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The pentlandite group $(Fe,Ni,Co)_9S_8$: New data and an appraisal of structure–composition relationships

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SUMMARY. Analyses are presented for an iron-rich pentlandite associated with native copper and troilite from New Zealand and three cobalt-bearing pentlandites from Australia. Examination of 141 published analyses indicates that pentlandites, regardless of their Co content, can be classified on the basis of cell size, Fe content, Fe:Ni ratio, and the sulphide assemblage in which they occur. The cobaltian varieties show two separate trends.

ELECTRON microprobe analyses together with cell sizes are presented for four pentlandites from Australasia (Table I). These exhibit extreme ranges of cobalt content, Fe:Ni ratio, and stoichiometry.

Within the pentlandite group the most frequently reported compositions for members containing little or no cobalt are nickel-rich with Fe:Ni ratios of somewhat less than 1 (0·7–0·9). The most nickel-rich contain up to 43·5 wt. % Ni (Naldrett *et al.*, 1972) and the most iron rich contain up to 40·5 wt. % Fe (Page, 1972). Little attention has been given in the literature, however, to the Fe:Ni ratio of pentlandites containing significant amounts of cobalt. Rather the emphasis has been on the amount of the cobalt present.

Cell-size values reported generally decrease from those for Co-free pentlandites to the refined value for Co_9S_8 given by Geller (1962) of 9·928±0·001 Å. For the Co-free pentlandites the highest nickel-rich ones give a value of 10·026±0·002 Å (Buchan and Blowes, 1968) and Kouvo *et al.* (1959) report a value of 10·067±0·001 Å for an iron-rich pentlandite. Apart from the cobalt end member Co_9S_8, synthetic equivalents are not comparable, because of their larger cell sizes (Knop *et al.*, 1965, Rajamani and Prewitt, 1975).

Analysis of published data. In order to establish relationships between composition, structure, assemblage, and stoichiometry within the pentlandite group, a comparison was made of 141 published analyses, excluding those containing significant silver values. This included 104 pentlandites containing less than (an arbitrary) 8 wt. % Co and thirty-seven analyses containing greater cobalt contents than this. Including data reported in the present work, sixteen of these analyses have cell-size information.

Results

Cell-size relationships. Fig. 1 illustrates the good correlation between cell-size and iron content for members of the $(Fe,Ni,Co)_9S_8$ group. The cobalt-rich and cobalt-poor members overlap, but the series is continuous. Ni and Co have no such constant effect on cell size. The relationship progresses from 0 % Fe for Co_9S_8 to about 38–41 atoms of Fe (25–27 wt. % Fe) where the overlap occurs with members deficient in cobalt, i.e. $(Fe,Ni)_9S_8$. The series then progresses from the nickel-rich to the most iron-rich pentlandites. The theoretical end member of the series (Fe_9S_8) has not been reported but the synthetic equivalent (Nakazawa *et al.*, 1973)

TABLE I. *Pentlandite data: Electron microprobe analyses**

Location		Co	Ni	Fe	S	Total	Fe:Ni	a, Å	Assemblage	Form & occurrence
Mount Dun area, Nelson Province	Wt%	4.1	19.3	43.1	33.6	100.1	2.233	10.170 ±0.003	Troilite, chalcopyrite, *native copper*, cuprite	Coarse grains in altered and contorted ultrabasic. 0.7 Wt% Ni present in native copper solid solution.
New Zealand	atoms ‡	0.5	2.5	6.0	8.0					
Lime Creek N.W. Queensland	Wt%	9.8	30.5	27.1	32.7	100.1	0.889	10.030 ±0.005	*Pyrrhotine*, chalcopyrite	Fine exsolutions in (hexagonal) pyrrhotine.
	atoms	1.3	4.0	3.7	7.8					
Mount Colin N.W. Queensland	Wt%	11.0	30.8	25.6	32.4	99.8	0.831	10.014 ±0.003	Pyrrhotine, pyrite, *smythite*	Coarse grains (up to 200 μm) and fine exsolutions in (monoclinic) pyrrhotine. Chalcopyrite, cobalt violarite, magnetite present as well.
	atoms	1.4	4.1	3.5	7.7					
Lord Brassey Mine N.W. Tasmania †	Wt%	43.8	18.7	5.0	31.8	99.3	0.267	9.960 ±0.003	*Heazlewoodite*	Coarse grains in ultrabasic with abundant magnetite.
	atoms	5.8	2.5	0.7	7.8					

* Analyses by P. K. Schultz, Australian Mineral Development Laboratories, Adelaide. Results are the average of the analysis of at least 3 separate grains. Little or no elemental variations being indicated from grain to grain.

