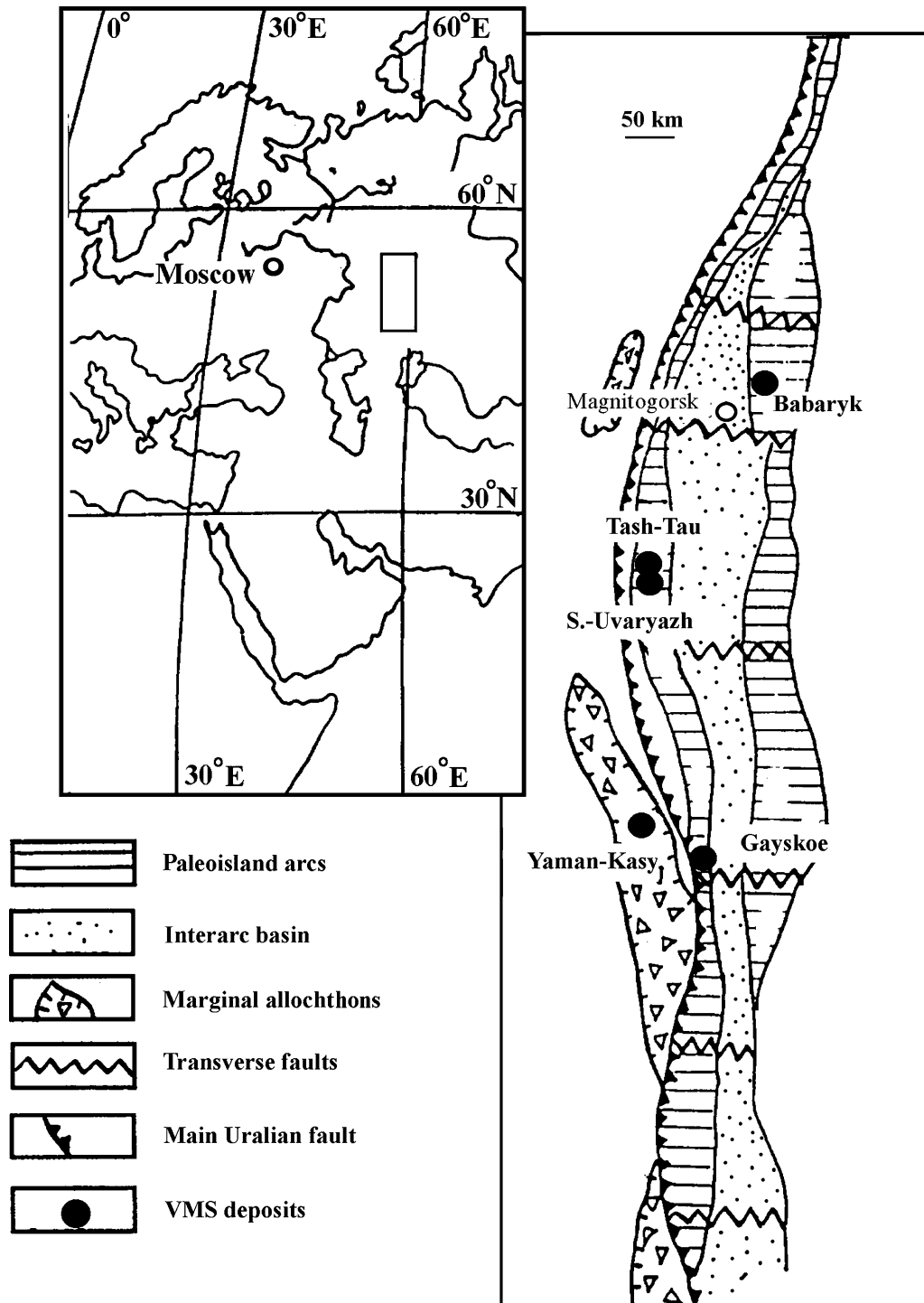


Fig. 1. Magnitogorsk-Mugodzhary paleoisland arc and position of VMS deposits (Zaykov et al., 2001b)

Table 1. *Comparative data for cervellite and cervelleite-like minerals*

| Occurrence  | Paragenetic position  | Reference                      |
|---|---|--------------------------------|
| <i>VHMS deposits</i>  |   |                                |
| Zyranovskoe, Altay<br>(phase z)   | in quartz veins with galena, chalcopyrite, sphalerite, pyrite, freibergite; anhedral 0.05 × 0.08 mm grains in galena with hessite and phase <i>u</i> (benleonardite-like).  | <i>Aksenov et al. (1969)</i>   |
| Bambolla, Mexico<br>(cervelleite)   | in silicified rhyolite vitrophyre as thin (30 μm) rims surrounding inclusions of acanthite in hessite, inclusions in hessite, finely intergrown with benleonardite.<br>Associated minerals: native silver, pyrite, sphalerite.  | <i>Criddle et al. (1989)</i>   |
| Um Samiuki, Egypt<br>(cervelleite)  | 1) as small (15–40 μm) subhedral crystals close to margins of hessite and galena grains; 2) as inclusions in sphalerite with silver-rich bornite, chalcopyrite and hessite.<br>Associated minerals: sphalerite, pyrite, chalcopyrite, galena, bornite, fahlore, hessite, and electrum.            | <i>Helmy (1999)</i>            |
| <i>Epithermal deposits</i>  |   |                                |
| Shadiitsa, Central<br>Rhodopes, Bulgaria<br>(Ag,Cu) <sub>4</sub> TeS  | anhedral grains and symplectitic intergrowths with hessite.   | <i>Gadzheva (1985)</i>         |
| Mayflower, Montana<br>(cervelleite)   | as irregular laths and masses (up to 150 μm) in contact with benleonardite and hessite. Associated minerals: tetrahedrite, hessite, sphalerite, gold.   | <i>Spry and Scott (1996)</i>   |
| Eniovche, Central<br>Rhodopes<br>(cervelleite?)   | irregular grains in galena anhedral <10 μm with phase A (skinnerite?). Ass. minerals: galena, pyrite, sphalerite, acanthite, freibergite, Ag-bearing tennantite.  | <i>Dobrev et al. (2002)</i>    |
| Larga, South<br>Apuseni Mts.,<br>Romania (cervelleite)  | in pyrite-arsenopyrite-gold vein mineralization as thin rims (5–10 μm) enclosing hessite and associated with galena and tetradymite, pyrite, arsenopyrite, gold, hessite, galena.   | <i>Cook and Ciobanu (2003)</i> |
| <i>Gold-quartz vein deposit</i>   |   |                                |
| Funan, China<br>(Ag,Cu) <sub>6</sub> TeS <sub>2</sub> –<br>(Ag,Cu) <sub>4</sub> TeS                           | anhedral grains 5–60 μm in size. Associated minerals: phase Ag <sub>9</sub> FeTe <sub>2</sub> S <sub>4</sub> , galena, hessite, stromeyerite, occasionally – acanthite, chalcopyrite.   | <i>Gu et al. (2003)</i>        |
| <i>Pegmatite deposit</i>  |   |                                |
| Ivigtut, Greenland<br>(mineral B)   | ass. minerals: chalcopyrite, galena, sphalerite, fahlore, pyrite, pyrrotite, chalcocite, native silver, acanthite.  | <i>Karup-Møller (1976)</i>     |
| <i>Skarn deposits</i>   |   |                                |
| Ocna de Fier,<br>NW Banat, Romania<br>(cervelleite,<br>Ag <sub>2</sub> Cu <sub>2</sub> TeS)                   | inclusions (~30 μm) with wittichenite within diopside, chalcopyrite. Ass. minerals: galena, matildite, petzite, hessite, tetradymite, berryite, Cu–Ag–Pb–Bi sulphosalts.  | <i>Cook and Ciobanu (2003)</i> |
| Băița Bihor,<br>Northern<br>Apuseni Mts.,<br>Romania<br>(cervelleite,<br>Ag <sub>2</sub> Cu <sub>2</sub> TeS) | at the outermost margin of coarse bornite, as minor component of bornite–galena intergrowths; grains up to 20 μm, enclosed in, or forming a rim on hessite.<br>Associated minerals: wittichenite, hessite, chalcocite, galena, other – gold, other tellurides, rarely – siegenite and polydymite. | <i>Cook and Ciobanu (2003)</i> |

sulfide (VHMS) deposit, Russian Altay. Phase *u* occurs within a galena matrix as intergrowths with hessite and phase *z* (a cervelleite-like phase; 68 wt.% Ag, 22 wt.% Te, 7 wt.% S). Phase *x* forms platy grains intergrowths with hessite and tetrahedrite-tennantite. Benleonardite has since been reported from the Mayflower and Gies deposits, Montana, (*Spry and Scott, 1996*), from the Vorontsovskoe skarn magnetite deposit in the Urals (*Murzin, 1991*), and from a number of other occurrences.

The type locality (TL) of cervelleite,  $\text{Ag}_4\text{TeS}$ , is also the Bambolla Mine (*Criddle et al., 1989*). Before acceptance of the mineral, Ag sulfotellurides with minor Cu contents have been described by *Aksenov et al. (1969)* from sulfide ores at Zyranovskoe (phase *z*, above), by *Gadzheva (1985)* from the Shadiitsa epithermal deposit (Bulgaria), and by *Karup-Møller (1976)* from the Ivigtut cryolite deposit, Greenland. Cervelleite was later studied by *Spry and Scott (1996)* from the Mayflower deposit, Montana, and by *Helmy (1999)* in galena–bornite–sphalerite ores of the Um Samiuki volcanic hosted Zn–Cu–Pb–Ag deposit, Egypt. More recent occurrences of cervelleite include descriptions of the mineral in both Neogene epithermal and Cretaceous skarn ores from Romania (*Cook and Ciobanu, 2003*), including the world-class Neogene breccia deposit at Roșia Montană (*Ciobanu et al., 2004*).

