COMPOSITIONS OF COEXISTING PYRRHOTITES, PENTLANDITES AND PYRITES AT SPARGOVILLE, WESTERN AUSTRALIA

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Abstract

Seventy-eight electron probe analyses are presented of coexisting pyrrhotite, pentlandite and pyrite grains from the 5D orebody at Spargoville, Western Australia.

Monoclinic pyrrhotite, hexagonal pyrrhotite and smythite are present, indicating low-temperature equilibration of the assemblage, probably below 75° C. The nickel content of the pyrrhotites (including smythite) ranges from 0.24 to 0.65 at.% but shows little correlation with the nickel content of associated pentlandite; rather, position within the orebody seems to be the controlling factor.

The nickel content of the pentlandite falls within the range found for other pyrrhotite-pentlanditepyrite assemblages. The cobalt content ranges from 0.34 to 0.86 at. % and shows a positive correlation with the cobalt content of coexisting pyrite (which ranges from 1.02 to 2.51 at. %).

INTRODUCTION

Nickel sulphide mineralization at Spargoville, Western Australia, is associated with the basal, olivine-rich, unit (A-E, Fig. 1) of an altered Archean ultramafic body (Hancock et al. 1971). The sulphides are concentrated on the basal contact and consist predominantly of pyrrhotite and pentlandite with subordinate pyrite and minor chalcopyrite. X-ray diffraction using the method of Arnold (1966) indicates that most of the pyrrhotite is monoclinic but that some hexagonal pyrrhotite is also present (Hancock et al. 1971). Much of the pyrite occurs as complex intergrowths with the other sulphides and is believed to be secondary, possibly formed during alteration of the ultramafic host (Ramsden & Wilmhurst, in prep.). Some, however, occurs as well-developed euhedral crystals and may be primary.

The purpose of the present communication is to report on the compositions of coexisting grains of pyrrhotite, pentlandite and pyrite in this assemblage. The data (Table 1) were obtained from nine samples taken at increasing depths down an exploratory diamond drill hole (DDH-X, Fig. 1 and Hancock *et al.* 1971) and refer only to assemblages of grains that were in contact with one another. The analyses were carried out with a Cambridge Microscan V electron probe and care was taken to reduce the possibility of spurious counts from associated minerals by analyzing well away from grain boundaries. In the case of pyrrhotite, special care was taken to avoid the minute exsolved pentlandite lamellae present in some grains. Analyses were made for sulphur, iron, nickel, copper and cobalt using pyrite, metallic nickel, metallic copper and metallic cobalt as standards. Corrections were made using the MAGIC IV programme of Colby (1971).

For the sulphur and iron analyses, precision is about $\pm 1\%$ of the amount present in pyrrhotite and pentlandite, and about $\pm 2\%$ of the amount present in pyrite. The precision for nickel is about $\pm 1\%$ of the amount present in pentlandite, but only about $\pm 20\%$ of the amount present in pyrrhotite and pyrite. For cobalt the precision is about $\pm 5\%$ of the amount present in the pentlandite and pyrite and



FIG. 1. Cross-section of ultramafic body as revealed by DDH-X and adjacent drill holes.

about $\pm 20\%$ of the amount present in the pyrrhotite. The copper analyses are rough estimates only.

RESULTS AND DISCUSSION

Ternary phase relations

Figure 2 shows a plot of the data (atomic per cent) on the Fe-Ni-S ternary diagram. Follow-