† Sample obtained from the Director, Mines Department, Tasmania. Chemical analysis also reported in Misra and Fleet (1973).

‡ Calculated on basis of 9 metal atoms.

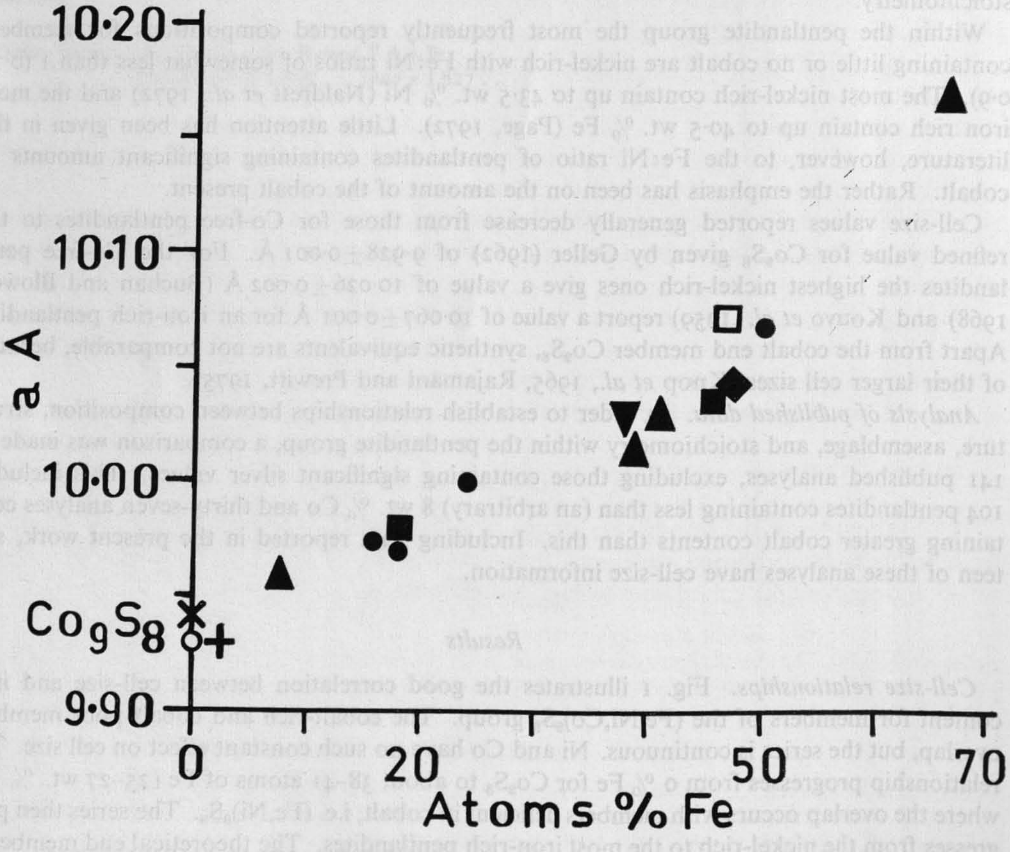

FIG. 1. Variation of cell size with Fe content (atoms % Fe of total metal atoms) for members of the pentlandite group $(Fe,Ni,Co)_9S_8$. ▲ Present study. ● Kuovo *et al.*, 1959. ■ Rajamani and Prewitt, 1973, 1975. ◆ Robinson and Brooker, 1952. ▼ Buchan and Blowes, 1968. ○ Synthetic Co_9S_8, Ibrahim, 1959. × Petruk *et al.*, 1969. + Stumpfl and Clark, 1964, using Geller's (1962) cell size. □ Berry and Thompson, 1962.

gives a cell size of 10·5 Å. Their composition of Fe_9S_8, however, of theoretical 66·2 wt. % Fe was inferred because of the difficulties of direct composition-analysis of thin films.

Cobalt substitution. The plot of Co against the Fe:Ni ratio of all pentlandites (fig. 2) indicates that cobalt replaces iron or nickel in two separate series. The former is typical of the nickel-and-cobalt-rich localities of Canada and the latter is common in the iron-and-copper-rich assemblages of Europe. The two series originate at about Fe:Ni—0·8 with an Fe content somewhat < 30 wt. % Fe. These trends could represent the two kinds of cobalt atoms identified by Geller (1962), one showing octahedral and the other tetrahedral coordination.