Cervelleite from the Eniovche epithermal deposit in the Central Rhodopes of Bulgaria (*Dobrev et al., 2002*) has a significant (up to 12.51 wt.%) admixture of copper (Fig. 1). In the vein Funan gold vein deposit, China (*Gu et al., 2003*), Ag-sulfotellurides with essential Cu contents form a series of unnamed phases within the range  $(\text{Ag,Cu})_6\text{TeS}_2 - (\text{Ag,Cu})_4\text{TeS}$ . An unnamed phase with the composition of one end member of this series ( $\text{Ag}_2\text{Cu}_2\text{TeS}$ ) was identified by *Cook and Ciobanu (2003)*. This is associated with cervelleite in the Băița Bihor and Ocna de Fier skarns, Romania. Comparative compositional data for all these ‘cervelleite-like’ phases are given in Table 1.

There are a number of occurrences of Ag-sulfotellurides in VHMS deposits of the South Urals: Gayskoe, Yaman-Kasy, Babaryk, Severo-Uvaryazhskoe and Tash-Tau. In this study, we compile published data for the Gayskoe and Yaman-Kasy occurrences and give new data for specimens from Severo-Uvaryazhskoe, Babaryk and Tash-Tau. Investigation of Ag-sulfotellurides in these VHMS deposits is important to understand trace mineral distributions within VHMS deposits in the Southern Urals, to understand genetic and transformation processes within the deposits, and the possible genetic relationships between VHMS and epithermal ores.

### Occurrences in the Southern Urals

The Urals is the world’s largest Paleozoic VHMS province. The deposits are, in general, related to paleo-island arc structures and minor spreading basins of the Urals Paleoocean (Fig. 1). Gold-enriched Zn–Cu–barite deposits of Kuroko type and Cu deposits of Cyprus type occur alongside the dominant Cu–Zn deposits of Uralian type (*Prokin and Buslaev, 1999*). There are several main ore types in each deposit, such as pyritic, Cu, and Zn–Cu ores, but the relative proportions of the different ore types varies from deposit to deposit. A highly schematic distribution scheme for the different ore types can be given as follows: Massive pyritic ore usually forms the central part of an ore lode. A stockwork zone, tracing the zone of

hydrothermal fluid infiltration is found beneath the massive pyrite zone. Ores at the upper and lateral parts of the ore bodies are enriched in Cu, Zn, and to a lesser extent in Au and Ag. Multiple generations of hydrothermal activity and tectonic overprinting have led to some remobilization and redeposition of ore minerals. Minerals such as sphalerite, galena, tetrahedrite-tennantite and gold (electrum) tend to be enriched in these later mineral assemblages. The main ore minerals are pyrite, chalcopyrite and sphalerite in various ratios; galena, pyrrhotite, magnetite and tennantite-tetrahedrite are also common. Accessory minerals in the deposits number more than 30 (Zaykov et al., 2001b). Gold-, Ag- and Pb-tellurides are widespread accessory minerals.

The VHMS deposits addressed in this study belong to the West-Magnitogorsk (Gayskoe, Yaman-Kasy, Tash-Tau, Severo-Uvaryazhskoe) and East-Magnitogorsk (Babaryk) paleo island arc structures (Fig. 1). The giant Gayskoe deposit (ore reserves >300 Mt, average grades are 1.57 wt.% Cu, 0.74 wt.% Zn, 0.06 wt.% Pb, 1.2 g/t Au, 77 g/t Ag and 30 g/t Te) is typical of the Uralian type. It is situated in the southern part of the West-Magnitogorsk paleoisland arc, on the flank of a volcanic edifice. The host rocks belong to the Baymak-Buribay suite, a bimodal rhyolite-basalt formation of Eifelian age. Felsic volcanic rocks from the ore-bearing zones are altered to sericite-quartz assemblages. The largest (northern) ore-bearing zone has a length of ca. 1600 m with a total thickness of ca. 200 m. The ores are both massive and disseminated. The massive ores display massive, banded, brecciated, taxitic, collomorphic, and bedded structures and each orebody is zoned. The central part of the ore bodies is represented by pyrite-chalcopyrite and pyrite ores, which contain tellurides (hessite, altaite, coloradoite, calaverite, krennerite and tellurobismuthite). The bornite-bearing ores contain a distinct mineral suite, including tennantite, gold, germanite, mawsonite, stannoidite, and betekhtinite (Prokin and Buslaev, 1999), and are placed on the flanks of the orebodies. No tellurides are reported from the bornite ores, but Ag-sulfotellurides have been determined (Moloshag and Gulyayeva, 1990).

The Yaman-Kasy Cu-Zn sulfide deposit is of Uralian type (ore reserves 1623 Mt, average grade 2.56 wt.% Cu, 5.56 wt.% Zn, 3.3 g/t Au, 33.5 g/t Ag, 204 g/t Te) and is situated in the Sakmarian Zone, interpreted as a marginal allochthon by Zaykov et al. (2001b). The deposit is located on the periphery of a volcanic dome. The host Silurian (?) Blavinskaya suite consists mostly of effusive and extrusive rhyolite-dacite. Rhyolite as well as basalt lava flows are known. Volcaniclastic rocks overlie the orebody. Quartz-sericite alteration is characteristic for the underlying rocks. The orebody has a lenticular form, attaining a maximum thickness of 37 m. It has been reconstructed as a sulfide hill containing numerous relics of vent chimneys and a near-vent fauna similar to that from modern black smoker edifices (Zaykov et al., 2001b). The dominant ore minerals are pyrite, sphalerite and chalcopyrite; marcasite, galena, wurtzite and barite are minor. Altaite, sylvanite, hessite, coloradoite, covellite, bornite, tellurobismuthite, tennantite, native tellurium and native gold are accessories. Silver sulfotellurides were identified in the chimney relics by Maslennikov (1999).

The Severo-Uvaryazhskoe and Tash-Tau deposits are of Kuroko type. They are located in the Baymak ore district, a system of paleovolcanic ridges hosting numerous occurrences of Kuroko-(Baymak) type sulfide ores. Formation of the

Severo-Uvaryazhskoe deposit is related to an effusive-extrusive rhyolite-dacite dome. Stockwork ores occupy the northern flank of the deposit. Massive brecciated and banded ores lie stratigraphically above and occupy the southern part of the deposit. Sulfide mineralization is accompanied by quartz-sericite alteration. Barite–sphalerite ore with Au and Ag contents up to 26 g/t and 330 g/t, respectively, occur within the stockwork zone (Zaykov et al. 2001a). Two mineralization stages are recognized: 1) pyrite with minor chalcopyrite; and 2) polymetallic ore with dominant sphalerite, galena and tetrahedrite-tennantite. Electrum, native silver, argentite, hessite, and cervelleite are accessories of the second stage (Zaykov et al., 2001a).

The Tash-Tau deposit occurs in the apical part of a basalt ridge, with adjacent and partly overlapping andesites, dacites and rhyolites flows. The rocks hosting the ore are Na-enriched rhyolite-basalt formations of Middle Devonian age (Baymak-Buribay Suite). The southern ore body contains ca. 70% of the total reserves and has a lens shape, 430 m in length and 80–160 m in width. Pyrite, chalcopyrite, and sphalerite are the main minerals; galena, tennantite, and bornite are minor. Native gold, electrum, hessite, jalpaite, germanite, a cervelleite-like phase and stromeyerite are accessories in bornite-bearing ores from the roof of the orebody. These ores are significantly enriched in Au and Ag (up to 80 and 400 g/t, respectively; Kuleshov and Zaykov, 2005).

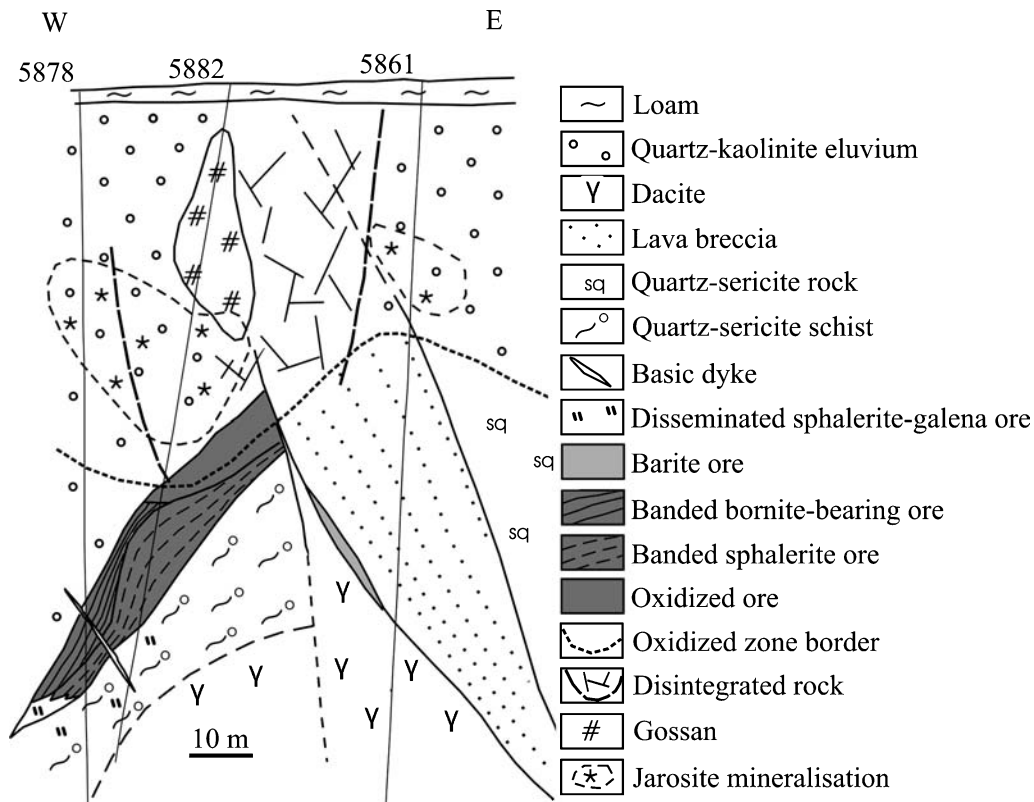


Fig. 2. Generalized cross-section of Babaryk deposit (Novoselov and Belogub, unpublished data)

The small Babaryk deposit is of Kuroko type too (average grade 2.15% Cu, 5.56% Zn, 1.93% Pb, 0.88 g/t Au, 108.6 g/t Au) and is located in the Alexandrinsky ore district of the East-Magnitogorsk paleo-island arc. The structure of this deposit is complicated by tectonics and is still much debated (Fig. 2). The ore lens lies within altered volcanic and volcanoclastic rocks of dacitic compositions (Alexandrinskaye strata in the upper part of the Karamalytash Formation, D<sub>2</sub>ef-zv). Both massive banded and veinlet-disseminated ores are found. The banded ore is enriched in Au (1.5 g/t), Ag (150 g/t) and Te (up to 57 g/t). On the base of mineralogical composition, several ore types can be distinguished: pyrite, pyrite–chalcopyrite–sphalerite–galena–bornite, sphalerite–barite and pyrite–barite. The principal ore minerals are sphalerite, chalcopyrite, bornite, and pyrite; galena, tetrahedrite and tennantite are less abundant. Accessory minerals are native gold (electrum), germanite, colusite, argyrodite, renierite (?), Ag-bearing chalcocite, stromeyerite and a cervelleite-like sulfotelluride. Gangue minerals are quartz, barite, calcite and sericite.

