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The bournonite–seligmannite solid solution

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Abstract

Electron microprobe analyses of bournonite–seligmannite samples from the Casapalca and Guignol Mines of central Peru reveal extensive solid solution between bournonite and seligmannite, The analyses indicated that As substitutes for Sb in bournonite to at least an As/(As + Sb) value (atomic) = 0.54. We suspect a complete solid solution exists between bournonite and seligmannite. Analyses of both bournonite–seligmannite and tennantite–tetrahedrite from the Casapalca Mine suggest that the distribution coefficient of Sb/As between the two solid-solution series is close to unity. The Sb/As ratios of bournonite–seligmannite and geocronite in the Guignol Mine suggest that Sb favors bournonite–seligmannite while As favors geocronite.

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The solid solution between bournonite ($PbCuSbS_3$) and seligmannite ($PbCuAsS_3$) is much more extensive than previously postulated. The extent of As substitution for Sb in bournonite has been estimated not to exceed As/(As + Sb) = 0.20 (Ramdohr, 1969; Schaber, 1965; Palache *et al.,* 1944). In this paper, elemental ratios in solid solutions are reported in atom number ratios. Seligmannite had been reported to contain 0.64 percent Sb substituting for As, giving an As/(As + Sb) value = 0.98 (Palache *et al.,* 1944). Electron microprobe analyses of bournonite–seligmannite samples from the Casapalca and Guignol Mines of central Peru reveal a more extensive solid solution than previously reported. Some of the analyses are reported in Table 1, and they indicate that As substitutes for Sb in bournonite to at least an As/(As + Sb) value = 0.54. In addition to the analyses tabulated in Table 1, 56 other analyses of bournonite–seligmannite had As/(As + Sb) values in the same range. All analyses are plotted in Figure 1. The authors suspect a complete solid solution exists between bournonite and seligmannite.

Bournonite and seligmannite are isotypic in space group $Pn2_1m$ (Edenharter *et al.,* 1970). In the structure, Pb is both 7- and 8-coordinated by S, As and Sb combine with 3 S atoms to form trigonal pyramids, and Cu is coordinated by a slightly deformed tetrahedron of S atoms. There are two isolated AsS_3 or SbS_3 trigonal pyramids in the unit cell. The average As–S bond distance in each of the trigonal pyramids of seligmannite is 2.296 and 2.271A, and the average Sb–S bond distance in the trigonal pyramids in bournonite is 2.502 and 2.409A (Edenharter *et al.,* 1970). These bond distances are consistent with those reported for other minerals with similar coordination polyhedra. Since the pure isotypic end members exist and since a solid solution is seen at least 50 percent of the way from bournonite to seligmannite, it is reasonable that the complete solid solution exists.

Most bournonite–seligmannite crystals from the Casapalca Mine have well-developed tabular forms. A paragenetic study (Wu, 1975) indicates that the crystals were deposited during or immediately after the last stage of tennantite–tetrahedrite ($Cu_{12}As_xSb_{4-x}S_{13}$, $0 \leq x \leq 4$) crystallization. The As/(As + Sb) values of tennantite–tetrahedrite and bournonite–seligmannite are 0.33–0.47 and 0.30–0.48, respectively. In the Guignol Mine, the predominant

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Table 1. Analyses of bournonite–seligmannite

Sample	Weight %						Atomic Ratios
	Pb	Cu	Sb	As	S	Total	As/(As+Sb)
PRF 120-1a[1]	43.26	14.86	22.62	0.72	19.10	100.56	0.05
PRF 120-1b[1]	44.92	14.67	17.00	4.54	19.71	100.84	0.30
PRF 150-1a[1]	45.55	15.50	17.29	4.26	20.15	102.75	0.29
PRF 150-1b[1]	46.77	15.26	11.56	8.23	20.38	102.20	0.54
PRF 200-5a[1]	45.14	14.94	15.35	5.57	19.92	100.92	0.37
CAS 17-265a[2]	*	13.4	14.7	*	*		0.43
CAS 17-265b[2]	*	13.2	17.4	*	*		0.32
CAS 17-265c[2]	*	13.3	17.9	*	*		0.30
CAS 17-265d[2]	*	13.3	17.7	*	*		0.31
CAS 17-265e[2]	*	13.5	16.1	*	*		0.37
CAS 17-265f[2]	*	13.4	17.9	*	*		0.30
CAS 17-265g[2]	*	13.5	16.6	*	*		0.35
CAS 17-265h[2]	*	13.5	18.5	*	*		0.27
CAS 17-265i[2]	*	13.7	14.7	*	*		0.43
CAS 17-265j[2]	*	13.7	13.6	*	*		0.48