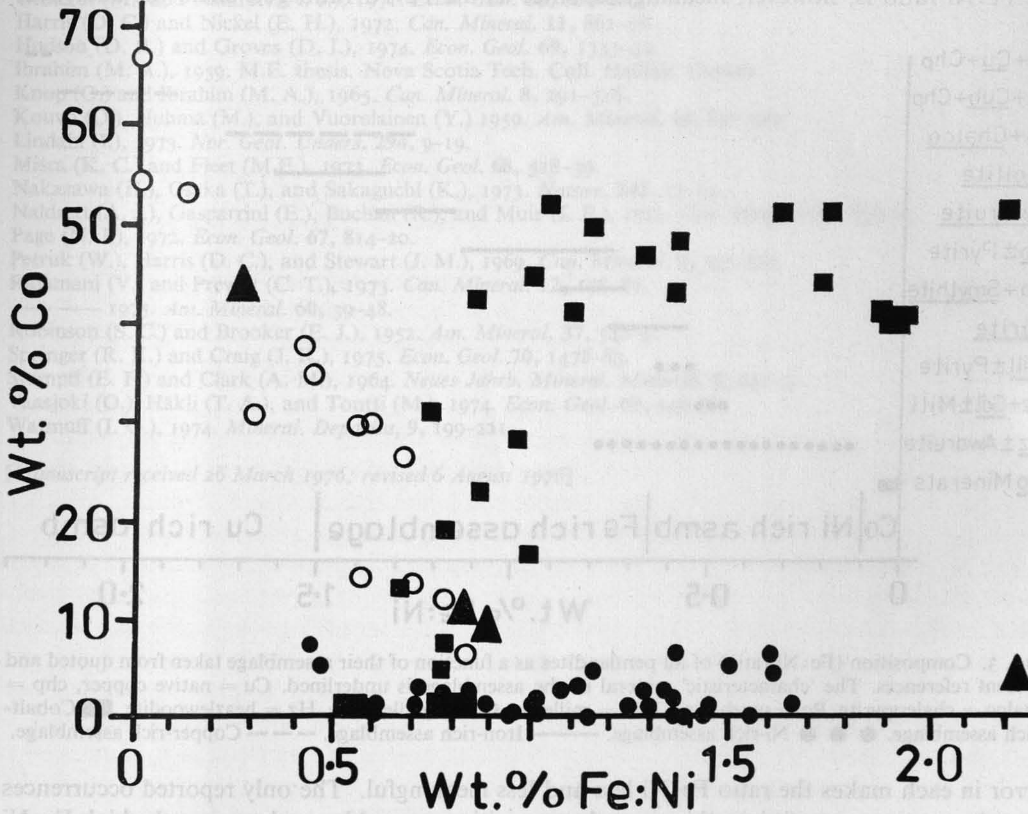

FIG. 2. Variation of cobalt with Fe:Ni ratio for all pentlandites. ▲ Present study, ■ European cobalt pentlandites from Fe-and-Cu-rich assemblages, ○ Canadian cobalt pentlandites from Co-and-Ni-rich provinces. ● Pentlandites with no appreciable Co content (< 8 wt. %). ■■ The most frequently reported Co-free pentlandites. Sources in addition to those listed with fig. 1, include Graterol and Naldrett (1971), Harris and Nickel (1972), Page (1972), Naldrett *et al.* (1972), Vaasjoki *et al.* (1974), Lindahl (1973), Watmuff (1974), Hudson and Groves (1974), Craig and Higgins (1975), Springer and Craig (1975).

Composition–assemblage relationships. A relationship is present between the Fe:(Fe:Ni) ratio of cobalt-deficient pentlandites and the mineral assemblage in which they occur (Graterol and Naldrett, 1971). An association with heazlewoodite is observed for the lower Fe:(Fe:Ni) ratios, ranging to an association with troilite for the higher values. Harris and Nickel (1972) concluded similarly using the Fe:Ni ratio. Fig. 3 represents the relationships between the composition of all pentlandites expressed as the Fe:Ni ratio and the assemblage in which they occur. It demonstrates the overlap present in any general relationship of this type and highlights the position of the 'characteristic' mineral.