### Mineral assemblages and associations

Cervelleite was found within different mineral associations in deposits of the Southern Urals. *Moloshag* and *Gulyaeva* (1990) report that samples containing an unnamed Ag-sulfotelluride came from bornite-bearing ores of the “Sterzhnevaya Linza” ore body from the Northern ore zone of the Gayskoe deposit. The phase

Table 2. Comparative data for cervelleite-like minerals from VHMS deposits in the Urals

| Occurrence  | Paragenetic position   | Reference                                  |
|---|--|--|
| Gayskoe<br>(phase Ag <sub>3</sub> TeS)              | in tennantite–pyrite–sphalerite ores as isometric, anhedral to subhedral grains, 0.1–0.2 mm in size, impregnations in galena veinlets.   | <i>Moloshag</i> and <i>Gulyaeva</i> (1990) |
| Yaman-Kasy,<br>(cervelleite/<br>benleonardite-like) | in outer part (chalcopyrite zone) of marcasite–chalcopyrite–sphalerite chimneys as separate grains, intergrown with hessite and coloradoite, thin (10 μm) veinlets in sylvanite and hessite.   | <i>Maslennikov</i> et al. (1997)           |
| Severo-Uvaryazhskoe,<br>(cervelleite)               | in chalcopyrite–sphalerite–pyrite–fahlore ores as anhedral grains, up to 20 μm in size, in galena, intergrowths with hessite. Associated minerals are electrum, native silver and acanthite  | <i>Zaykov</i> et al. (2001)                |
| Tash-Tau  | in chalcopyrite–fahlore–sphalerite–pyrite–bornite ores as inclusions (~0.03 mm) in galena, galena–bornite–pyrite border. Associated mineral is gold.   | <i>Kuleshov</i> and <i>Zaykov</i> (2005)   |
| Babaryk,<br>(cuprous<br>cervelleite-like)           | in banded pyrite–chalcopyrite–sphalerite–bornite–galena ores with tennantite–tetrahedrite as anhedral to elongated grains up to 0.2 mm in size within galena, at the galena–bornite grain boundary. Associated minerals are chalcocite, stromeyerite and electrum. | <i>Novoselov</i> and <i>Belogub</i> (2004) |

was found in association with tennantite, pyrite, sphalerite (luminescent in ultra-violet light), galena, and bornite. It forms subhedral isometric grains up to 15  $\mu\text{m}$  in size included within galena (Table 2). Electrum occurs within this ore type (*Prokin and Buslayev, 1999*).

*Maslennikov et al. (1997)* reported Ag-sulfotellurides in a marcasite–sphalerite–chalcopyrite chimney relic from the Yaman-Kasy deposit, where, the sulfotellurides form isolated inclusions in chalcopyrite, intergrowths with hessite and coloradoite, and microveinlets (10  $\mu\text{m}$ ) in sylvanite or hessite within the chalcopyrite zone of the chimney.

In the Severo-Uvaryazhskoe deposit, cervelleite was found in samples from prospecting borehole 4324 at a depth 43–45 m from the surface (Fig. 3). This drillhole is located on the northern flank of the deposit and intersects ore between 39.0 and 55.6 m (*Zaykov et al., 2001a*). Cervelleite forms anhedral, elongated grains up to 100  $\mu\text{m}$  in size within galena from the pyrite–sphalerite–galena–chalcopyrite–tennantite stockwork ores (Table 2). Cervelleite sometimes forms simple intergrowths with hessite (Fig. 4a). Rarely, hessite replaces cervelleite (Fig. 4b); both electrum ( $\text{Au}_{0.60}\text{Ag}_{0.40}$ ) and acanthite are accompanying Ag minerals.

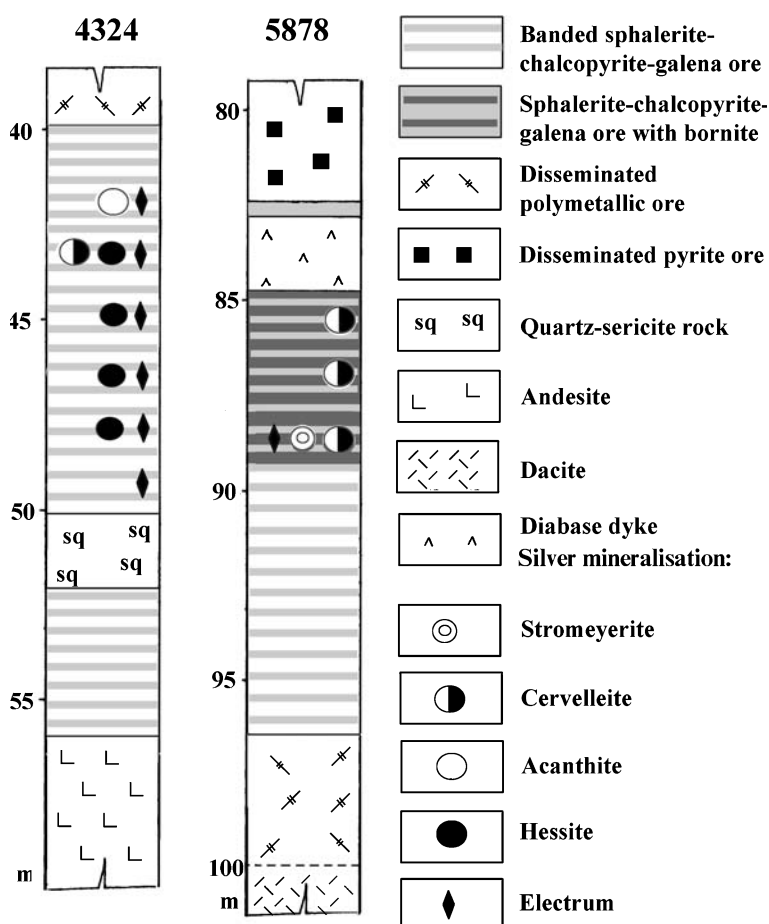


Fig. 3. Location of the occurrence of cervelleite (Severo-Uvaryazhskoe deposit, drillhole 4324) and Cu-bearing cervelleite-like mineral (Babaryk deposit, drillhole 5878)



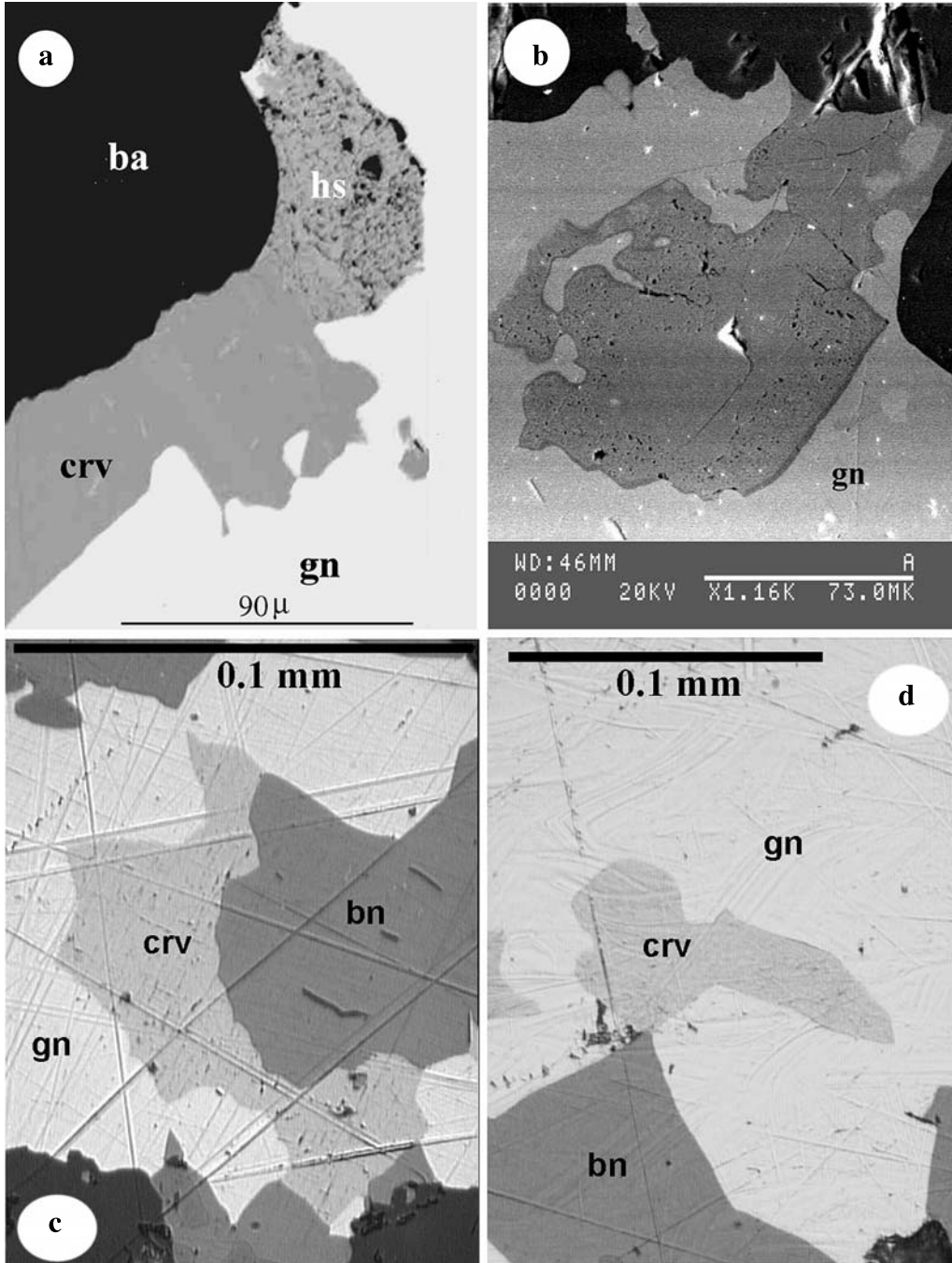


Fig. 4. Cervelleite-bearing assemblages from the Severo-Uvaryazhskoe (back-scattered electron images – **a**, **b** and Babaryk deposit (reflected light images – **c**, **d**). Crv – cervelleite, gn – galena, bn – bornite, hs – hessite, ba – barite

In the Tash-Tau deposit, a cervelleite-like mineral occurs as small isometric inclusions ( $\sim 30 \mu\text{m}$ ) at the boundary between galena and bornite in massive sphalerite–chalcopyrite–bornite ores from the roof of the sulfide mound. Large aggregates of

gold (up to 4 mm in size) with varying compositions ( $\text{Au}_{0.76-0.86}\text{Ag}_{0.24-0.14}$ ) are associated with cervelleite in the same sample.