* *not analyzed for*

1. *from Guignol Mine, Peru (Birnie, 1975)*
2. *from Casapalca Mine, Peru (Wu, 1975). The Cu and Sb values were corrected by applying ZAF correction factors obtained from the complete bournonite analyses. As/(As+Sb) values based on theoretical formula, $PbCu(As,Sb)S_3$*

sulfosalt is bournonite–seligmannite with lesser amounts of geocronite ($Pb_{28}As_{4+x}Sb_{8-x}S_{46}$, $0 \le x \le 8$) (Birnie, 1975). The As/(As + Sb) values of bournonite–seligmannite and geocronite range between 0.05–0.54 and 0.54–0.60, respectively. These data suggest that the distribution coefficient of Sb/As between tennantite–tetrahedrite and bournonite–seligmannite is close to unity, and that Sb favors bournonite–seligmannite and As favors geocronite in the bournonite–seligmannite and geocronite assem-

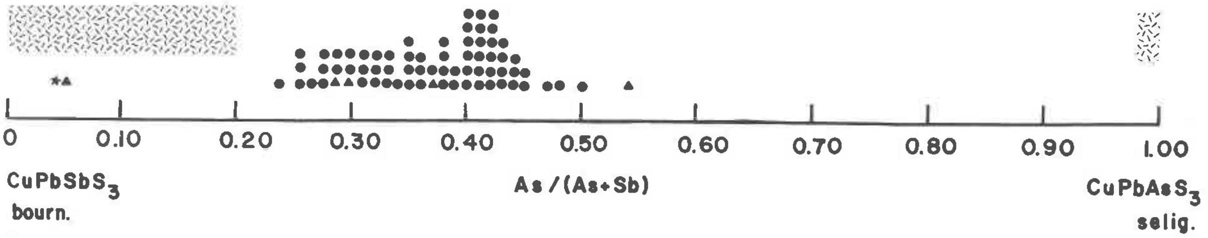

Fig. 1. Compositional range of bournonite–seligmannite. Stippled regions cover range of analyses reported by Ramdohr (1969), Schaber (1965), and Palache *et al.* (1944). Star represents analysis of bournonite from Chichibu Mine, Japan (Harada *et al.*, 1970). Triangles are from the Guignol Mine and circles from the Casapalca Mine, Peru.

blage. However, since equilibrium conditions cannot be established with certainty for either of the two sulfosalt assemblages, no firm conclusion as to the Sb/As distribution coefficient can be drawn.

Birnie and Burnham (1976) note that there are numerous limited solid solutions of As for Sb and Sb for As in the Pb–As–Sb–S sulfosalts. However, in the Ag–As–Sb–S and Cu–As–Sb–S sulfosalts, many complete solid-solution series are known. They proposed that the difference in the extent of As substitution for Sb and Sb substitution for As in these solid-solution series could be accounted for by the relative bond strengths of the metal–sulfur bonds as calculated by Povarennykh (1968; 1971) (Table 2). The stronger Cu–S and Ag–S bonds probably hold their structures together across a solid-solution series, whereas the weaker Pb–S bonds do not hold the structures together when different-sized semimetals are substituted for each other.

