

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

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Abstract

Prouditite, from the Juno Mine at Tennant Creek, Northern Territory, Australia, is monoclinic, space group $C2/m$, with $a = 31.96(1)$, $b = 4.12(1)$, $c = 36.69(3)$ Å, $\beta = 109.52(3)^\circ$ and has a known range of solid solution expressed by the general formula $Cu_xPb_{7.5}Bi_{0.67-0.33x}(S_y, Se_{1-y})_{22}$, 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 pack; 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 $Pb_{7.5}Bi_{0.67}(S, Se)_{22} \approx CuPb_{7.5}Bi_{0.33}(S, Se)_{22}$ 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 prouditite is closely related to that of junosite, $Cu_2Pb_3Bi_6(S, Se)_{16}$, the other main selenium-rich mineral intergrown with prouditite 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 sulphosalt 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 $Bi_2S_3-Bi_2Se_3$ (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 clausenthalite, $PbSe$, isomorphous with galena; guanajuatite, $Bi_2(S, Se)_3$, isomorphous with bismuthinite; and paraganajuatite, Bi_2Se_3 , which has a structure analogous to tetradymite (Bi_2Te_2S). 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, $Pb_3Bi_2(S, Se)_6$, and selenogoongarite, $Pb_4Bi_2(S, Se)_7$ (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, $Bi_4(S, Se)_3$ (Kato, 1959), are reported to be isostructural with joseite-A, $Bi_{4+x}Te_{1-x}S_2$.

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

H	K	L	Y(OBS)	Y(CALC)
36	0	1	420.23	263.27
36	0	2	746.53	754.10
36	0	3	440.60	200.67
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	840.54	940.69
36	0	16	484.05	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	740.66
34	0	3	518.95	795.07
34	0	6	523.49	322.65
34	0	7	372.80	212.98
34	0	9	376.92	253.30
34	0	10	926.62	985.30
34	0	11	840.06	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	2148.20
34	0	22	2569.40	2565.50
32	0	23	774.18	426.32
34	0	24	867.50	842.71
34	0	26	830.51	344.15
32	0	5	1156.27	1091.45
32	0	3	514.61	209.71
32	0	7	979.63	903.10
32	0	1	2050.09	2165.44
32	0	10	1204.31	1039.50
32	0	1	1722.35	1952.16
32	0	2	777.67	814.62
32	0	3	784.02	770.30
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	1287.06

36	0	20	471.57	278.81
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	3	518.95	795.07
34	0	4	523.49	322.65
34	0	5	372.88	212.98
34	0	6	376.92	253.30
34	0	7	926.62	985.30
34	0	8	848.06	1082.45
34	0	9	1201.17	1163.04
34	0	10	753.96	786.44
34	0	11	750.40	606.42
34	0	12	2221.73	2148.28
34	0	13	2569.40	2565.50
32	0	14	774.18	426.32
32	0	15	867.50	842.71
32	0	16	838.51	344.15
32	0	17	1156.27	1091.45
32	0	18	514.61	209.71
32	0	19	979.63	903.10
32	0	20	2058.89	2165.44
32	0	21	1204.31	1039.58
32	0	22	1722.35	1952.16
32	0	23	777.67	814.62
32	0	24	784.02	770.38
32	0	25	683.63	114.93
32	0	26	793.90	908.76
32	0	27	2204.18	2101.47
32	0	28	987.33	529.66
32	0	29	1397.69	1453.31
32	0	30	1276.45	1201.02
32	0	31	1141.54	939.95
32	0	32	984.73	655.10
32	0	33	283.53	312.85
32	0	34	397.94	387.36
32	0	35	395.90	95.04
32	0	36	552.27	676.74
32	0	37	1222.30	1287.06
30	0	10	1191.22	1281.12
30	0	9	708.39	801.67
30	0	8	1027.90	789.36
30	0	7	770.19	556.27

H	K	L	Y(OBS)	Y(CALC) (2)
36	0	1	920.23	263.27
36	0	2	746.53	754.10
36	0	3	940.60	200.67
36	0	4	1035.55	1072.88
36	0	5	820.14	742.23
36	0	6	337.61	257.29
36	0	7	339.85	305.95
36	0	8	840.54	940.69
36	0	9	484.05	174.61
36	0	10	681.76	253.59
36	0	11	987.09	325.04
36	0	12	471.57	278.81