A Cu-bearing cervelleite-like mineral was found in banded pyrite–chalcopyrite–sphalerite–bornite–galena ores from the Babaryk deposit (Fig. 3). Intermediate tennantite–tetrahedrite with high Zn (up to 14.55%) and low Fe (0 to 3.97%) contents occur in this ore. Sphalerite shows blue luminescence colors in ultraviolet light. Cervelleite forms elongate isometric anhedral grains up to 0.2 mm in size, which are included within galena or are restricted to bornite–galena grain boundaries (Fig. 4c, d). Sometimes, cervelleite is associated with stromeyerite, Ag-bearing chalcocite and electrum (Novoselov and Belogub, 2004).

### Compositional data

In the deposits discussed here, sulfotellurides are either minerals that resemble cervelleite or appear to be phases derived from cervelleite in terms of composition, variation in stoichiometry and physical properties. Microprobe analyses from all occurrences are summarized in Table 3. The composition of species from the Gayskoye deposit is cited from *Moloshag* and *Gulyayeva* (1990). Cervelleite from the Severo-Uvaryazhskoe and Tash-Tau deposits was analyzed by Cameca SX-50 electron microprobe at the Natural History Museum, London (courtesy of *T. Williams* and *J. Spratt*). Specimens from the Yaman-Kasy deposit were studied using the same instrument, but at a different period in time (courtesy of *C. Stanley* and *V. Masselnikov*). The chemical composition of Cu-bearing cervelleite-like mineral from the Babaryk deposit was established using a REMMA-2M SEM instrument equipped with EDAX, at the Institute of Mineralogy, Miass, Russia (analyst *V. A. Kotlyarov*). Natural  $\text{FeS}_2$ , Cu, Ag, and HgTe were used as standards.

#### *Silver sulfotellurides without significant copper*

The specimens from the Severo-Uvaryazhskoe deposit give compositions which are most similar to ideal cervelleite:  $(\text{Ag}_{1.79}\text{Cu}_{0.09})_{1.88}(\text{Te}_{0.50}\text{S}_{0.50})_{1.00}$ . The minerals have S/Te ratios  $\sim 1$ , like TL cervelleite (*Criddle* et al., 1989). The only minor elements detected are Fe, Zn and Sb (Table 3). The Ag content of the associated tennantite was about 3%. No other minerals in the assemblage contained Ag, except for rare acanthite, which has Cu contents up to as much as  $\text{Ag}_{1.7}\text{Cu}_{0.3}\text{S}$ . A decrease in the Ag content of cervelleite (from 69 to 59 wt.%), and corresponding increase in Te content, is said to correspond to depth in the drillhole at the Severo-Uvaryazhskoe deposit (*Zaykov* et al., 2001a). These authors also described a phase transitional between cervelleite and hessite occurring as a rim between the two minerals (Fig. 4b).

Sulfotellurides from the Gayskoye deposit also have S/Te ratios  $\sim 1$ , but there is some deficit in cation site occupancy relative to ideal cervelleite. The chemical composition can be given as  $(\text{Ag}_{1.46}\text{Cu}_{0.03})_{1.48}(\text{Te}_{0.50}\text{S}_{0.50})_{1.00}$ . Both the associated bornite and tennantite are characterized by detectable Ag contents, but bornite has 2–3 times more Ag than does the tennantite (*Prokin* and *Buslaev*, 1999).

According to *Maslennikov* et al. (1997), Ag-sulfotellurides from the chimneys of the Yaman-Kasy deposit have considerable contents of As (up to 1.80 wt.%)

Table 3. Chemical composition (wt.%) and formulae of cervelleite and cervelleite-like minerals from the Urals VHMS deposits

|     | Ag    | Cu    | S    | Te    | Fe   | Zn   | Sb   | Pb   | Total  | Formula   |
|-----|-------|-------|------|-------|------|------|------|------|--------|---|
| 1.  | 65.42 | 0.85  | 6.63 | 26.51 | —    | —    | —    | 0.25 | 99.41  | (Ag <sub>1.46</sub> Cu <sub>0.03</sub> ) <sub>1.48</sub> (Te <sub>0.50</sub> S <sub>0.50</sub> ) <sub>1.00</sub>                    |
| 2.  | 66.18 | 1.27  | 7.42 | 24.21 | 1.20 | 0.23 | 0.01 | —    | 100.52 | (Ag <sub>1.66</sub> Cu <sub>0.09</sub> Fe <sub>0.06</sub> ) <sub>1.81</sub> (Te <sub>0.56</sub> S <sub>0.44</sub> ) <sub>1.00</sub> |
| 3.  | 68.47 | 1.50  | 6.08 | 21.93 | 1.07 | 0.01 | 0.02 | —    | 99.08  | (Ag <sub>1.80</sub> Cu <sub>0.11</sub> Fe <sub>0.04</sub> ) <sub>1.95</sub> (S <sub>0.51</sub> Te <sub>0.49</sub> ) <sub>1.00</sub> |
| 4.  | 69.52 | 1.58  | 5.30 | 22.72 | 0.05 | 0.00 | 0.16 | —    | 99.33  | (Ag <sub>1.84</sub> Cu <sub>0.12</sub> ) <sub>1.96</sub> (S <sub>0.53</sub> Te <sub>0.47</sub> ) <sub>1.00</sub>                    |
| 5.  | 68.2  | 1.70  | 5.82 | 22.8  | 0.03 | 0.66 | 0.16 | —    | 99.37  | (Ag <sub>1.76</sub> Cu <sub>0.07</sub> Zn <sub>0.04</sub> ) <sub>1.87</sub> (Te <sub>0.50</sub> S <sub>0.50</sub> ) <sub>1.00</sub> |
| 6.  | 69.29 | 2.00  | 5.66 | 21.96 | 0.04 | 0.59 | 0.16 | —    | 99.70  | (Ag <sub>1.76</sub> Cu <sub>0.07</sub> Zn <sub>0.03</sub> ) <sub>1.86</sub> (S <sub>0.52</sub> Te <sub>0.48</sub> ) <sub>1.00</sub> |
| 7.  | 65.34 | 2.07  | 5.14 | 26.15 | 0.32 | 0.12 | 0.21 | —    | 99.35  | (Ag <sub>1.82</sub> Cu <sub>0.16</sub> Fe <sub>0.02</sub> ) <sub>2.00</sub> (S <sub>0.53</sub> Te <sub>0.47</sub> ) <sub>1.00</sub> |
| 8.  | 68.63 | 2.74  | 5.89 | 20.63 | 0.02 | 1.44 | 0.19 | —    | 99.54  | (Ag <sub>1.84</sub> Cu <sub>0.09</sub> Zn <sub>0.06</sub> ) <sub>1.99</sub> (Te <sub>0.52</sub> S <sub>0.48</sub> ) <sub>1.00</sub> |
| 9.  | 68.14 | 3.52  | 5.84 | 20.99 | 0.02 | 1.24 | 0.15 | —    | 99.90  | (Ag <sub>1.88</sub> Cu <sub>0.07</sub> Zn <sub>0.06</sub> ) <sub>2.01</sub> (Te <sub>0.52</sub> S <sub>0.48</sub> ) <sub>1.00</sub> |
| 10. | 64.26 | 7.51  | 7.07 | 21.13 | 0.23 | —    | 0.10 | 0.28 | 101.48 | (Ag <sub>1.54</sub> Cu <sub>0.31</sub> Fe <sub>0.01</sub> ) <sub>1.86</sub> (S <sub>0.57</sub> Te <sub>0.43</sub> ) <sub>1.00</sub> |
| 11. | 65.89 | 7.26  | 6.26 | 20.73 | 0.60 | —    | 0.00 | 0.28 | 101.02 | (Ag <sub>1.71</sub> Cu <sub>0.32</sub> Fe <sub>0.02</sub> ) <sub>2.05</sub> (S <sub>0.55</sub> Te <sub>0.45</sub> ) <sub>1.00</sub> |
| 12. | 65.07 | 10.05 | 8.76 | 16.09 | —    | —    | —    | —    | 99.97  | (Ag <sub>1.51</sub> Cu <sub>0.40</sub> ) <sub>1.91</sub> (S <sub>0.68</sub> Te <sub>0.32</sub> ) <sub>1.00</sub>                    |
| 13. | 63.50 | 11.28 | 8.43 | 16.77 | —    | —    | —    | —    | 99.98  | (Ag <sub>1.49</sub> Cu <sub>0.45</sub> ) <sub>1.94</sub> (S <sub>0.67</sub> Te <sub>0.33</sub> ) <sub>1.00</sub>                    |
| 14. | 63.71 | 11.43 | 8.68 | 16.26 | —    | —    | —    | —    | 100.08 | (Ag <sub>1.48</sub> Cu <sub>0.45</sub> ) <sub>1.93</sub> (S <sub>0.68</sub> Te <sub>0.32</sub> ) <sub>1.00</sub>                    |
| 15. | 63.16 | 11.67 | 8.25 | 16.91 | —    | —    | —    | —    | 99.99  | (Ag <sub>1.50</sub> Cu <sub>0.47</sub> ) <sub>1.97</sub> (S <sub>0.66</sub> Te <sub>0.34</sub> ) <sub>1.00</sub>                    |
| 16. | 64.26 | 11.74 | 8.51 | 15.61 | —    | —    | —    | —    | 100.12 | (Ag <sub>1.54</sub> Cu <sub>0.48</sub> ) <sub>2.02</sub> (S <sub>0.68</sub> Te <sub>0.32</sub> ) <sub>1.00</sub>                    |
| 17. | 64.11 | 12.09 | 8.19 | 15.81 | —    | —    | —    | —    | 100.20 | (Ag <sub>1.57</sub> Cu <sub>0.50</sub> ) <sub>2.07</sub> (S <sub>0.67</sub> Te <sub>0.33</sub> ) <sub>1.00</sub>                    |
| 18. | 63.07 | 12.94 | 9.47 | 14.63 | —    | —    | —    | —    | 100.11 | (Ag <sub>1.43</sub> Cu <sub>0.50</sub> ) <sub>1.93</sub> (S <sub>0.72</sub> Te <sub>0.28</sub> ) <sub>1.00</sub>                    |
| 19. | 64.16 | 13.14 | 8.57 | 14.23 | —    | —    | —    | —    | 100.10 | (Ag <sub>1.51</sub> Cu <sub>0.40</sub> ) <sub>1.91</sub> (S <sub>0.68</sub> Te <sub>0.32</sub> ) <sub>1.00</sub>                    |
| 20. | 62.27 | 13.17 | 9.23 | 15.51 | —    | —    | —    | —    | 100.18 | (Ag <sub>1.41</sub> Cu <sub>0.51</sub> ) <sub>1.92</sub> (S <sub>0.70</sub> Te <sub>0.30</sub> ) <sub>1.00</sub>                    |
| 21. | 63.13 | 13.33 | 8.98 | 14.55 | —    | —    | —    | —    | 99.99  | (Ag <sub>1.49</sub> Cu <sub>0.53</sub> ) <sub>2.02</sub> (S <sub>0.71</sub> Te <sub>0.29</sub> ) <sub>1.00</sub>                    |
| 22. | 61.02 | 13.44 | 8.04 | 17.56 | —    | —    | —    | —    | 100.06 | (Ag <sub>1.46</sub> Cu <sub>0.54</sub> ) <sub>2.00</sub> (S <sub>0.65</sub> Te <sub>0.35</sub> ) <sub>1.00</sub>                    |
| 23. | 63.63 | 13.45 | 9.05 | 13.96 | —    | —    | —    | —    | 100.09 | (Ag <sub>1.51</sub> Cu <sub>0.54</sub> ) <sub>1.95</sub> (S <sub>0.72</sub> Te <sub>0.28</sub> ) <sub>1.00</sub>                    |
| 24. | 61.42 | 13.60 | 8.52 | 16.76 | —    | —    | —    | —    | 100.30 | (Ag <sub>1.43</sub> Cu <sub>0.54</sub> ) <sub>1.97</sub> (S <sub>0.67</sub> Te <sub>0.33</sub> ) <sub>1.00</sub>                    |
| 25. | 62.85 | 14.07 | 9.08 | 14.09 | —    | —    | —    | —    | 100.09 | (Ag <sub>1.48</sub> Cu <sub>0.56</sub> ) <sub>2.04</sub> (S <sub>0.72</sub> Te <sub>0.28</sub> ) <sub>1.00</sub>                    |
| 26. | 60.59 | 14.40 | 8.11 | 17.00 | —    | —    | —    | —    | 100.10 | (Ag <sub>1.45</sub> Cu <sub>0.59</sub> ) <sub>2.05</sub> (S <sub>0.65</sub> Te <sub>0.35</sub> ) <sub>1.00</sub>                    |
| 27. | 64.26 | 7.51  | 7.07 | 20.13 | —    | —    | —    | —    | 98.97  | (Ag <sub>1.71</sub> Cu <sub>0.32</sub> ) <sub>2.03</sub> (S <sub>0.55</sub> Te <sub>0.45</sub> ) <sub>1.00</sub>                    |

