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TEXTURAL AND COMPOSITIONAL VARIATIONS IN A Ni-Co-As ASSEMBLAGE

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ABSTRACT

A Ni-Co-As assemblage from Cobalt, Ontario, consisting of plumose rosettes of rammelsbergite enclosing large prismatic crystals of pararammelsbergite and rimmed by cobaltite and safflorite has been examined by electron microprobe analysis for Fe, Ni, Co, S, As and Sb. Approximate average metal compositions for these phases are: pararammelsbergite, axial blades, $Ni_{.96}$ $Co_{.03}$ $Fe_{.01}$, interlocking crystals at the cores of rosettes, $Ni_{.92}$ $Co_{.07}$ $Fe_{.01}$; rammelsbergite, $Ni_{.67}$ $Co_{.30}$ $Fe_{.03}$; cobaltite, $Ni_{.50}$ $Co_{.40}$ $Fe_{.10}$ to $Ni_{.20}$ $Co_{.76}$ $Fe_{.04}$; and safflorite, inner zone, $Ni_{.20}$ $Co_{.60}$ $Fe_{.20}$, outer zone, $Ni_{.32}$ $Co_{.38}$ $Fe_{.30}$. The rammelsbergite is relatively homogeneous but there are significant compositional variations within the cobaltite zone. Ni decreases and Co increases outward, and Fe and S distributions across the cobaltite zone have fairly pronounced V-shaped profiles, both tending to be relatively enriched toward the inner and outer margins.

Although pararammelsbergite appears to have formed by inversion of rammelsbergite, the Co released in this process has migrated away from pararammelsbergite and must have been redistributed within the remaining rammelsbergite and, probably, within the cobaltite. Also, the V-shaped Fe and S profiles across the cobaltite zone, idiomorphic cobaltite grains cutting across the grain boundaries of rammelsbergite and of safflorite, and cobaltite islands enclosed in rammelsbergite and safflorite are inconsistent with sequential, primary deposition from the ore-forming fluid. Thus, whilst the gross chemical zoning may be primary, other features in these rosettes seem to be the result of later chemical readjustments through solid state diffusion.

INTRODUCTION

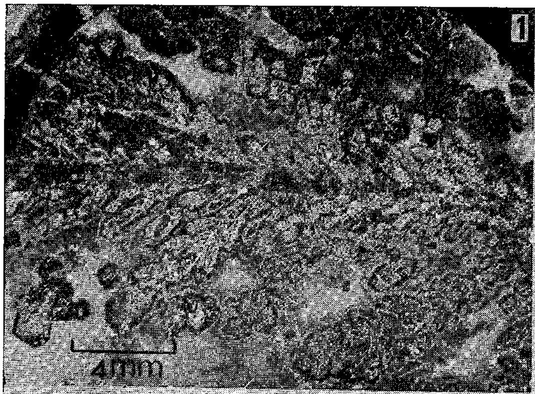
The mineralogy of the Ni-Co-Fe arsenide and sulpharsenide assemblages associated with the silver-bearing veins in the Cobalt-Gowganda region of Ontario has been described by Petruk (1971a) and Petruk *et al.* (1971). In the present work we have investigated in detail the textural and compositional variations in a Ni-Co-As assemblage from the Cobalt area, hoping to clarify the mode of formation and chemical history of its constituent phases. The material studied was obtained from Ward's Natural Science Establishment, Rochester, New York, and was used originally as the source of pararammelsbergite for the crystal structure investigation of Fleet (1972). A preliminary discussion of the texture of the assemblage and of the chemistry of the pararammelsbergite was included in his paper.

