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Pekoite from Narechen, Bulgaria—a possible solution to the bonchevite problem

A NUMBER of Pb–Bi–S minerals, including bonchevite (Kostov, 1958), galenobismutite and lillianite (Kupcik *et al.*, 1969), have been recorded from scheelite-bearing quartz veins near the town of Narechen, in the Southern Rhodope Mountains, Bulgaria. The quartz veins are up to 0.5 m thick and cut muscovite–biotite schists of the Rhodopian Complex (Bonev, 1982). One of the authors (W.D.B.) collected several specimens of quartz from a vein north of Narechen during the International Mineralogical Association excursion in September 1982. The specimens contain thin bladed crystals, up to 1 mm wide and 2 cm long of a soft, steel-grey mineral which gave an X-ray powder diffraction pattern close to that of bismuthinite. However, long-exposure Weissenberg X-ray films taken of a small fragment of the mineral revealed weak superlattice spots characteristic of pekoite (Mumme and Watts, 1976*a, b*). Several small fragments from the same X-rayed crystal were mounted, polished, and examined under reflected light. The pekoite was very weakly pleochroic, cream in colour, and strongly anisotropic. The prismatic crystals were made up of a mosaic of grains elongated roughly parallel to a well-defined 010 cleavage. No inclusions were observed.

Electron microprobe analyses (Table I), obtained from the same fragments, show a range in composition within a single crystal, deviating from the standard formula for pekoite ($\text{PbCuBi}_{11}\text{S}_{18}$). The mole % of Bi_2S_3 ranges from 74 to 83, largely within the pekoite compositional field reported by Harris

TABLE I. *Electron microprobe analyses (in wt. %) of pekoite from Narechen, Bulgaria*

	1	2	3	4	5	6
Cu	2.41	1.71	1.75	1.59	1.52	1.59
Pb	8.31	5.98	5.68	5.26	5.25	5.20
Bi	70.44	73.56	74.04	74.55	74.81	74.36
S	17.32	17.35	17.63	17.48	17.64	17.69
Total	98.48	98.60	99.10	98.88	99.22	98.84
Formulae (S = 18.00)						
Cu	1.27	0.90	0.92	0.83	0.79	0.82
Pb	1.33	0.96	0.88	0.83	0.82	0.82
Bi	11.23	11.71	11.59	11.79	11.72	11.61
S	18.00	18.00	18.00	18.00	18.00	18.00

Notes. Analysis was by a JEOL microprobe with a beam voltage of 20 kV and a specimen current of 0.018 μA . Standards used were pure metals (Bi, Cu, Sb, Ag, Zn, Fe) troilite (S), and galena (Pb). Sb, Ag, Fe, and Zn were below detection limits at all points analysed. (Analyst: W. Birch.)

and Chen (1976). The increase in Bi is matched by a decrease in Cu and Pb, but with the Cu/Pb ratio remaining close to unity. These data are plotted in the Cu_2S –PbS– Bi_2S_3 system in fig. 1.

The physical and optical properties of the Narechen pekoite are similar to those of the incompletely characterized mineral bonchevite, as described from Narechen by Kostov (1958). On the basis of the X-ray powder diffraction data, Kostov suggested that the mineral was related to galenobismutite and bismuthinite. However, Fleischer

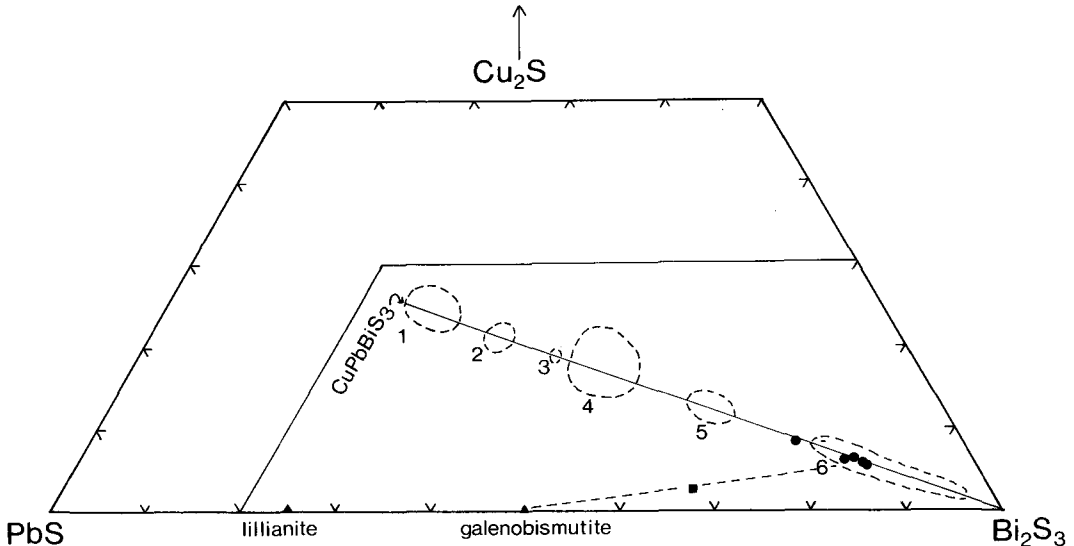


FIG. 1. Composition fields of sulphosalts in the aikinite-bismuthinite series (after Harris and Chen, 1976). The fields are: 1. aikinite; 2. hammarite; 3. lindstromite; 4. krupkaite; 5. gladite; 6. pekoite. The Narechen pekoite compositions are shown by closed circles. The square is the original bonchevite analysis (Kostov, 1958), which lies midway between galenobismutite and the pekoite composition of this study.

