

Proudite from Tennant Creek, Northern Territory, Australia: its crystal structure and relationship with weibullite and wittite

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Abstract

Proudite, from the Juno Mine at Tennant Creek, Northern Territory, Australia, is monoclinic, space group $C2/m$, with $a = 31.96(1)$, $b = 4.12(1)$, $c = 36.69(3) \text{ \AA}$, $\beta = 109.52(3)^\circ$ and has a known range of solid solution expressed by the general formula $\text{Cu}_x\text{Pb}_{7.8}\text{Bi}_{9.67-0.83x}(\text{S}_y, \text{Se}_{1-y})_{22}$, where $0.04 < x < 0.98$ and $0.57 < y < 0.82$. Single-crystal X-ray data were collected using the integrating Weissenberg equi-inclination method with multiple film packs; and the structure was solved by the Patterson method and refined by a least-squares procedure to give a final R of 0.17. The asymmetric unit contains 8 Pb, 10 Bi, 1 Cu, and 23 S atom sites. The Cu site, one Bi, and two S sites are partially occupied and the solid solution $\text{Pb}_{7.8}\text{Bi}_{9.67}(\text{S}, \text{Se})_{22} \rightleftharpoons \text{CuPb}_{7.8}\text{Bi}_{9.33}(\text{S}, \text{Se})_{22}$ probably exists. Pb and Bi atoms may be distinguished with only a moderate degree of confidence on the basis of differences in their bonding geometry; the selenium is preferentially ordered into seven of the anion lattice sites. The structure of proudite is closely related to that of junoite, $\text{Cu}_2\text{Pb}_3\text{Bi}_8(\text{S}, \text{Se})_{18}$, the other main selenium-rich mineral intergrown with proudite at Juno. This study also incorporates new X-ray and chemical data on the little studied seleniferous sulphosalts wittite and weibullite, and proves that all three are distinct mineral species. Zoning of bismuth-rich sulphosalts in the ore bodies at Juno is discussed.

Introduction

Selenium substitutes for sulphur in many sulphide and sulphosalts minerals, so that distinct Se minerals rarely occur in massive sulphide deposits. Sulphides and selenides are present together because they have formed either at different periods of mineralization or at times when the mineralizing solutions were considerably deficient in S. In contrast to sulphur, which under natural conditions forms compounds of one type or another with at least 40 chemical elements, selenium does so with just a few of higher atomic number. Selenium compounds with light metals do not exist in nature, and there is a predominance of selenides of copper, silver, and bismuth, and notably a lack of compounds with gold which is so specific for its analog tellurium (Sindeeva, 1964).

Although relatively few selenium minerals have been reported as distinct species, there are many descriptions of selenium-bearing minerals in the literature. Sulphur-selenium isomorphism in them is extensive and often unlimited, as is illustrated both in synthetic compounds and in natural specimens, e.g.

the solid solutions PbS-PbSe and $\text{Bi}_2\text{S}_3-\text{Bi}_2\text{Se}_3$ (Earley, 1950), where 1:1 replacement of S by Se is possible. In particular, the selenide minerals of lead and bismuth included in this type are clausthalite, PbSe , isomorphous with galena; guanajuatite, $\text{Bi}_2(\text{S}, \text{Se})_3$, isomorphous with bismuthinite; and paraguanajuatite, Bi_2Se_3 , which has a structure analogous to tetradymite ($\text{Bi}_2\text{Te}_2\text{S}$). Other reported occurrences of somewhat more complex lead-bismuth sulphosalts which also fall into this category of sulphur-selenium isomorphism are laitakarite, Bi_4SSe_2 , (Vorma, 1960); selenocosalite (Ödman, 1941); selenolillianite, $\text{Pb}_3\text{Bi}_2(\text{S}, \text{Se})_6$, and selenogoongarite, $\text{Pb}_4\text{Bi}_2(\text{S}, \text{Se})_7$, (by Isaksson; see Grip and Wirstam, 1970). These occurrences, at Orijarvi, Finland, and the Boliden Mine, Sweden, must be regarded as somewhat doubtful, particularly selenocosalite which appears to have the wrong composition for it to be a Se-isomorph of cosalite, and selenogoongarite for the reason that goongarite itself is a discredited mineral. Laitakarite and ikunolite, $\text{Bi}_4(\text{S}, \text{Se})_3$ (Kato, 1959), are reported to be isostructural with joseite-A, $\text{Bi}_{4+x}\text{Te}_{1-x}\text{S}_2$.