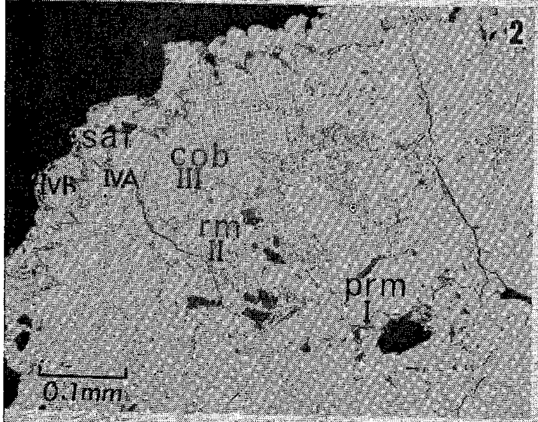
ORE MINERALOGY

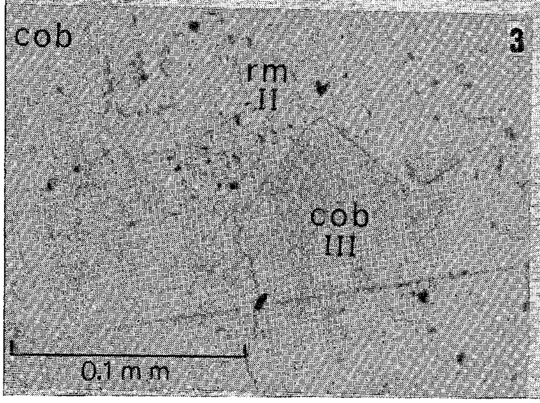
The ore mineral assemblage in the specimen consists of pararammelsbergite, rammelsbergite, cobaltite, safflorite and skutterudite in a cherty matrix. Petruk (1971a) classified the arsenide assemblages of the Cobalt-Gowganda area into five gradational classes: (1) Ni-As, (2) Ni-Co-As, (3) Co-As, (4) Co-Fe-As, and (5) Fe-As. Although the assemblage under study does not fit strictly into any of the above classes, it most nearly corresponds to the Ni-Co-As assemblage of Petruk, which is transitional between the Ni-As and Co-As assemblages: the Ni-As assemblage is characterized by nickeline as the main Ni-arsenide and the presence of rammelsbergite, and the Co-As assemblages by pararammelsbergite as the main Ni-arsenide rather than nickeline. The phases notably absent in the present assemblage are nickeline, breithauptite, "Ag-Sb minerals", gersdorffite and sulphides.

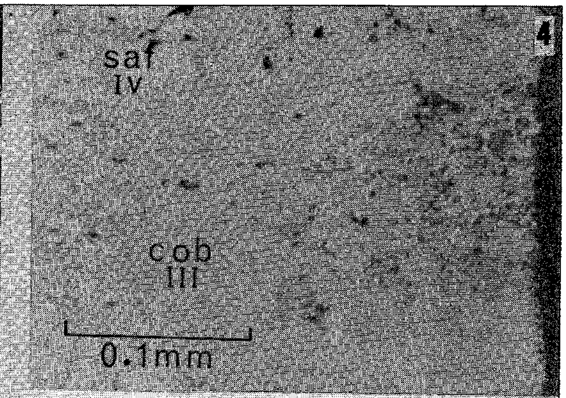
Dendrites and zoned rosettes

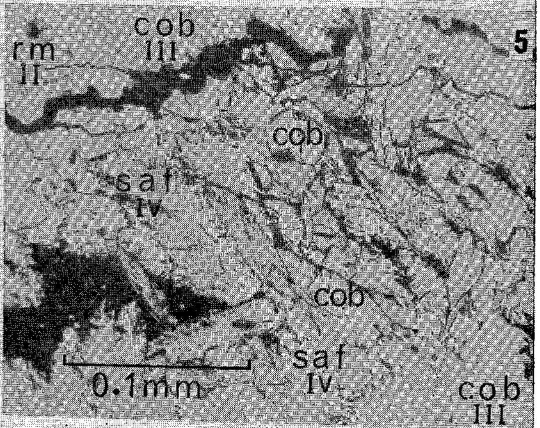
The most striking textural features of the specimen are the over-all dendritic, almost fern-like, habit of the arsenide assemblage (Fig. 1), and the consistent zonal arrangement of the arsenide minerals in individual rosettes. A typical dendrite is about 5 cm long and 5 mm across, the main and subsidiary branches of which are characterized by narrow (less than 1 mm across) axial zones of bladed pararammelsbergite (and