(1958) pointed out that the differences between the bonchevite, galenobismutite, and bismuthinite X-ray patterns were only marginal and that the validity of the new mineral should be substantiated by X-ray single crystal analysis. Bonchevite was also described from Mo-W greisen deposits in Karaoba, central Kazakhstan, USSR, by Nechelyustov and Lebedev (1967). Their powder pattern (ASTM 25-430) is not significantly different from that of a mixture of bismuthinite and galenobismutite. The average chemical analysis gave Pb 17.60; Ag 0.03; Cu 0.10; Fe 0.32; Bi 63.42; Sb 0.75; S 17.25 wt. %, indicating a formula $Pb_{1.09}(Bi_{3.94}Sb_{0.08})_{24.02}S_{7.00}$, close to the ideal $PbBi_4S_7$. Kupcik *et al.* (1969) examined specimens of so-called bonchevite from the type locality and showed them to consist of two phases coexisting in needle-shaped crystals. The major phase was galenobismutite (60%) and the other phase was subsequently identified as lillianite, $Pb_3Bi_2S_6$ (Bonev, 1982). Accordingly, the formula for bonchevite quoted by Fleischer (1983) is that of lillianite.

During the late 1960s a number of studies of phase relations in the $PbS-Bi_2S_3$ system were undertaken (Craig, 1967; Otto and Strunz, 1968; Salanci and Moh, 1969). These studies and a later one by Takeuchi *et al.* (1974) showed that a synthetic phase V (close to $PbBi_4S_7$), occurring in three forms (V-1, V-2, V-3), was stable only between

about 680 and 740°C. At lower temperatures it exsolved to form a lamellar intergrowth of galenobismutite and bismuthinite (Craig, 1967; fig. 26), indicating that it is unlikely that a low temperature, unsubstituted form of $PbBi_4S_7$ can exist.

The original bonchevite analysis (Kostov, 1958) can be recast to give a formula $Cu_{0.45}Pb_{2.56}Bi_{11.01}S_{18.00}$, in contrast to $Pb_{0.94}Bi_{4.00}S_{6.54}$ (Bonev, 1982), or the ideal $PbBi_4S_7$ quoted by Kostov and Minceva-Stefanova (1981). It is evident (fig. 1) that one explanation for the composition is a near 50:50 mixture of galenobismutite and the pekoite determined in this study. Fig. 1 also shows that a mixture of lillianite and galenobismutite (Kupcik *et al.*, 1969) could not explain the original bonchevite composition.

Perhaps a substituted low-temperature 'bonchevite' ($\sim PbBi_4S_7$) structure-type awaits discovery. However, in view of the reported X-ray data for the type specimen (Kostov, 1958; Table 1 and fig. 4), the phase equilibria studies and the present work, it appears most likely that, for original bonchevite at least, X-ray and chemical data were reported for a mixture of galenobismutite and partially (Cu, Pb) substituted bismuthinite, namely pekoite as it is now known.

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The identification of two fibrous sulphosalts from l'Etacq, Jersey

IN 1911 or 1912 wulfenite was discovered by Teilhard de Chardin and Pelletier (1921) at l'Etacq, Jersey, accompanied by some other minerals. The first published account of the discovery is by Lacroix (1913) who states: 'Iles anglo-normandes— Jersey. Je dois au P. Pelletier un échantillon de quartz d'un filon qui traverse le granite de l'Etacq; il renferme de la molybdénite; il est creusé de géodes, renfermant, les unes des aiguilles de stibine ferrifère, et les autres des cristaux blancs de wulfénite ($b^{1/2} \frac{1}{2} h^5$, avec souvent en outre $p(001)$, soit à peine indiqué (fig. 1), soit prédominant). L'intérêt de cet échantillon est de montrer l'association de la molybdénite à la wulfénite, occupant la place de galène disparue.'

We have, however, Teilhard de Chardin's contemporary account of the identification of these minerals in the following extracts from two hitherto unpublished letters addressed to Pelletier:

13, Rue du Vieux-Colombier (Paris 6)
13 Octobre 1912

Je passerai demain au laboratoire de Minéralogie pour avoir vos déterminations et vos échantillons (on m'y a fait allusion, donc ils ne sont pas jetés) . . .

Lundi soir—j'ai passé ce matin au Laboratoire de Minéralogie:

a) On m'a dit que vos échantillons étaient classés et catalogués; cela m'a enlevé tout moyen de les redemander, en tout ou en partie.

b) Il y a dans ces échantillons: de la wulfénite, comme vous saviez, et de la stibine (ferrifère); M. Lacroix ne m'a fait allusion à rien d'autre. Il m'a seulement dit que l'association wulfénite et Pb-Molybdénite (apparente) était intéressante. Il a mis quelques lignes là-dessus dans la nouvelle édition de la Minéralogie de la France (sous presse). En général, quand on trouve la wulfénite, les minéraux qui lui ont donné naissance ont complètement disparu. — Cela fait tout de même deux choses nouvelles pour Jersey, à moins que ce que nous avons baptisé mispickel aciculaire (Prelec) fut déjà de la stibine.

Louvain, 1er Janvier 1913.

D'abord je vous avouerai que je n'ai pas osé insister encore près de M. Lacroix pour faire reviser l'analyse de la pseudo-stibine de l'Etacq; mais à l'occasion j'en glisserai un mot.

It is obvious from these letters that Teilhard de Chardin was doubtful about Lacroix's identification of stibnite (stibine, Sb_2S_3). Eight years later, Teilhard de Chardin and Pelletier (1921) published