Table 2. Relative bond strengths*

Element and Coordination	Relative Bond Strength
$Pb-S_8$	0.03
$Pb-S_6$	0.08
$Cu-S_4$	0.11
$Ag-S_3$	0.12
$Cu-S_2$	0.19
$Ag-S_2$	0.20
$Si-O_4$	0.41

Povarennykh (1968 and 1971)

The bournonite–seligmannite solid-solution series is a mixed series with respect to bond strengths, because both Pb–S and Cu–S coordination polyhedra are present in the structure. However, Takeuchi and Haga (1969) show that the essential feature of the crystal structure of seligmannite is a linked framework of $Cu-S_4$ and $As-S_3$ pyramids. The Pb atoms merely occupy interstices in the framework. This interpretation of the structure is supported by the fact that the $Cu-S_4$ tetrahedra and $As-S_3$ trigonal pyramids are only slightly distorted, while the Pb coordination polyhedra are highly irregular (Takeuchi and Haga, 1969). The structure of bournonite–seligmannite is therefore more closely related to that of a Cu sulfosalt such as tennantite–tetrahedrite than that of a Pb sulfosalt such as geocronite. On these grounds, it is reasonable to expect that bournonite–seligmannite represents a complete As–Sb solid-solution series as seen in Cu–As–Sb–S sulfosalts. The relatively strong Cu–S bonds hold the structure together and permit the complete solid solution.

No mineral syntheses have been conducted with compositions along the bournonite–seligmannite binary join. If these experiments are ever undertaken, they will shed interesting light on our proposal.

The crystal structure of aikinite ($PbCuBiS_3$), the Bi analog of bournonite and seligmannite, has been determined by Kohatsu and Wuensch (1971) and is clearly different from bournonite–seligmannite. The Cu–S tetrahedra in aikinite are more distorted than those of bournonite–seligmannite, and aikinite is essentially a stuffed derivative of bismuthinite. Therefore, an analogy for solid solution between aikinite–bournonite or aikinite–seligmannite cannot be drawn on the same grounds as bournonite–seligmannite.

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References

Birnie, R. W. (1975) *The Crystal Chemistry and Paragenetic Association of Geocronite.* Ph.D. thesis, Harvard University, Cambridge, Massachusetts.

—— and C. W. Burnham (1976) The crystal structure and extent of solid solution of geocronite. *Am. Mineral., 61,* 963–970.

Edenharter, A., W. Nowacki and Y. Takeuchi (1970) Verfeinerung der Kristallstruktur von Bournonit $[(SbS_3)_2|Cu_2^{IV}Pb^{VII}Pb^{VIII}]$ und von Seligmannit $[(AsS_3)_2|Cu_2^{IV}Pb^{VII}Pb^{VIII}]$. *Z. Kristallogr., 131,* 397–417.

Harada, K., O. Sakamoto, K. Nakao, and K. Nagashima (1970) Bournonite from Daikoku, Chichibu mine, Saitama, Japan. *Mineral. J., 6,* 186–188.

Kohatsu, I. and B. J. Wuensch (1971) The crystal structure of aikinite, $PbCuBiS_3$. *Acta Crystallogr., B27,* 1245–1252.

Palache, C., H. Berman and C. Frondel (1944) *Dana's System of Mineralogy.* Vol. 1. John Wiley and Sons, New York.

Povarennykh, A. S. (1968) The strength of bonding forces in mineral structures. *Papers and Proc. 5th Gen. Meet. I.M.A.,* Mineral. Soc., London, 6–12.

—— (1971) Crystallochemistry of complex sulfides of arsenic, antimony, and bismuth. *Soc. Mineral Geol. Japan Spec. Issue 2,* 42–46.

Ramdohr, P. (1969) *The Ore Minerals and Their Intergrowths.* Pergamon Press, New York.

Schaber, G. G. (1965) *Mineralogy and Crystal Chemistry of the Sulfosalt Minerals: Bournonite, Seligmannite, Aikinite, Diaphorite, and Freieslebenite.* Ph.D. thesis, Univ. Cincinnati, Cincinnati, Ohio.

Takeuchi, Y. and N. Haga (1969) On the crystal structures of seligmannite, $PbCuAsS_3$, and related minerals. *Z. Kristallogr., 130,* 254–260.

Wu, I. (1975) *Geochemistry of Tetrahedrite–Tennantite at Casapalca, Peru.* Ph.D. thesis, Harvard University, Cambridge, Massachusetts.

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