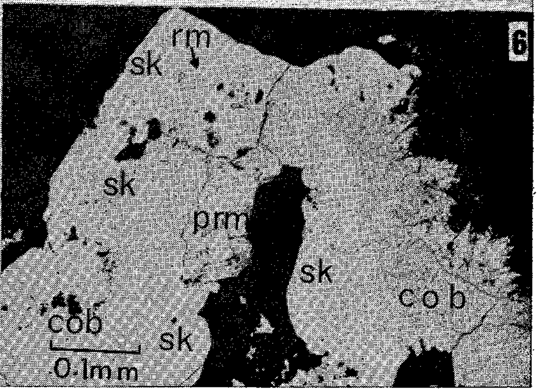


FIG. 1. A portion of the specimen showing a typical dendrite, with axial pararammelsbergite (black) and plumose rosettes, occurring in a cherty matrix.

FIG. 2. Photomicrograph of a portion of a typical zoned rosette showing roughly concentric zones of pararammelsbergite (white, interlocking prismatic crystals in the core, prm), rammelsbergite (greyish white, rm), cobaltite (light grey, cob) and safflorite (greyish white, conical prismatic crystals at the rim, saf). The safflorite zone consists of two subzones (IVA and IVB); the sharp boundary between them is marked with minute inclusions of gangue.

FIG. 3. Photomicrograph showing nature of the boundary between rammelsbergite (light grey) and cobaltite (medium grey) zones. The idiomorphic grain boundaries of relatively large cobaltite crystals cut across many smaller grains of recrystallized, polygonal rammelsbergite.

FIG. 4. Photomicrograph showing a typical gradational boundary between the cobaltite (medium grey) and safflorite (greyish white) zones.

FIG. 5. Photomicrograph showing the junction between outward growing safflorite (light grey) zones of two rosettes. Many of the islands of euhedral cobaltite (medium grey) in the safflorite zones cut across the grain boundaries of prismatic safflorite.

FIG. 6. Photomicrograph showing idiomorphic skutterudite (light grey, sk) transecting zone boundaries in a rosette, and containing islands of pararammelsbergite (white, prm), rammelsbergite (greyish white, rm) and cobaltite (medium grey, cob). Note the discontinuity of the safflorite zone (greyish white, conical prismatic crystals, saf) as a result of the growth of the skutterudite.

chert) and longitudinal and lateral envelopes of plumose rosettes (Fig. 1).

The rosettes, which apparently are lateral sections of dendrite branches, range from less than 1 mm to about 3 mm in diameter, and are characterized by arsenide minerals arranged in well-defined, roughly concentric zones. The sequence of phase zoning outward from the core in a typical rosette (Fig. 2) is: pararammelsbergite (zone I), rammelsbergite (zone II), cobaltite (zone III), and safflorite (zone IV). This zonal pattern is consistent in all the rosettes associated with dendrites. The same zonal pattern may be observed in isolated rosettes embedded in the cherty matrix, but many of them lack either the pararammelsbergite zone or the pararammelsbergite and rammelsbergite zones. The rosettes have preferred orientation within a dendrite, so that their appearance varies with the orientation of a section. No case of oscillatory or reverse zoning was observed among the hundreds of rosettes studied in polished sections of different orientation. An outer cobaltite zone following the safflorite zone, as reported by Petruk (1971a, Fig. 57) was not found in the present assemblage.

Pararammelsbergite

Two textural varieties of pararammelsbergite can be recognized in the specimen: (1) axial blades, some of which are up to 2 cm long, that mark the axial zones of the main and subsidiary branches of dendrites, and (2) interlocking aggregates of prismatic crystals, with minor amounts of interstitial rammelsbergite, in cores of rosettes (Fig. 2) which represent the terminal and lateral limbs of the axial blades. Three compositionally distinct textural varieties of pararammelsbergite were recognized by Fleet (1972) in a crushed concentrate of the present assemblage. The first two of these correspond to the axial blades and interlocking aggregates described above; the third variety was possibly rammelsbergite. Isolated prismatic crystals of pararammelsbergite occur in the rammelsbergite zone, but never beyond this zone.