(continued)

Table 3 (continued)

|     | Ag    | Cu   | S    | Te    | Fe   | Zn | Sb   | As   | Total  | Formula   |
|-----|-------|------|------|-------|------|----|------|------|--------|---|
| 28. | 63.61 | 0.64 | 6.72 | 29.01 | 0.52 | –  | 0.16 | –    | 100.66 | (Ag <sub>1.35</sub> Cu <sub>0.02</sub> Fe <sub>0.02</sub> ) <sub>1.39</sub> (Te <sub>0.52</sub> S <sub>0.48</sub> ) <sub>1.00</sub> |
| 29. | 66.82 | 0.11 | 7.11 | 27.44 | 0.06 | –  | 0.15 | –    | 101.69 | Ag <sub>1.58</sub> (S <sub>0.64</sub> Te <sub>0.36</sub> ) <sub>1.00</sub>  |
| 30. | 62.55 | 0.24 | 5.39 | 29.4  | 0.15 | –  | 0.1  | 1.80 | 99.63  | (Ag <sub>1.46</sub> As <sub>0.06</sub> Cu <sub>0.01</sub> ) <sub>1.53</sub> (Te <sub>0.58</sub> S <sub>0.42</sub> ) <sub>1.00</sub> |
| 31. | 63.03 | 0.28 | 4.29 | 30.11 | 0.04 | –  | 0.2  | 1.58 | 99.53  | (Ag <sub>1.59</sub> As <sub>0.05</sub> Cu <sub>0.01</sub> ) <sub>1.65</sub> (Te <sub>0.68</sub> S <sub>0.32</sub> ) <sub>1.00</sub> |
| 32. | 62.99 | 0.29 | 7.5  | 30.59 | 0.14 | –  | 0.23 | –    | 101.74 | (Ag <sub>1.23</sub> Cu <sub>0.01</sub> ) <sub>1.24</sub> (Te <sub>0.51</sub> S <sub>0.49</sub> ) <sub>1.00</sub>                    |
| 33. | 65.3  | 0.29 | 3.5  | 29.3  | 0.21 | –  | 0.14 | 0.56 | 99.30  | (Ag <sub>1.79</sub> As <sub>0.02</sub> Cu <sub>0.01</sub> ) <sub>1.82</sub> (Te <sub>0.68</sub> S <sub>0.32</sub> ) <sub>1.00</sub> |
| 34. | 64.34 | 0.42 | 4.53 | 28.71 | 0.29 | –  | 0.05 | 0.93 | 99.27  | (Ag <sub>1.63</sub> As <sub>0.03</sub> Cu <sub>0.02</sub> ) <sub>1.68</sub> (Te <sub>0.61</sub> S <sub>0.39</sub> ) <sub>1.00</sub> |
| 35. | 66.17 | 0.55 | 7.36 | 27.99 | 0.37 | –  | 0.12 | –    | 102.56 | (Ag <sub>1.37</sub> Cu <sub>0.02</sub> Fe <sub>0.01</sub> ) <sub>1.40</sub> (S <sub>0.51</sub> Te <sub>0.49</sub> ) <sub>1.00</sub> |
| 36. | 68.26 | 1.46 | 6.48 | 24.26 | –    | –  | –    | –    | 100.46 | (Ag <sub>1.61</sub> Cu <sub>0.06</sub> ) <sub>1.72</sub> (S <sub>0.52</sub> Te <sub>0.48</sub> ) <sub>1.00</sub>                    |

Analysis 1 – Guyskoe (*Moloshag and Gulyaeva, 1990*); analyses 2–11 – Severo-Uvaryazhskoe; analyses 12–26 – Babaryk; analysis 27 – Tash-Tau; analyses 28–36 – Yaman-Kasy (*Masternikov et al., 1997*)

“–” indicates that element content is below detection limit

Table 4. Chemical composition of the Ag-bearing minerals associated with Cu-bearing cervelleite from the Babaryk deposit (wt.%)

|              | S     | Cu    | Ag    | Au    | Total  |
|--------------|-------|-------|-------|-------|--------|
| Stromeyerite | 15.81 | 32.10 | 52.07 | 0     | 99.98  |
| Stromeyerite | 15.63 | 32.39 | 51.96 | 0     | 99.98  |
| Stromeyerite | 15.90 | 31.64 | 52.49 | 0     | 100.03 |
| Stromeyerite | 16.02 | 31.29 | 52.89 | 0     | 100.20 |
| Stromeyerite | 16.02 | 31.33 | 52.78 | 0     | 100.13 |
| Stromeyerite | 15.92 | 31.31 | 52.76 | 0     | 99.99  |
| Stromeyerite | 15.61 | 31.90 | 52.76 | 0     | 100.27 |
| Electrum     | 0     | 0     | 26.49 | 73.49 | 99.98  |
| Electrum     | 0     | 0     | 28.68 | 71.49 | 100.17 |
| Chalcocite   | 20.33 | 78.58 | 1.89  | 0     | 100.80 |

Analyses were made using REMMA-202M instrument. Standards: native elements (Cu, Au and Ag), FeS<sub>2</sub> (S). Analyst VA Kotlyarov

and Sb (up to 2.26 wt.%). The ratio between Ag and  $\Sigma(S + Te)$  varies from 1.3:1 to 1.8:1.

#### *Silver sulfotellurides with significant copper content*

The Ag-sulfotelluride from the Tash-Tau deposit has significant contents of Cu, up to 0.32 atoms per formula unit,  $(Ag_{1.71}Cu_{0.32})_{2.03}(S_{0.55}Te_{0.45})_{1.00}$ . The phase also has a high sulfur content compared to TL cervelleite, with S also prevailing also Te. The  $\Sigma(Ag + Cu)/\Sigma(Te + S)$  ratio is 2:1. The Ag content in associated bornite reaches 2.7 wt.% (Kuleshov and Zaykov, 2005).