TABLE 7 (Structure factor table: approx. 1300 entries)

H	K	L	Y(OBS)	Y(CALC)
36	0	-1	920.23	263,27
36	0	-2	746.33	754,10
36	0	-3	440.60	208,67
36	0	-6	1035.55	1072,88
36	0	-8	820.14	742,23
36	0	-9	537.61	257,29
36	0	-10	339.85	305,95
36	0	-15	840.34	940,69
36	0	-16	484.85	174,61
36	0	-17	681.76	253,59
36	0	-18	587.09	325,04
36	0	-20	471.57	278.81
36	0	-21	1475.03	1363,65
36	0	-22	1660.15	1130,61
36	0	-23	907.03	979,46
34	0	0	967.45	945,76
34	0	-1	1101.56	771,72
34	0	-2	866.97	748,66
34	0	-5	518.95	795,07
34	0	-6	523.49	322,65
34	0	-7	372.88	212,98
34	0	-9	376.92	253,30
34	0	-10	926.62	985,30
34	0	-11	848.06	1082,45
34	0	-12	1201.17	1163,04
34	0	-17	753.96	786,44
34	0	-18	750.40	606,42
34	0	-20	2221.73	2148,28
34	0	-22	2569.40	2363,50
32	0	-23	774.18	426,32
34	0	-24	867.50	842,71
34	0	-26	838.51	344,15
32	0	-3	1156.27	1091,45
32	0	-5	514.61	209,71
32	0	-1	979.63	903,10
32	0	0	2050.89	2165,44
32	0	-8	1209.31	1039,58
32	0	-11	1722.35	1952,16
32	0	-2	777.67	814,62
32	0	-3	784.02	778,38
32	0	-4	683.63	114,93
32	0	-5	793.90	908,76
32	0	-9	2204.18	2101,47
32	0	-10	987.33	529,66
32	0	-11	1397.69	1453,31
32	0	-12	1276.45	1201,02
32	0	-13	1141.54	939,95
32	0	-16	984.73	655,10
32	0	-17	283.53	316,85
32	0	-19	397.94	387,36
32	0	-20	395.90	95,04
32	0	-22	552.27	676,74
32	0	-29	1222.30	1287,26

36	0	718	361,69	322,63
36	0	720	471,57	278,81
36	0	721	1475,03	1363,65
36	0	722	1660,15	1130,61
36	0	723	907,03	979,46
34	0	724	967,45	945,76
34	0	725	1101,56	771,72
34	0	726	866,97	748,66
34	0	727	518,95	795,07
34	0	728	523,49	322,65
34	0	729	372,88	212,98
34	0	730	376,92	253,30
34	0	731	926,62	985,30
34	0	732	848,06	1082,45
34	0	733	1201,17	1163,04
34	0	734	753,96	786,44
34	0	735	750,40	606,42
34	0	736	2221,73	2148,28
34	0	737	2569,40	2565,50
32	0	738	774,18	426,32
34	0	739	867,50	842,71
34	0	740	838,51	344,15
32	0	741	1156,27	1091,45
32	0	742	514,61	209,71
32	0	743	979,63	903,10
32	0	744	2058,89	2165,44
32	0	745	1204,31	1039,58
32	0	746	1722,35	1952,16
32	0	747	777,67	814,62
32	0	748	784,02	770,38
32	0	749	683,63	114,93
32	0	750	793,90	908,76
32	0	751	2204,18	2101,47
32	0	752	987,33	529,66
32	0	753	1397,69	1453,31
32	0	754	1276,45	1201,02
32	0	755	1141,54	939,95
32	0	756	984,73	655,10
32	0	757	283,53	314,85
32	0	758	397,94	387,36
32	0	759	395,90	95,04
32	0	760	552,27	676,74
32	0	761	1222,30	1287,06
32	0	762	1191,22	1281,12
30	0	763	708,39	801,67
30	0	764	1027,90	789,36
30	0	765	770,19	556,27
30	0	766	1501,47	1494,00

H	K	L	Y(CALC)	(2)
36	0	721	420,23	263,27
36	0	722	746,53	754,10
36	0	723	840,68	200,67
36	0	724	1035,55	1072,88
36	0	725	820,14	742,23
36	0	726	337,61	257,29
36	0	727	339,85	305,95
36	0	728	840,54	940,69
36	0	729	489,05	174,61
36	0	730	681,76	253,59
36	0	731	587,09	325,05
36	0	732	471,97	278,81

MUMME - TABLE 7 ("Statistical Factor-table")

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(4)