Rammelsbergite

The pararammelsbergite zone is invariably followed by a rammelsbergite zone, the width of which tends to be inversely proportional to the width of the central pararammelsbergite zone. The boundary between the two zones is gradational. The rammelsbergite interstitial and adjacent to pararammelsbergite has a distinctive turbid appearance whereas further away it is clear and granular (Fig. 2). However, there is no consistent compositional difference between the two types, and the turbid appearance appears to be due to a contrast in polishing characteristics of the two minerals, or to minute inclusions of gangue phases in rammelsbergite, or to a combination of both.

Cobaltite

Cobaltite is easily identified in the present assemblage because of its high relief and its pinkish tinge, under reflected light, against the white of the other arsenide minerals. The wavy nature of the boundary between rammelsbergite and cobaltite zones (see Fig. 2) is due to idiomorphic outlines of relatively large cobaltite crystals that terminate against several smaller grains of rammelsbergite (Fig. 3). On careful examination one can discern suggestions of outlines of relict rammelsbergite grains within the cobaltite areas, and, along cobaltite-rammelsbergite grain boundaries, these relict outlines appear to pass into the grain boundaries of the rammelsbergite. The boundary between the cobaltite and safflorite zones may be sharp locally, but typically it is gradational, with the contact zone marked by innumerable islands of cobaltite, often with idiomorphic outlines, in safflorite and a few tiny islands of safflorite in cobaltite (Fig. 4). The resulting texture resembles the pseudo-eutectic texture of Lindgren (1930). Pods of polygonal rammelsbergite in the cobaltite zone and islands of cobaltite in the rammlesbergite zone are common, and in all such cases cobaltite shows its characteristic idiomorphic outline against rammelsbergite. Islands of cobaltite are also common in the safflorite zone and many of them are euhedral grains cutting across the boundaries of safflorite prisms (Fig. 5). They also occur in the pararammelsbergite zone at the core of rosettes, but invariably enclosed in patches of rammelsbergite that are interstitial to the pararammelsbergite.

Safflorite

Safflorite in the present assemblage shows its typical habit of interfingering, conical, prismatic crystals, with their apices pointing away from the core of the rosette. The texture is highly suggestive of outward growth of the safflorite crystals in an open-space environment, and is documented best where two adjacent rosettes coalesce through the outward growth of their respective safflorite zones (Fig. 5). The safflorite zone consists of two subzones (IVA and IVB) which often can be recognized under reflected light by slight differences in colour and reflectivity. The boundary between the two subzones is usually well-defined, marked by inclusions of gangue (Fig. 2), and is easily correlated with the marked compositional discontinuity across a typical safflorite zone (discussed later).

Skutterudite

Skutterudite is not a constituent of the zonal pattern of the arsenide assemblage. It occurs either as clusters of small euhedral crystals at cores of rosettes, embedded in the cherty gangue, or as isolated, stout euhedral to subhedral crystals in the rosette, without any preference for a particular zone and often transecting one or more of the zone boundaries. The former type is free of inclusions whereas the latter type usually contains corroded islands of pararammelsbergite, rammelsbergite and cobaltite (Fig. 6) which may be interpreted as relicts of the phases the skutterudite has replaced. Islands of safflorite have not been observed in skutterudite, but skutterudite often grows into and beyond the safflorite zone, abruptly terminating the safflorite layer on either side (Fig. 6) — a texture suggestive of later development of the skutterudite.

COMPOSITION OF PHASES

All the compositional data on the arsenide phases of the assemblage were obtained with a three-channel MAC-400 electron microprobe analyzer under the following operating conditions: 20 kv, 0.12μamp on willemite, counting time 20 to 60 secs, and spot diameter of about 1μm. All the phases were analyzed for Ni, Fe, Co, Sb, As, S. The count data were obtained for $K\alpha$ lines ($L\alpha$ line for Sb) using LiF (for Fe, Ni, Co, As) and PET (for S, Sb) analyzing crystals. The standards used were: synthetic maucherite, $Ni_{11}As_8$ (Fleet 1973) for Ni and As, synthetic $Fe_{49.87}S_{50.13}$ (Misra & Fleet 1973) for Fe and S, and pure metals for Co and Sb. The data were reduced using program EMPADR-VII (Rucklidge & Gasparrini 1969). Some typical compositions of the phases are given in Table 1.