The composition of the Cu-bearing sulfotelluride from the Babaryk deposit,  $(Cu_{0.48}Ag_{1.49})_{1.97}(S_{0.69}Te_{0.31})_{1.00}$ , is specific to this deposit and cannot be equated with any named mineral. Its S/Te ratio is  $\sim 2$ , and Cu contents can be as much as 14.4 wt.%. The composition is constant whichever mineral it is hosted in, or associated with. Silver was not found in the associated chalcopyrite, tennantite-tetrahedrite, bornite or galena; compositions of the accompanying Ag-bearing minerals are given in Table 4.

#### **Appearance and physical properties**

All of the Ag-sulfotellurides discussed in this study are trace components of the ores, typified by very small grain size, irregular habit and common intergrowths. We have, nevertheless undertaken a baseline study of their optical and physical properties. Table 5 summarizes our data for the Urals specimens and compares them with other published data for the mineral family, underlining the large variation in optical properties and hardness (Table 5).

#### *Optical properties*

A quantitative study of optical properties was made using a MSF-10 microscope-microphotometer (LOMO, Russia) at Saint-Petersburg State University. SiC was

Table 5. Optical and physical properties of cervelleite-like sulphotellurides in comparison with similar minerals from Bambolla and Zyranovskoe

| Occurrence                                     | Optical properties  | Hardness                               |
|--|---|--|
| Zyranovskoe, phase Z<br>(Aksenov et al., 1969) | R: 40 (442)–40.1 (465)–39.9 (493)–39.5 (523)–39 (551)–38.1 (588)–37.4 (621)–36.2 (667)–35.9 (698); isotropic; gray with bluish-green or greenish shade. | VHN 84–87;<br>hessite > h < galena     |
| Gayskoe<br>(Moloshag<br>and Gulyaeva, 2002)    | Anisotropic.  | no data                                |
| Bambolla<br>(Criddle et al., 1989)             | R: 39.75 (400)–39.8 (470)–38.15 (546)–35.6 (650)–34.4 (700); isotropic; bluish to greenish white; positive photochemical reaction.                      | VHN <sub>10</sub> 26                   |
| Yaman-Kasy<br>(Maslennikov et al., 1997)       | anisotropic; dark gray with brown shade; strong positive photochemical reaction.  | no data                                |
| Severo-Uvaryazhskoe<br>(this study)            | R: 36.5 (460)–37.1 (520)–35.8 (620)–35.1 (700); isotropic; gray with greenish shade.  | VHN <sub>20</sub> 119.4;<br>H > galena |
| Babaryk (this study)                           | R: 32.9 (400)–32.5 (460)–32.1 (520)–30.6 (620)–29.9 (700); isotropic; gray with greenish, bluish-greenish shade.  | VHN <sub>10</sub> 44.5;<br>h < galena  |

R – reflectivity, % (in brackets wavelength, nm); VHN – microhardness, kg/mm<sup>2</sup>; h – polishing hardness

used as standard. The reflectance spectrum of cervelleite from the Severo-Uvaryazhskoe deposit differs from that of TL cervelleite given by Criddle et al. (1989). Maximum reflectivity was observed at a wavelength of around 550 nm; for

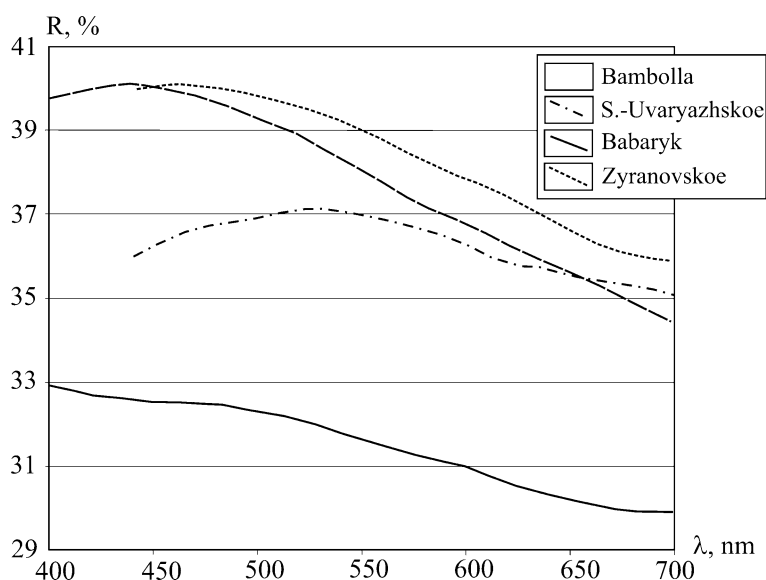


Fig. 5. Reflectance spectra of Urals species of cervelleite-like minerals in comparison with cervelleite from the Bambolla Mine (Criddle et al., 1989), and phase z from the Zyranovskoe deposit (Aksenov et al., 1969). MSF-10, SiC standard (Saint-Petersburg University): Babaryk – analyst V. Yakovleva, average from 12 measurements; Severo-Uvaryazhskoe – analyst Yu. Polyakhovsky

TL cervelleite it was 450 nm (Fig. 5). The distinctive greenish shade observed in reflected light is concordant with the shape of the reflectivity spectrum. The reflectivity spectrum of the Cu-bearing cervelleite-like mineral from Babaryk is characterized by much lower R values (Fig. 5). A distinctive feature of the cervelleite-like minerals from Gayskoe and Yaman-Kasy deposit is their optical anisotropy.

Microhardness values were estimated using a PMT-3 microhardness tester (LOMO, Russia). Values for cervelleite-like minerals from the Urals cover a wide range from 44.5 to 119.4 kg/mm<sup>2</sup> (Table 5). This large range can be hardly explained by the variations in chemical composition. It is possible that these variations are heavily influenced by grain size and cleavage. The microhardness measurements for TL cervelleite are unique because of the extremely small grain size of the material. Our results for the Urals samples should, therefore, be of better quality because of the coarser, more representative material. Cervelleite-like phase *z* from the Zyranovskoe deposit (Aksenov et al., 1969) has a microhardness value comparable with the Urals samples. It is possible to assert that cervelleite actually has a higher microhardness than had been reported for TL material. The described polishing relief of minerals tends to confirm this hypothesis. An imprint of Vickers indenter is light, salient, and isometric; concentric cracks occur close to the indentation mark. In some grains, we can see fine rough parallel fractures which can be considered as imperfect cleavage.

Criddle et al. (1989) pointed out that only a very mild photochemical reaction was observed for TL cervelleite that had been isolated from other Ag-minerals (acantite and hessite). In contrast, intergrowths of cervelleite with other Ag-minerals lead to aggravation of the photochemical reaction. Our study indicated that the Ag-sulfotellurides are chemically stable. Experiments with some of the cervelleite-like minerals from Babaryk and Severo-Uvryazhskoe deposits show negative or very weak (with HNO<sub>3</sub>) chemical or photochemical reaction. Breakdown of sulfotellurides during storage of the polished sections from Yaman-Kasy was, nevertheless, observed.

#### *Structure and X-ray investigations*

TL cervelleite has a primitive cubic cell with a 14.03 Å (Criddle et al., 1989). We undertook several attempts to obtain X-ray data for the Cu-bearing sulfotelluride from Babaryk, picking out the material with a needle under microscope. Reflection intensities are very weak: estimated as a weak (w), very weak (vw) or extremely weak (ew) (d (Å), intensity): 5.04, w; 4.16, ew; 3.08, w; 2.54, vw; 2.32, w. The spectrum we obtained is not similar to that of TL cervelleite, but the poor quality of the X-ray pattern means that it could not be compared with confidence.

## **Discussion**

### *Paragenesis*

It has been shown that cervelleite and cervelleite-like minerals occur in different types of ore deposits, including VHMS, epithermal, skarn, pegmatite and gold-quartz

veins (Table 1). Relationships between Ag-sulfotellurides and associated minerals in the VHMS deposits indicate that they may be formed in a number of different ways. They can occur as isolated subhedral grains in ores, as reaction products between Ag-sulfides and -tellurides, and, possibly, also as decomposition products of a higher-temperature solid solution phase. For example, the sulfotelluride from Babaryk forms subhedral inclusions in galena, which can be interpreted as crystallization of this mineral as a stable phase. In this case, however, it also forms symplectitic intergrowths with galena and chalcocite. In the Yaman-Kasy deposit, veinlets of non-stoichiometric sulfotellurides crosscut the tellurides, reflecting increasing  $fS_2$  and decreasing  $fTe_2$  during ore formation (Maslennikov et al., 1997). Cervelleite from the type locality forms as a reaction zone around acanthite in hessite (Criddle et al., 1989).

As stable independent compounds, the cervelleite-like minerals belong to the latest polymetallic mineral association in all listed ore deposit types, with the exception of Yaman-Kasy. Importantly, galena is always present in the same paragenesis (Table 1). Copper-minerals, such as members of the tennantite-tetrahedrite series, bornite, chalcocite, and chalcopyrite may also be associated in some of the occurrences; sometimes (but not always) these minerals are Ag-enriched. Silver-bearing native gold, electrum or native silver, hessite and acanthite are the associated Ag-bearing minerals; hessite is a common telluride in this association. The coexistence of stromeyerite was established only for the Babaryk deposit. Native tellurium, coloradoite, a benleonardite-like mineral, and Bi-sulfotellurides are rare and were found only in the chimney relic from the Yaman-Kasy deposit. It would appear that this mineral association does not represent an equilibrium assemblage.

### *Compositional series*

Wide variations in chemistry seem to be characteristic for cervelleite and related sulfotellurides. According to published data (e.g., Criddle et al., 1989; Helmy, 1999; Cook and Ciobanu, 2003; Gu et al., 2003; Novoselov and Belogub, 2004), the main variations can be expressed in terms of (i) variation in S/Te ratio, (ii) contents of Cu substituting for Ag, and (iii) varying ratios between  $\Sigma(Ag + Cu)$  and  $\Sigma(S + Te)$ .

Hessite ( $Ag_2Te$ ), chalcocite ( $Cu_2S$ ), acanthite and argentite ( $Ag_2S$ ), stromeyerite ( $AgCuS$ ), jalpaite ( $Ag_3CuS$ ), henryite ( $Ag_3Cu_4Te_4$ ) and cervelleite ( $Ag_4TeS$ ) are named mineral species in the system Ag–Cu–Te–S. Besides these, the synthetic phase  $AgCuTe_{0.5}S_{0.5}$  is reported to be stable over a wide range of temperature (Yu. Asadov, pers. comm). Like hessite, acanthite and chalcocite, this phase has both cubic (high-temperature) and monoclinic (low-temperature) polymorphs.