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1308, 79
619, 28
534, 14

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1	-23	1035	,63	855	,54
1	-28	920	,23	874	,33
1	-25	666	,79	313	,96
1	-27	568	,80	444	,42
1	-29	732	,90	1008	,41
1	-10	832	,88	410	,17
1	-11	782	,87	402	,11
1	-13	1054	,68	1672	,40
1	-14	1490	,65	454	,67
1	-15	688	,77	1267	,37
1	-16	918	,82	1614	,37
1	-17	424	,56	225	,49
1	-18	759	,63	902	,51
1	-19	1012	,65	1349	,61
1	-20	809	,55	1056	,98
1	-22	1490	,33	1553	,86
1	-23	626	,36	481	,02
1	-26	553	,35	730	,29
1	-28	377	,40	164	,36
1	-30	2663	,41	2629	,05
1	-9	2915	,65	2737	,42
1	-10	1353	,98	1184	,36
1	-11	877	,39	1289	,30
1	-12	2068	,31	2820	,05
1	-13	1387	,69	997	,52
1	-14	1289	,65	1442	,79
1	-15	386	,64	1146	,80
1	-16	682	,68	866	,23
1	-17	588	,64	1028	,30
1	-18	964	,65	849	,24
1	-19	3373	,06	3589	,56
1	-20	924	,56	1380	,00
1	-21	877	,86	36	,30
1	-24	741	,04	828	,36
1	-26	873	,88	951	,13
1	-28	577	,57	382	,58
1	-30	4553	,09	4405	,07
1	-8	1332	,84	840	,75
1	-9	8282	,35	8829	,49
1	-10	1451	,73	1132	,14
1	-11	681	,89	748	,80
1	-12	1238	,82	1444	,69
1	-13	749	,09	397	,73
1	-15	853	,09	1095	,32
1	-17	1093	,49	527	,61
1	-18	2080	,48	3051	,77
1	-20	653	,16	752	,03
1	-23	764	,84	465	,66
1	-6	1666	,77	1490	,47
1	-7	3442	,52	3267	,37
1	-8	994	,03	1008	,58
1	-10	847	,41	458	,94
1	-13	494	,32	581	,89
1	-14	517	,73	974	,15
1	-15	668	,66	177	,98
1	-16	892	,80	1513	,18
1	-17	2468	,78	2271	,93
1	-18	1368	,15	182	,42
1	-19	1536	,74	1458	,32
1	-27	1516	,39	897	,41
1	-59	1810	,04	998	,31
1	-48	868	,86	884	,74

111	643,29	1393,52
112	479,24	264,38
113	390,08	169,59
114	910,05	1002,67
115	1642,09	1771,83
116	1322,97	1197,24
117	2074,34	1635,83
118	978,49	456,15
119	2664,62	2899,10
120	584,36	199,21
121	535,23	429,81
122	1826,67	2058,95
123	987,17	1259,14
124	4727,85	4586,82
125	1380,88	1328,27
126	556,55	1058,76
127	2356,00	1884,84
128	945,34	2126,85
129	1581,80	327,92
130	1763,44	1468,96
131	2185,40	2097,17
132	2061,97	2036,68
133	210,45	2427,92
134	495,88	160,61
135	5342,74	846,86
136	612,96	5311,80
137	977,87	1011,71
138	454,39	313,87
139	963,23	403,45
140	1576,17	1891,49
141	2966,88	1221,67
142	1388,95	2138,33
143	728,36	1383,44
144	4381,70	668,79
145	2024,39	4562,11
146	725,99	2381,43
147	681,93	1163,69
148	764,52	1246,33
149	1099,88	1533,91
150	1497,78	109,68
151	1833,12	1311,16
152	1076,63	2073,60
153	983,84	115,80
154	1632,39	638,82
155	711,13	1874,58
156	3301,68	108,81
157	913,63	2978,38
158	387,71	759,65
159	332,91	374,81
160	1099,37	159,52
161	1774,71	374,81
162	612,28	1923,19
163	2531,38	644,17
164	937,66	2299,85
165	1229,69	2172,38
166	1363,68	321,73
167	769,18	1998,65
168	788,93	288,34
169	785,71	1877,87
170	1692,27	1833,36
171	1332,51	1623,32
172		918,61

1575.01
596.78
194.96
2336.66
387.49
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1785.60
3923.18
1203.97
524.33
1019.74
1427.24
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1152.30
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1504.89
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15	969	.28	918	.71
15	1638	.55	1473	.64
15	847	.85	846	.20
15	728	.47	334	.69
15	1382	.86	1188	.23
15	417	.68	723	.31
17	735	.78	335	.48
17	1787	.83	723	.42
17	2282	.37	2231	.87
17	1381	.86	177	.87
17	1129	.38	773	.38
17	1025	.67	1569	.71
17	732	.32	392	.79
17	985	.16	836	.19
17	2689	.71	2637	.63
17	559	.57	334	.77
17	1014	.31	747	.75
19	2322	.18	2079	.08
19	1189	.47	1962	.15
19	1019	.98	1087	.41
19	882	.56	662	.52
19	1234	.14	778	.49
19	1088	.42	1199	.43
19	2683	.55	2393	.04
19	2368	.09	2122	.13
19	2024	.97	2066	.21
19	1154	.82	458	.64
19	510	.71	564	.86
19	1488	.97	564	.86
19	1406	.82	1148	.65
19	984	.31	768	.84
19	1531	.78	1020	.88
19	1898	.09	2287	.13
19	2299	.55	1610	.59
21	1592	.86	1419	.05
21	4131	.78	4064	.47
21	1744	.47	1982	.14
21	1338	.72	1317	.84
21	938	.50	282	.68
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21	1592	.94	1896	.03
21	1053	.65	146	.31
21	1489	.75	651	.71
21	2101	.51	2486	.43
23	2787	.04	493	.79
23	685	.52	1187	.68
23	927	.53	237	.27
23	1299	.34	371	.58
23	1274	.22	287	.45
23	972	.85	265	.48
23	1377	.96	487	.97
23	557	.69	134	.48
25	1048	.39	817	.33
25	1593	.86	1331	.78
25	488	.51	431	.85
25	1338	.05	1278	.88
25	836	.98	411	.86
25	582	.87	89	.72
25	831	.75	528	.34
25	829	.69	58	.47
27	684	.18	274	.88
27	1816	.68	1750	.87

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