TABLE 1. COMPOSITIONS OF CO-EXISTING PYRRHOTITES, PENTLANDITES, AND PYRITES

Mi-			k	lt. %					At. %			Depth,
neral	\$	Fe	Ni	Cu	Со	Total	S	Fe	Ni	Cu	Co	meters
Po	38.9	60.6	0.46	0.05	0.15	100.2	52.6	46.9	0.34	0.03	0.11	178.3
Pn	32.8	30.8	34.4	0.05	1.05	99.1	47.0	25.3	26.9	0.04	0.82	
Po	39.5	61.1	0.53	0.04	0.08	101.2	52.7	46.8	0.38	0.03	0.06	
Pn	33.0	31.3	34.4	0.05	1.12	100.5	47.3	25.3	26.5	0.04	0.86	
Pu Pn	33.0	31 5	3/1 1	0.03	0.12	100.6	52.4	47.1	0.35	0.02	0.09	
Po	39.2	60.8	0.52	0.09	0 12	100.1	47.3	25.0	20.3	0.06	0.80	
Pn	33.9	31.8	33.1	0.08	1.09	100.0	47 9	25 7	25 5	0.00	0.09	
Po	37.3	59.3	0.49	0.03	0.12	97.3	52.1	47 5	0 37	0.05	0.04	222 2
Pn	31.4	28.7	34.9	0.10	0.64	95.9	46.6	24.5	28.3	0.07	0.52	LLL , L
Po	37.7	59.4	0.60	0.06	0.10	97.8	52.2	47.2	0.46	0.04	0.05	
Pn	32.3	30.3	32.5	0.13	0.62	95.6	47.6	25.6	26.1	0.10	0.50	
Po	37.9	59.4	0.44	0.03	0.07	97.8	52.4	47.2	0.33	0.02	0.06	
Pn	31.7	28.0	35.3	0.04	0.63	95.6	47.0	23.8	28.6	0.03	0.51	
PQ Dm	3/.0	29.1	0.58	0.09	0.09	97.5	52.3	47.1	0.44	0.06	0.07	
Po	37 0	50 6	0.10	0.00	0.70	- 97.9	40.8	24.3	28.3	0.00	0.60	000 0
Pn	32 5	29 0	35 8	0.04	0,12	98.0	17 0	4/.4	20.30	0.03	0.09	225.8
Po	38.3	60.4	0.53	0.00	0.08	90.4	52 2	47 3	0.30	0.00	0.00	
Pn	33.2	30.2	35.9	0.07	0.56	99.8	47.1	24 6	27 8	0.00	0.00	
Po	38.0	59.7	0.38	0.01	0.11	98.2	52.3	47.3	0.29	0.01	0.08	
Pn	32.6	29.6	36.0	0.04	0.58	98.8	46.8	24.4	28.3	0.03	0.45	
Po	38.3	60.4	0.50	0.01	0.13	99.4	52.2	47.3	0.37	0.01	0.10	
Pn	32.4	28.8	36.4	0.09	0.74	98.5	46.7	23.9	28.7	0.07	0.58	
PO	39.5	58.8	0.43	0.00	0.14	99.0	53.6	45.9	0.32	0.00	0.10	233.2
Pn Du	53.1	28.0	35.8	0.13	0.14	97.8	47.8	23.3	28.3	0.09	0.55	
P0	38.7	56 0	0.41	0.10	1.80	98.8	5/.1	31.3	0.28	0.10	1.23	
Pn	33.2	27.5	36 1	0.02	0.10	90.1	04.U	40.0	20 5	0.02	0.14	
Py	51.3	40.9	1.02	0.05	3.56	96.8	66.4	30 4	0 72	0.03	2 51	
Po	39.0	58.3	0.46	0.06	0.15	97.9	53.5	46.0	0.34	0.04	0.12	
Pn	33.3	28.2	35.5	0.03	0.75	97.8	48.0	23.4	27.9	0.02	0.59	
Po	39.3	58.4	0.36	0.00	0.14	98.2	53.7	45.9	0.27	0.00	0.10	
Pn	32.9	28.8	35.2	0.22	0.74	97.9	47.6	23.9	27.8	0.16	0.58	
Po	41.6	60.0	0.42	0.03	0.14	102.1	54.5	45.1	0.30	0.02	0.10	237.1
Pn	34./	30.3	36./	0.09	0.53	102.2	47.9	24.0	27.7	0.06	0.40	
Pn Dn	36.1	30.3	26 7	0.02	0.11	100.4	54.9	44.5	0.4/	0.01	0.08	