The two end-member classifications of cobalt-rich (linnaeite–carrollite, siegenite, bravoite) and copper-rich (chalcopyrite, cubanite, native copper) assemblages are based on scant data. Stumpfl and Clark (1964) and Petruk *et al.* (1969) provided data for the very low Fe:Ni ratios, Lindahl (1973) plus the present work give data for the high Fe:Ni ratios. The Co_9S_8 end member of Stumpfl and Clark (1964) occurs in an assemblage rich in both copper and cobalt; the Fe:Ni ratio is, however, meaningless, since as the Fe:Ni ratio gets small the analytical error in each makes the ratio Fe:Ni less and less meaningful. The only reported occurrences that do not appear to fit into this general composition–assemblage scheme are the high Fe:Ni (1·158–1·356) pentlandites associated with awaruite (Harris and Nickel, 1972). These could, however, be iron-rich awaruites.

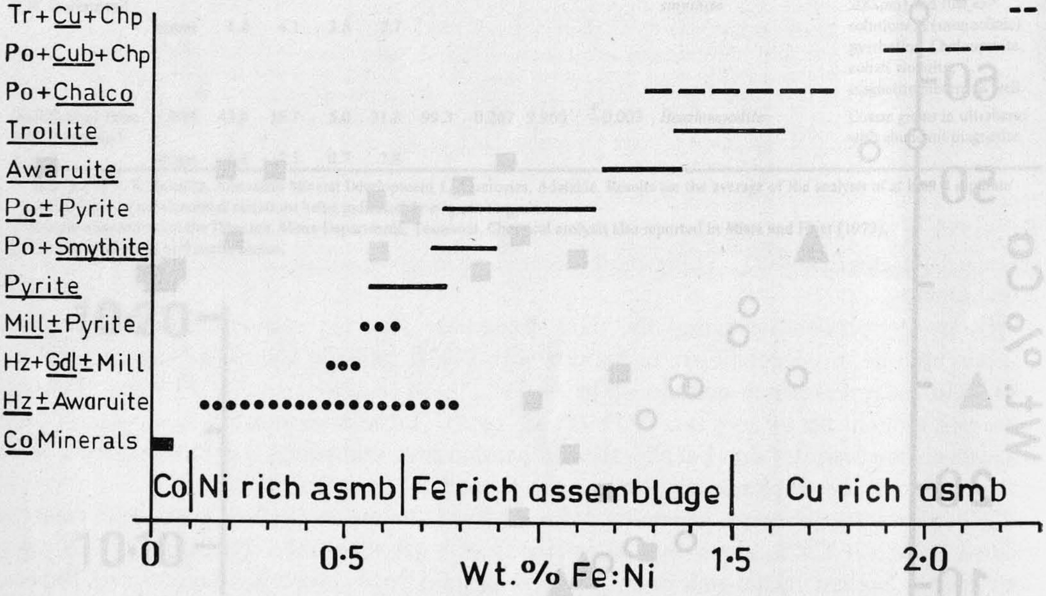

FIG. 3. Composition (Fe:Ni ratio) of all pentlandites as a function of their assemblage taken from quoted and present references. The 'characteristic' mineral in the assemblage is underlined. Cu = native copper, chp = chalco = chalcopyrite. Po = pyrrhotine, Mill = millerite, Gdl = godlevskite, Hz = heazlewoodite. ■ Cobalt-rich assemblage. ● ● ● Ni-rich assemblage. ——— Iron-rich assemblage. — — — Copper-rich assemblage.

Within the nickel-and-iron-rich assemblages there appears to be a trend in the stoichiometry of the 'characteristic' mineral that is consistent with the trend in the Fe:Ni ratio of the pentlandite. Thus with increasing Fe:Ni the metal to sulphur ratio of the characteristic mineral in the nickel-rich assemblages progresses from 1·5 (heazlewoodite) to 1·17 (godlevskite) to 1·0 (millerite). In the iron-rich assemblages pyrite–smythite–pyrrhotine–troilite show a M:S progression from 0·5 to 0·82, 0·9, and 1·0.

Metal to sulphur ratios. Harris and Nickel (1972) considered that evidence for appreciable deviation of pentlandite compositions from a 9:8 metal to sulphur ratio was not strong. Rajamani and Prewitt (1973), however, concluded that there was a loose correlation between nickel content and stoichiometry. $M_{9-x}S_8$ was indicated for nickel-rich species and $M_{9+x}S_8$ for iron-rich ones. In the present study no relationship between metal:sulphur ratio and any other factor can be established.

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