MUMME - TABLE 7 (Structure factor table)

1473	1669	1363	63
987	987	1130	61
967	967	979	43
1101	1101	905	79
866	866	771	72
918	918	746	66
923	923	705	87
572	572	322	65
576	576	212	98
926	926	253	38
848	848	988	38
1201	1201	1002	45
753	753	1163	84
758	758	786	44
2221	2221	686	42
2569	2569	2180	28
774	774	2563	58
867	867	426	32
838	838	842	71
1156	1156	384	13
518	518	1041	45
979	979	209	71
2058	2058	903	18
1805	1805	2165	44
1722	1722	1039	58
777	777	1952	16
784	784	814	62
683	683	770	38
793	793	114	93
2204	2204	988	76
987	987	2181	47
1397	1397	529	66
1276	1276	1453	31
1141	1141	1201	82
988	988	939	93
283	283	655	18
397	397	316	85
393	393	387	36
552	552	93	84
1222	1222	676	74
1191	1191	1287	86
788	788	1281	12
1827	1827	881	67
778	778	789	36
1296	1296	556	27
1145	1145	1684	89
785	785	965	60
818	818	622	12
883	883	488	33
1012	1012	788	84
1013	1013	1206	26
827	827	1094	58
414	414	899	48
414	414	194	34
716	716	219	86
983	983	488	58
828	828	642	73
942	942	1883	64
513	513	812	41
1201	1201	283	84
838	838	1053	82
838	838	1887	25

28	0	10	269,48	130,62
28	0	9	349,19	90,58
28	0	7	692,08	551,69
28	0	6	699,36	476,44
28	0	5	713,10	719,29
28	0	0	829,02	365,84
28	0	1	386,48	308,75
28	0	2	414,12	173,52
28	0	3	383,12	610,30
28	0	4	826,69	696,59
28	0	5	823,96	130,69
28	0	6	383,60	733,60
28	0	7	828,88	832,28
28	0	8	824,62	768,50
28	0	9	824,57	854,91
28	0	10	412,56	24,40
28	0	11	412,83	393,59
28	0	12	713,64	631,18
28	0	13	413,56	318,20
28	0	14	1433,99	1493,32
28	0	15	814,31	688,36
28	0	16	293,16	227,93
28	0	17	293,25	356,51
28	0	18	383,87	890,16
28	0	19	291,61	283,39
28	0	20	1732,67	1728,57
28	0	21	2293,14	2428,80
28	0	22	1382,48	1613,98
28	0	23	553,20	89,31
28	0	24	343,70	266,84
28	0	25	266,32	312,22
26	0	26	1068,89	942,17
26	0	27	389,63	334,82
26	0	28	408,42	333,88
26	0	29	414,70	759,83
26	0	30	823,21	733,62
26	0	31	821,17	670,53
26	0	32	497,57	289,99
26	0	33	1310,61	1337,60
26	0	34	2847,51	2876,86
26	0	35	2273,33	2354,60
26	0	36	480,90	843,92
26	0	37	696,17	348,73
26	0	38	1277,81	1362,57
26	0	39	1288,84	1428,83
26	0	40	1817,80	1747,72
26	0	41	1153,47	1276,28
26	0	42	418,71	684,28
26	0	43	1809,29	884,73
26	0	44	1813,39	1856,12
26	0	45	1638,72	1741,51
26	0	46	1434,75	1184,84
26	0	47	1752,18	1869,48
26	0	48	211,82	338,16
26	0	49	1158,39	1163,79
24	0	16	1331,67	1138,29
24	0	15	1382,86	1386,32
24	0	14	696,33	389,81
24	0	13	1786,89	1322,84
24	0	12	2166,88	2163,48
24	0	11	1628,42	1676,92