Pn	40.1	57 0	0 65	0.07	0.53	07.0	48.1	24.0	2/.4	0.05	0.39	
Pn	34.7	31.2	35.9	0.19	0.50	102.4	17 R	24.0	27 0	0.04	0.09	
Po	40.9	58.1	0.49	0.03	0.13	99.6	54.8	44.7	0 36	0.13	0.37	
Pn	34.0	30.6	36.7	0.18	0.45	101.9	47.3	24.4	27.8	0.12	0.34	
Po	40.5	57.9	0.62	0.05	0.16	99.2	54.6	44.8	0.45	0.03	0.11	
<u>Pn</u>	35.0	32.2	34.1	0.16	0,48	101.9	48.3	25.5	25.7	0.11	0.36	
Po	39.0	57.8	0.63	0.01	0.08	97.6	53.7	45.7	0.47	0.01	0.06	238.3
Pn	32.9	30.1	37.1	0.06	0.53	100.7	46.5	24.4	28.6	0.04	0.41	
PO Po	30.0	20.4	0.8/	0.00	0.13	98.3	53.3	46.0	0.65	0.00	0.09	
Po	20 3	29.0 58 A	0 97	0.09	0.07	99.0	40.5	24.4	28.6	0.06	0.40	
Pn	31.5	29.9	36.8	0.00	0.07	90.0	33.0	40.7	20 7	0.00	0.05	
Po	39.2	59.2	0.50	0.03	0.12	90.9	53 3	46 2	0 27	0.07	0.40	220 0
Pn	32.0	29.3	37.3	0.06	0.61	99.4	46.0	24.2	29.3	0.00	0.09	229.9
Po	38.9	58.8	0.76	0.00	0.06	98.5	53.2	46.2	0.57	0.00	0.05	
Pn	32.3	28.8	37.2	0.03	0.57	98.9	46.5	23.8	29.2	0.02	0.45	
Po	40.1	60.2	0.72	0.07	0.14	101.2	53.4	45.9	0.52	0.04	0.10	240.6
Pn	33.4	28.7	36.8	0.14	0.54	99.5	47.5	23.4	28.6	0.10	0.42	
Py Du	54.7	44.6	0.36	0.47	1.52	101.6	67.1	31.3	0.24	0.29	1.01	
Po	24.5	44.U	0.75	0.35	1.53	101.2	6/.1	31.1	0.50	0.22	1.02	
Pn	33.4	28 5	37 4	0.03	0.11	100.7	53.2	40.2	0.55	0.02	80.0	
Po	39.9	59 7	0 69	0.10	0.01	100.0	47.3	23.2	28.9	0.07	0.47	
Pn	33.4	28.8	37.1	0.08	0.59	100.0	47 3	23 5	28 7	0.03	0.10	
Po	40.3	59.7	0.73	0.11	0.18	101.0	53 6	45 7	0.53	0.00	0.45	
Pn	33.3	28.7	36.8	0.14	0.60	99.5	47.4	23.4	28.6	0.10	0.46	
Po	40.1	60.0	0.83	0.05	0.12	101.1	53.4	45.9	0.60	0.04	0.09	
Pn	<u>33.3</u>	28.5	37.3	0.09	0.61	99.9	47.3	23.3	28.9	0.06	0.47	
Pn	32.8	29.3	36.6	0.16	0.46	99.3	46.9	24.0	28.6	0.12	0.36	241.1
ry	52.8	43.9	2.47	0.06	1.51	100.7	65.8	31.4	1.68	0.04	1.03	
FU Pv	53.5	49.U	00.0	0.14	0.51	39.5	4/.3	23.7	28.4	0.10	0.39	
Pn	22.5	20 0	36 5	0.10	1./5	100.2	47 4	31.5	0.58	0.10	1.19	
Pv	53.6	44.2	0.84	0.27	1.74	100 6	4/.4 66 F	23./	10.4	0.11	0.38	
Po	40.1	60.1	0.89	0.05	0.14	101.3	53.3	45.0	0.65	0.17	1.10	
Pn	33.2	28.8	36.7	0.17	0.51	99.4	47.3	23.6	28.5	0.12	1.40	
Po	39.7	60.3	0.83	0.07	0.10	100.9	53.0	46.2	0.60	0.05	0.07	
Pn	33.1	28.7	37.0	0.14	0.54	99.5	47.2	23.9	28.8	0.10	0.42	
Ро	39.4	59.3	0.65	0.05	0.19	99.6	53.3	46.0	0.48	0.03 (0.14	
rn	32.7	28.2	36.5	0.11	0.52	98.1	47.3	23.4	28.9	0.08 (0.41	