Contents of Ag, Cu, S and Te in natural cervelleite are characterized by strict element correlations defined by substitutions between cations or anions, i.e.,  $Ag \Leftrightarrow Cu$  and  $Te \Leftrightarrow S$  (Fig. 6). These observations are evidence of solid solution (isomorphism) in both the cation and anion pairs. Published data also show good positive correlations for the pairs Ag–Te and Cu–S within stoichiometric limits. The compositions of some extremely Cu-enriched cervelleite grains from the Romanian deposits (Cook and Ciobanu, 2003) are, however, an apparent exception to this trend.



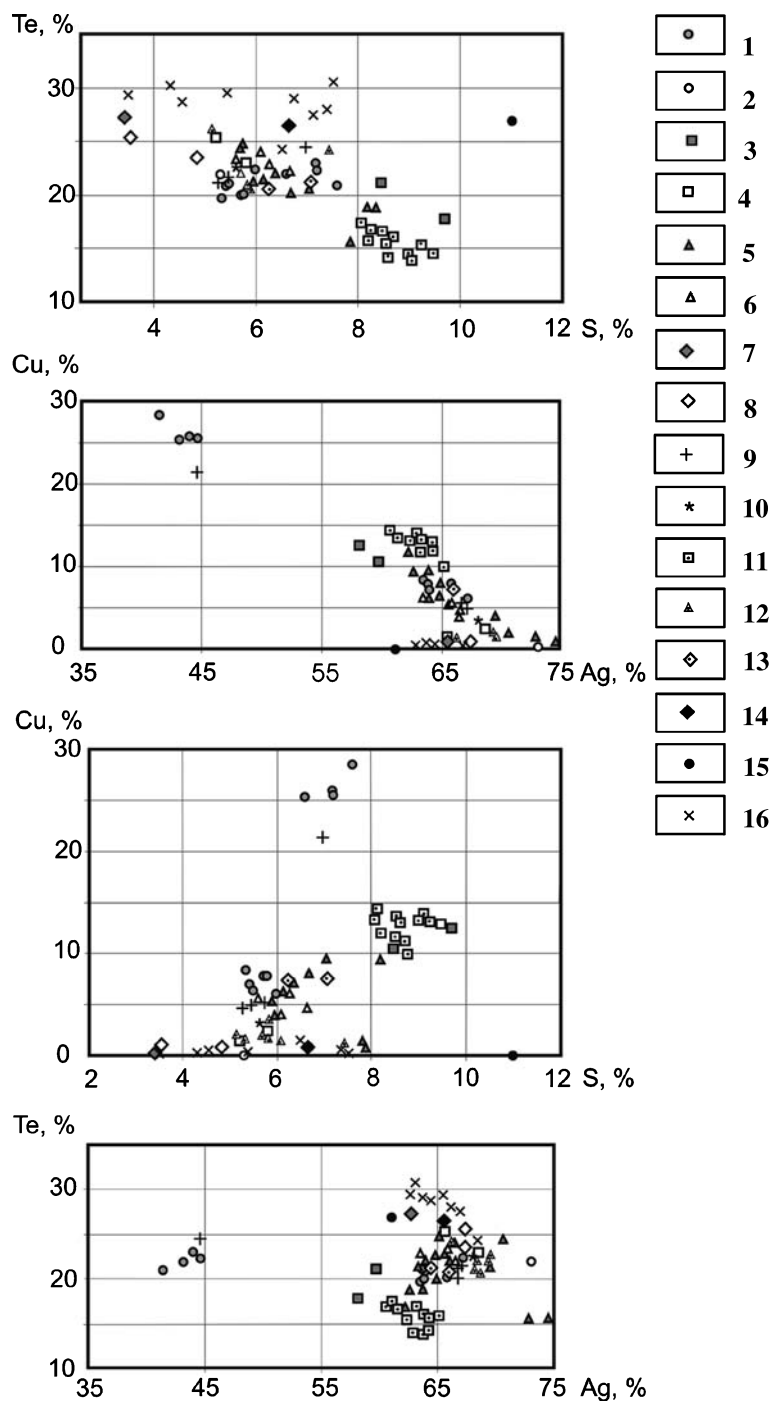


Fig. 6. Plots illustrating compositional correlations in the cervelleite-like phases. **1** Băița Bihor (Cook and Ciobanu, 2003), **2** Bambolla (Criddle et al., 1989), **3** Eniovche (Dobrev et al., 2002), **4** Ivigtut (Karup-Møller, 1976), **5** Funan (Gu et al., 2002), **6** Um Samiuki (Helmy, 1999), **7** Larga (Cook and Ciobanu, 2003), **8** Mayflower (Spry and Scott, 1996), **9** Ocna de Fier (Cook and Ciobanu, 2003), **10** Shadiitsa (Gadzheva, 1985), **11** Babaryk (Novoselov and Belogub, 2004), **12** Severo-Uvaryazhskoe, **13** Tash-Tau, **14** Gayskoye (Moloshag and Gulyaeva, 1990), **15** Zyryanovskoye (Aksenov et al., 1969), **16** Yaman-Kasy (Maslennikov et al., 1997)

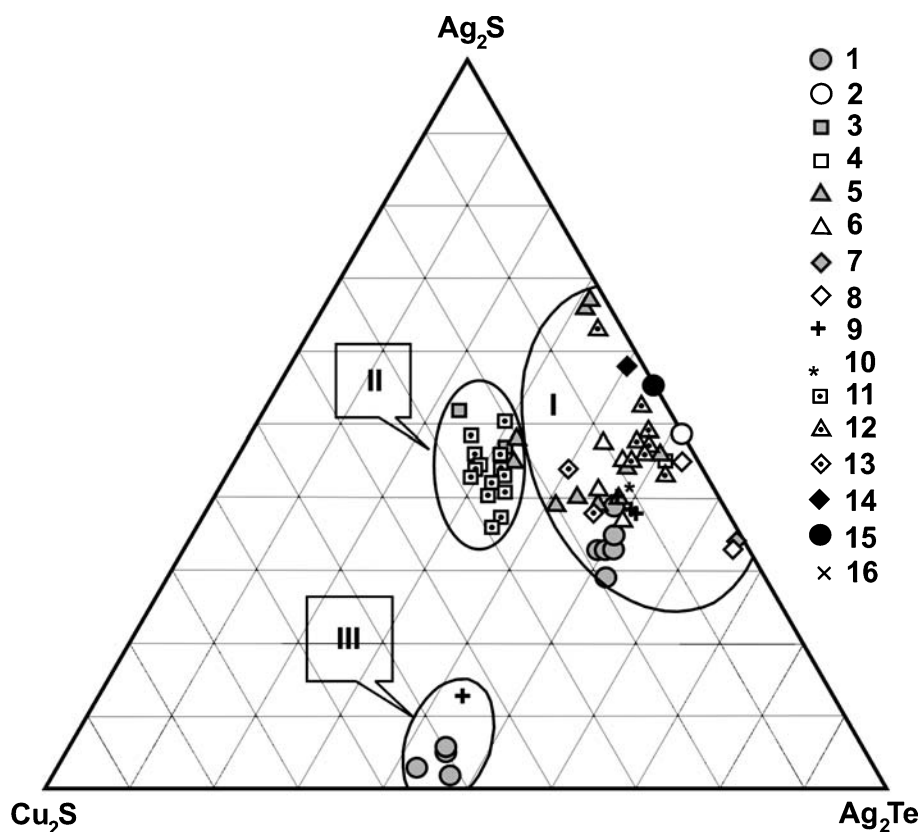


Fig. 7. Composition of cervelleite-like minerals plotted in the  $\text{Cu}_2\text{S}$ – $\text{Ag}_2\text{S}$ – $\text{Ag}_2\text{Te}$  ternary diagram. Fields: **I** cervelleite with Cu admixture, **II** copper-bearing cervelleite, **III** Ag-sulfotelluride with extremely high Cu content. Numbers in legend correspond to Fig. 6. Yaman-Kasy cervelleite-like minerals are not marked because their anion:cation ratios substantially diverge from 2:1

Compiling our new data with previously published data into the  $\text{Cu}_2\text{S}$ – $\text{Ag}_2\text{S}$ – $\text{Ag}_2\text{Te}$  ternary composition diagram, we depict the composition of cervelleite and cervelleite-like minerals in Fig. 7. Three distinct compositional fields can be seen. Cervelleite, without significant impurities, but with varying S/Te ratios, forms the first field, which lies at the mid-point along the hessite-acanthite join. Copper-bearing cervelleite from Babaryk (plus published data for the Eniovche and Funan deposits) plots in a second field close to the center of triangle. The main compositional variation in this subset is the coordinated changes in Cu and S contents. The first and second fields do not overlap with one another, suggesting the presence of a miscibility gap between the two. The third field is isolated from the other two and contains compositions of the extremely Cu-enriched phases reported by *Cook* and *Ciobanu* (2003) from the Băița Bihor and Ocna de Fier deposits, Romania.

Based on the available compositional data, it can be supposed that there exists extensive solid solution in cervelleite and related Ag-sulfotellurides. There are possibly both isomorphic and crystallochemical (i.e., different sites for metals) ways in which Cu can enter the structure of cervelleite-like minerals. The latter way may lead to the formation of derivative structures, distinct from cervelleite.

Variable and apparently non-stoichiometric ratios between  $\Sigma(\text{Ag} + \text{Cu})$  and  $\Sigma(\text{Te} + \text{S})$  may be explained by the presence of very thin intergrowths of different mineral phases, such as cervelleite, benleonardite, hessite or acanthite.

### Relationship between physical and chemical properties

Unfortunately, quantifiable physical features were only obtained for Ag-sulfotellurides from some of the deposits. The shape of reflectance spectra for stoichiometric cervelleite from Severo-Uvaryazhskoe and cervelleite-like phase  $z$  from Zyranovskoe (Aksenov et al., 1969) approximately resembles that of TL cervelleite (Criddle et al., 1989). The reflectance spectrum of the Cu-rich phase from the Babaryk deposit has a distinct shape (Fig. 5).