0000000000	1	1129,79	1049,49
0000000000		792,02	813,01
0000000000		782,09	463,21
0000000000		2738,93	2634,39
0000000000		2338,36	2381,77
0000000000		883,74	471,54
0000000000		2210,58	1831,64
0000000000		382,58	172,62
0000000000	11	1211,63	1203,16
0000000000	12	861,28	912,46
0000000000	13	1640,38	1382,84
0000000000	14	1737,43	1667,87
0000000000	15	1180,74	979,84
0000000000	16	967,41	930,28
0000000000	17	975,83	628,17
0000000000	18	1135,71	977,34
0000000000	19	1161,94	919,38
0000000000	20	1607,65	1815,88
0000000000	21	1323,91	1437,33
0000000000	22	2024,01	2048,69
0000000000	23	827,81	563,82
0000000000	24	386,34	849,72
0000000000	25	382,13	173,11
0000000000	26	374,89	325,38
0000000000	27	1388,73	1529,13
0000000000	28	1491,36	1578,32
0000000000	29	1677,47	1348,87
0000000000	30	274,31	783,73
0000000000	31	1218,39	1384,55
0000000000	32	671,44	687,83
0000000000	33	1188,23	839,14
0000000000	34	1782,30	1343,15
0000000000	35	624,23	688,88
0000000000	36	721,77	399,83
0000000000	37	2928,13	2974,33
0000000000	38	1479,31	1512,28
0000000000	39	631,32	469,87
0000000000	40	699,98	688,38
0000000000	41	1118,81	1382,62
0000000000	42	399,22	128,00
0000000000	43	486,44	71,00
0000000000	44	921,16	1187,32
0000000000	45	382,92	464,76
0000000000	46	1321,28	1637,12
0000000000	47	787,43	783,88
0000000000	48	399,33	344,17
0000000000	49	286,89	88,29
0000000000	50	1333,27	1673,61
0000000000	51	717,98	494,81
0000000000	52	414,33	494,81
0000000000	53	978,71	1123,17
0000000000	54	998,71	1123,17
0000000000	55	1113,91	1249,33
0000000000	56	1181,38	1284,82
0000000000	57	638,18	846,88
0000000000	58	992,73	842,86
0000000000	59	381,43	872,33
0000000000	60	837,13	964,46
0000000000	61	336,83	333,79
0000000000	62	1257,71	1368,28
0000000000	63	824,42	672,34
0000000000	64	838,46	371,77

20	0	0	3000,25	2037,31
20	0	0	1549,33	1476,13
20	0	0	1110,24	1099,20
20	0	0	1176,63	1013,93
20	0	0	1769,33	1730,71
20	0	0	1622,31	1701,10
20	0	0	775,36	899,33
20	0	0	392,93	174,93
20	0	0	562,67	297,26
20	0	0	985,00	838,02
20	0	0	828,49	772,26
20	0	0	1172,96	1356,44
20	0	0	2617,30	2631,14
20	0	0	420,87	664,84
18	0	0	964,31	1350,47
18	0	0	407,81	343,66
18	0	0	411,89	240,02
18	0	0	1014,83	1011,36
18	0	0	260,24	191,93
18	0	0	400,08	70,40
18	0	0	807,52	1144,84
18	0	0	1260,02	1249,61
18	0	0	786,19	714,02
18	0	0	640,52	610,93
18	0	0	311,46	833,06
18	0	0	447,44	338,72
18	0	0	369,78	417,09
18	0	0	2271,79	2412,22
18	0	0	2110,70	2201,99
18	0	0	703,84	959,17
18	0	0	1330,82	1234,70
18	0	0	301,13	700,13
18	0	0	1031,22	1034,30
18	0	0	2027,70	2792,12
18	0	0	1273,25	1637,19
18	0	0	1113,43	892,27
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18	0	0	2293,84	2369,66
18	0	0	1367,11	1390,74
18	0	0	731,39	838,63
18	0	0	1000,93	702,43
18	0	0	473,60	436,66
18	0	0	692,34	687,20
18	0	0	809,49	939,08
18	0	0	1156,30	1090,19
18	0	0	1165,47	1220,00
18	0	0	2020,30	2110,31
18	0	0	1739,40	1766,09
16	0	0	490,61	343,61
16	0	0	394,60	301,77
16	0	0	1260,02	1107,67
16	0	0	8243,33	8310,74
16	0	0	1791,87	2005,27
16	0	0	973,43	1107,64
16	0	0	1501,31	1400,30
16	0	0	1122,27	392,33
16	0	0	647,94	392,33
16	0	0	1001,93	607,10
16	0	0	1131,93	929,89
16	0	0	2904,06	3171,17
16	0	0	309,70	299,60
16	0	0	714,06	100,00