ing the procedure of Harris & Nickel (1972), cobalt has been distributed equally between nickel and iron when plotting the pentlandite compositions, but in the case of pyrrhotite and pyrite it has been included with the iron. In all cases the (small) copper content has been ignored.

The phase relations in Figure 2 are consistent with the tentative low-temperature ($<135^{\circ}$ C) diagram proposed by Graterol & Naldrett (1971), but the pyrrhotites fall into three groups. On the basis of composition, these groups correspond to hexagonal pyrrhotite, monoclinic pyrrhotite and smythite in order of decreasing iron content.

X-ray diffraction analysis (Hancock *et al.* 1971) does not detect the presence of smythite, but shows monoclinic pyrrhotite to be the predominant phase, generally forming over 90% of these mixtures. The presence of smythite indicates equilibration of the assemblage below about 75°C (Taylor 1970). Nickel (1972) has suggested that it is probably a secondary phase formed by late-stage sulphurization of monoclinic pyrrhotite. However, later evidence (Nickel *et al.* 1974) suggests that smythite is more likely to be an "oxidation" product of pyrrhotite formed by the removal of iron rather than by the addition of sulphur.

Nickel content of the pyrrhotite

Figure 3 shows the nickel content of the pyrrhotites (including smythite) plotted against the nickel content of the associated pentlandite. There is little correlation, although regression analysis suggests that there may be a slight positive trend. Nor does there appear to be a correlation between nickel content and pyrrhotite type (as inferred from its composition — Table 1) although, on the basis of previous studies (Vaughan et al. 1971; Batt 1972; Nickel 1972) higher values would be expected with the hexagonal type. Figure 4, illustrating the relationship between nickel content and depth, suggests rather that there is an increase in nickel content related to the more massive part of the ore at the basal contact (indicated by the high sulphur content in the whole-rock analyses). The reason for this trend is at present unknown. The lack of any clear partitioning of nickel between the pyrrhotite types, however, may be due to the limited precision of the nickel analyses in the present study.

Cobalt content of pentlandite and pyrite

Figure 5 shows the cobalt content of pentlandite plotted against the cobalt content of the associated pyrite. Error limits estimated from



FIG. 2. Pyrrhotite, pentlandite and pyrite compositions plotted on the Fe-Ni-S diagram.

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FIG. 3. Nickel content of pentlandite/pyrrhotite.



FIG. 4. Variation in whole-rock sulphur content and nickel content of pyrrhotite in relation to position in the orebody.

many analyses in each sample (but not necessarily of grains in contact) are also indicated. The data are limited, but there is clearly a positive correlation consistent with partitioning of cobalt between the two phases either during crystallization and/or subsequent recrystallization. Regression analysis yields a curve which intercepts the pentlandite axis at 0.19 at. % Co, but the trend is strongly dependent on the single high cobalt determination and a slight error in this point could easily set the line through the origin.

Metal:sulphur ratios of the pentlandite

Figure 6 shows the frequency distribution of sulphur in the pentlandites. Following Harris & Nickel (1972), these have been plotted as atomic per cent.

The centre of gravity of the distribution is slightly on the sulphur-rich side of stoichiometric $M_{9}S_{8}$. This is contrary to the findings of Harris & Nickel (1972) for pentlandites from a variety of assemblages. However, as pointed out by these authors, one could expect to find sulphurrich pentlandites in sulphur-rich assemblages containing pyrite if, in fact, the mineral is a non-stoichiometric phase, since there should then be a correlation between sulphur and the mineral assemblage containing the pentlandite. However, Rajamani & Prewitt (1973) indicate that sulphur excess should be related to a high Ni:Fe ratio in non-stoichiometric pentlandite and no such correlation exists in the present data (Fig. 7). It is more likely, therefore, that the apparent non-stoichiometry here is due to analytical errors.

CONCLUSIONS

It is concluded that the compositions of coexisting pyrrhotite, pentlandite, and pyrite grains at Spargoville indicate low-temperature equilibration of the assemblage, the presence of smythite indicating temperatures below about 75°C.

The nickel content of the pyrrhotite seems to depend upon position within the orebody but shows little correlation with the nickel content of the associated pentlandite. A positive correlation exists between the cobalt contents of coexisting pentlandite and pyrite grains consistent with partitioning between the two minerals.



FIG. 5. Cobalt content of pentlandite/pyrite.



FIG. 6. Frequency distribution of sulphur in pentlandites.

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FIG. 7. Ni/Fe ratio of pentlandite plotted against sulphur content.

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Manuscript received October 1974, emended February 1975.