Silver and copper have similar electron energy level structures. Copper, however, has a higher excitation energy than silver. If the sulfotellurides from Babaryk and cervelleite from the Bambolla Mine have the same structure, then the decrease in reflectivity is explained by simple substitution of copper into the lattice (Burns and Vaughan, 1970). The low relative reflectance of Cu-rich sulfotellurides from Băița Bihor and Ocna de Fier (Cook and Ciobanu, 2003) is in agreement with such a hypothesis.

Published and obtained data on the microhardness of cervelleite are very limited (Table 5). Our data for cervelleite and related phases from Zyranovskoye, Severo-Uvaryazhskoye and Babaryk indicate there is a tendency for microhardness to increase with Cu content. The value for TL cervelleite from Bambolla Mine does not fit this trend, but was obtained on a single very thin grain in contact with very soft hessite.

### Conditions of formation

There have been few attempts to estimate the formation condition for cervelleite based on thermodynamic and paragenetic analysis. The crystallization temperature of phase B (cervelleite) from the Ivigtut deposit was estimated as  $<270^\circ\text{C}$  by Karup-Møller (1976), while Helmy (1999) considered cervelleite from Um-Samiuki to occupy a stability field at  $160^\circ\text{C}$  to  $260^\circ\text{C}$  with  $f\text{Te}_2$  in the range  $-23$  to  $-17$ . The formation of metastable sulfotelluride in association with native tellurium is limited by the stability field of native tellurium in the temperature interval  $100^\circ\text{C}$  to  $160^\circ\text{C}$  (Maslennikov, 1999). The calculated stability field for sulfotellurides in the Funan deposit covers the range  $\log f\text{Te}_2 = 13.4$  to  $-17.4$  and  $\log f\text{S}_2 = -13.8$  to  $-9$ . These conditions were modeled at  $250^\circ\text{C}$  based on fluid inclusion geothermometry (Gu et al., 2003). Based on the textural relationships and mineral associations, Cook and Ciobanu (2003) argued for initial deposition of a primary phase that resulted in subsequent crystallization of cervelleite and  $\text{Ag}_2\text{Cu}_2\text{TeS}$  at temperatures as high as  $420^\circ\text{C}$  to  $395^\circ\text{C}$  in the Băița Bihor skarn deposit. The latter authors also proposed relatively high  $f\text{S}_2$  and moderate  $f\text{Te}_2$  for cervelleite formation in the Larga epithermal deposit (Cook and Ciobanu 2003).

Tellurides are commonly associated with sulfides, oxides and native elements in many types of mineral deposits. The stability of these minerals is a function of the fugacities of oxygen, sulfur and tellurium, and the evolution thereof, in any

given ore-forming system. The competition between oxygen, sulfur and tellurium to form minerals can be quantitatively assessed using thermodynamic calculations, so as to predict the mineral assemblage at a defined range of temperature, pressure, and activities of the volatile components. Thermodynamic analysis of phase relations in the system of interest, the system Ag–Cu–S–Te, can, correspondingly, provide estimates of  $fS_2$ ,  $fTe_2$  and  $fO_2$  during mineral deposition. Unfortunately, it is either difficult or impossible to make a proper estimation of formation conditions for cervelleite-like minerals, since thermodynamic data for most three- and four-component sulfides and tellurides are unavailable at present.

Some indications of formation conditions can nevertheless be given based on the following facts. (1) Cervelleite is commonly closely associated with galena, but never with altaite. According to *Godovikov and Sindeeva (1959)*, the maximum Te content in galena is 2.8 wt.%. An increase in the Te content beyond this level leads to the crystallization of altaite. (2) Hessite (e.g., in Severo-Uvaryazhskoe and other

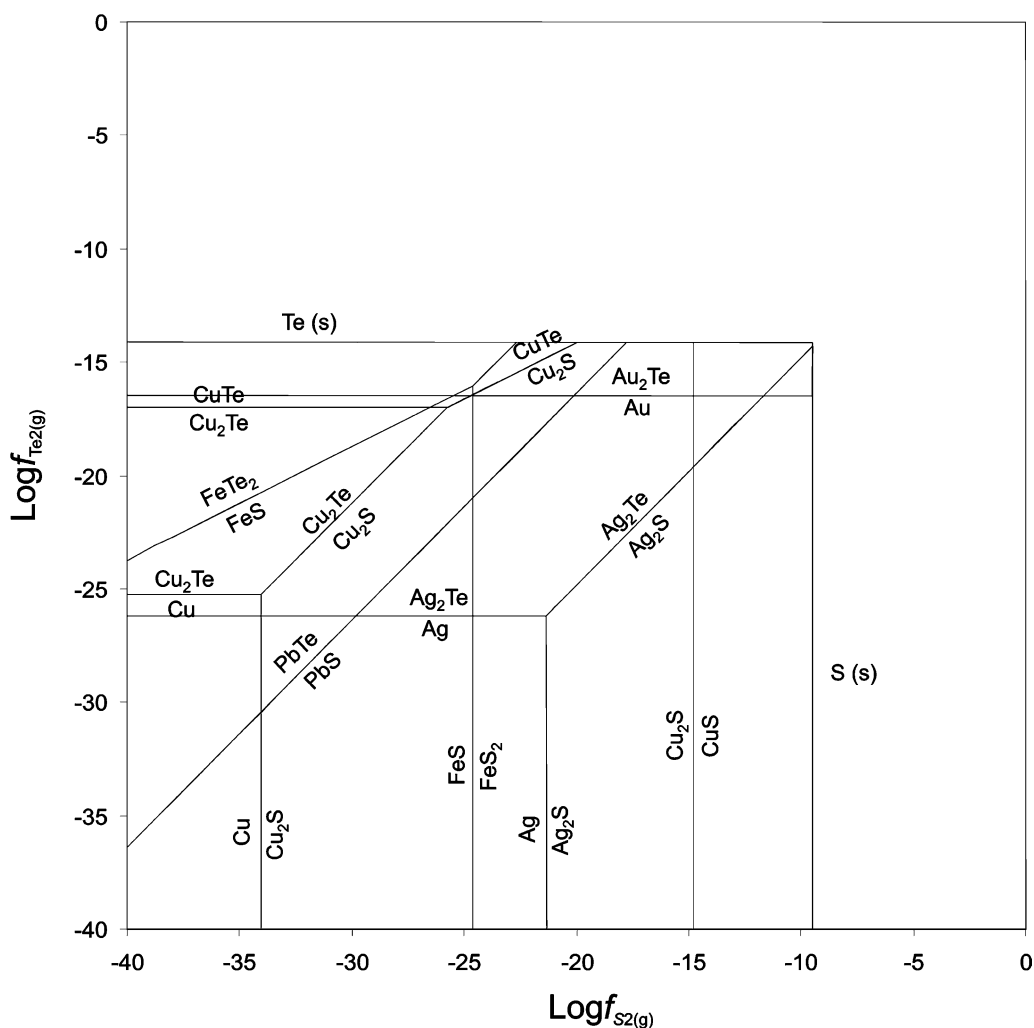


Fig. 8.  $fS_{2(\text{g})}$ – $fTe_{2(\text{g})}$  diagram at 100°C, showing the relative stability of some binary tellurides and their corresponding sulfides as a function of  $fS_{2(\text{g})}$  and  $fTe_{2(\text{g})}$

deposits) and stromeyerite (Babaryk) can be present in the ores and may concentrate tellurium or silver. (3) The cervelleite-bearing association in the VHMS deposits may be formed under low temperatures, maybe less than 78 °C (upper stability limit of orthorhombic stromeyerite) and high oxidation potential (necessary for formation of chalcocite and Cu<sup>2+</sup>-containing bornite. The paragenetic association between native Te and sulfotellurides in the Yaman-Kasy deposit indicates high  $fO_2$ , close to the hematite–pyrite–magnetite buffer within the stability field of native Te (e.g., Zhang and Spry, 1994).

Affi et al. (1988) estimated the relative stability fields of binary sulfides and tellurides up to 300 °C. By applying their data to the observed natural associations, it can be supposed that the cervelleite field lies concordantly with that of galena and native gold (i.e., different to the altaite and calaverite field), close to the hessite–argentite phase boundary. Such stability can be achieved at  $\log fS_2/\log fTe_2 = 0.775$ , within a  $\log fS_2$  range from –12 to –22 and  $\log fTe_2$  from –17 to –26 at 100 °C (Fig. 8). Realization of such conditions can occur at different stages in the development of a hydrothermal system, and in different part of the system, whenever interaction between high-temperature reducing hydrothermal fluid and low-temperature oxidizing sea water takes place (e.g., Large, 1977).

## Conclusions

Cervelleite and cervelleite-like minerals were found in the different genetic types of deposits in the Southern Urals, underlining the telluride trace signature of this metallogenic belt. These sulfotellurides are usually associated with Pb- and Zn-enriched ores, although Cu-rich cervelleite and unnamed Ag–Cu–Te–S phases are associated with Cu-bearing sulfides (bornite, tennantite-tetrahedrite, chalcocite, and chalcopyrite). Cervelleite *sensu stricto* is identified from Severo-Uvaryazhskoe, a cervelleite-like phase with variable (Ag + Cu)/(Te + S) ratio is identified from both Gayskoe and Yaman-Kasy. A sulfotelluride that represents a Cu-rich variety of cervelleite appears to be present in Tash-Tau, and an unnamed Ag–Cu–Te–S phase is reported from Babaryk. Formation of the sulfotellurides reflects a low  $fTe_2$  regime, too low for formation of most tellurides. Only the Ag-sulfotellurides in the Yaman-Kasy deposit were found to coexist with native tellurium. Broad variations in both composition and physical properties of cervelleite-like sulfotellurides, in corroboration with published data for occurrences elsewhere, allow us to suppose the existence of several mineral species, which differ and can be distinguished on the basis of their Cu contents, Te/S ratios, and in the case of possible polymorphs, by crystal structure. A better understanding of the phases within the system Ag–Cu–Te–S is impossible without detailed experimental studies, coupled with crystallographic structural characterization of natural and synthetic sulfotellurides.

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