16	0	3
16	0	3
16	0	6
16	0	8
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12	0	6
12	0	3
12	0	1

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1718,90
864,84
760,37
2230,29
821,48

11	0	04	822,18	284,35
11	0	07	3535,14	3535,78
11	0	08	838,85	647,86
11	0	09	1344,17	1398,54
11	0	11	1244,76	1269,63
11	0	13	375,19	276,64
11	0	15	965,26	128,35
11	0	16	3132,99	3388,44
11	0	17	3217,96	3398,32
11	0	19	1316,52	1358,88
11	0	21	568,81	85,15
11	0	27	2415,66	2127,15
11	0	29	975,82	659,19
11	0	21	688,21	751,82
11	0	28	664,18	655,65
11	0	19	1688,41	1578,91
11	0	18	1269,37	1338,28
11	0	13	825,67	552,38
11	0	14	925,47	1888,98
11	0	15	1899,59	724,22
11	0	11	1399,52	1284,14
11	0	18	1881,84	988,24
11	0	9	568,63	265,85
11	0	7	372,68	785,35
11	0	4	3588,79	3728,57
11	0	2	975,87	578,26
11	0	1	951,79	916,58
11	0	3	521,68	336,78
11	0	5	522,48	528,71
11	0	6	1368,11	998,21
11	0	7	974,88	881,18
11	0	8	1715,48	1837,83
11	0	10	924,92	1864,88
11	0	11	749,99	541,49
11	0	14	738,63	518,93
11	0	16	6816,75	6139,71
11	0	17	1133,24	955,62
11	0	18	826,75	711,31
11	0	19	892,95	658,17
11	0	20	1877,54	1886,25
11	0	22	739,15	198,59
11	0	23	1275,85	1188,71
11	0	26	3848,24	3281,35
11	0	27	847,87	1272,15
11	0	31	1155,45	1172,15
11	0	25	816,88	1898,87
11	0	21	757,68	788,56
11	0	28	1279,27	1572,22
11	0	19	622,34	146,71
11	0	15	3392,89	3264,26
11	0	12	486,88	462,92
11	0	6	1137,17	1851,11
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11	0	4	866,56	1364,44
11	0	3	985,68	528,25
11	0	2	1219,78	1744,87
11	0	04	1188,87	1151,69
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11	0	06	1784,75	1751,88
11	0	10	451,45	255,47
11	0	14	1921,96	1577,55
11	0	15	3865,18	3282,58

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0	0	18	404.22	191.79
0	0	19	836.76	186.41
0	0	21	1613.19	1571.93
0	0	22	1729.32	1862.42
0	0	24	1630.93	1548.61
0	0	25	1753.98	1684.89
0	0	26	889.69	338.52
6	0	19	4688.61	4261.11
6	0	19	153.54	119.48
6	0	16	3257.65	3388.38
6	0	15	847.87	837.81
6	6	14	817.54	982.99
6	0	13	2156.92	652.46
6	0	12	1257.15	1877.24
6	0	10	788.52	687.83
6	0	9	237.77	137.23
6	0	7	2374.31	2643.22
6	0	6	4186.84	4128.93
6	0	5	4742.92	4283.28
6	0	3	1344.61	1452.57
6	0	4	1421.68	1416.87
6	0	11	426.88	178.83
6	0	12	1334.29	1296.86
6	0	13	1037.36	1628.68
6	0	14	541.88	115.74
6	0	18	399.83	475.22
6	0	19	293.37	293.83
6	0	20	1426.54	1376.12
6	0	21	1092.38	2133.65
6	0	22	1129.88	356.22
6	0	24	483.44	1052.61
6	0	29	375.65	329.23
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4	0	27	2562.81	2399.67
4	0	26	781.51	103.72
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4	0	23	526.33	886.92
4	0	18	839.83	779.72
4	0	17	2371.58	2214.79
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4	0	14	2282.61	2861.31
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27	0	14	819.66	228.72
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27	0	0	802.82	643.61
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27	1	07	952.37	618.88
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27	1	09	823.37	236.86
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27	1	11	838.58	279.86
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27	1	14	684.97	518.32
27	1	15	1914.53	2134.43
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15	1	0.14	1105.22	1214.52
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9	1	918,82	1614,37
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7	1	1095,49	527,61
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23	1		1278,22	287,45
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