TABLE 1. TYPICAL CHEMICAL COMPOSITIONS OF PARARAMMELSBERGITE, RAMMELSBERGITE, COBALTITE, AND SAFFLORITE (ELECTRON MICROPROBE SPOT ANALYSES)

	weight %							atomic %					
	Fe	Ni	Co	S	As	Sb	Total	Fe	Ni	Co	S	As	Sb
Pararammelsbergite *axial blades*	0.1	26.9	1.2	1.8	70.6	0.3	100.9	0.1	30.9	1.4	3.8	63.6	0.2
	0.1	27.0	1.2	2.1	70.6	0.3	101.3	0.1	30.8	1.4	4.4	63.1	0.2
	0.3	27.0	0.5	1.9	69.6	0.2	99.5	0.3	31.4	0.7	4.1	63.4	0.1
acre aggregate	0.2	26.0	2.5	2.4	68.5	0.4	100.05	0.2	29.9	2.9	5.1	61.7	0.2
	0.2	26.6	2.4	2.6	67.3	0.5	99.6	0.2	30.6	2.8	5.5	60.6	0.3
	0.2	26.2	2.4	1.7	68.9	0.3	99.4	0.2	30.5	2.7	3.6	62.8	0.2
	0.2	26.5	2.3	2.2	69.0	0.4	100.6	0.2	30.4	2.6	4.6	62.0	0.2
	0.2	26.7	2.1	2.3	68.2	0.4	99.9	0.2	30.8	2.4	4.9	61.5	0.2
Rammelsbergite	0.8	19.1	9.7	0.7	68.9	0.3	99.5	1.0	22.5	11.3	1.5	68.5	0.2
	0.9	18.5	8.7	0.6	69.9	0.3	98.9	1.1	22.0	10.3	1.3	65.1	0.2
	0.8	18.8	8.6	0.9	69.6	0.2	98.9	1.0	22.3	10.1	2.0	64.5	0.1
	0.8	19.0	8.6	1.2	70.4	0.3	100.3	1.0	22.1	10.0	2.5	64.2	0.2
	0.9	19.5	8.6	1.5	69.7	0.2	100.4	1.1	22.5	9.9	3.2	63.2	0.1
	0.9	19.4	8.1	0.8	70.4	0.2	99.8	1.1	22.8	9.5	1.7	64.8	0.1
Cobaltite	2.0	5.9	25.6	18.1	46.9	0.0	98.5	2.1	5.7	24.7	32.0	35.5	0.0
	2.4	9.9	23.0	17.3	48.5	0.0	101.1	2.4	9.4	21.8	30.2	36.2	0.0
	4.0	11.4	20.2	18.0	46.1	0.0	99.7	4.0	10.9	19.2	31.4	34.5	0.0
	2.9	11.8	19.8	16.3	48.9	0.0	99.7	3.0	11.5	19.1	29.1	37.3	0.0
	3.2	14.2	16.5	17.5	48.3	0.0	99.7	3.2	13.7	15.9	30.8	36.4	0.0
	3.2	18.3	13.4	16.1	49.9	0.0_4	100.9	3.3	17.6	12.9	28.5	37.7	0.0_2
Safflorite *inner subzone*	5.1	3.2	20.1	2.8	67.5	0.3	99.0	6.2	3.7	23.1	5.8	61.0	0.2
	6.1	4.3	18.0	1.8	67.4	0.4	98.0	7.5	5.1	21.1	3.8	62.3	0.2
	6.0	5.4	18.0	2.8	68.2	0.4	100.8	7.1	6.1	20.3	5.8	60.5	0.2
	6.2	5.4	16.6	3.0	66.9	0.1	98.2	7.5	6.2	19.1	6.4	60.7	0.1
outer subzone	7.3	8.7	12.1	0.2	71.3	0.2	99.8	9.1	10.3	14.2	0.3	66.0	0.1
	6.6	9.3	11.7	0.2	70.8	0.2	98.8	8.3	11.1	13.9	0.4	66.2	0.1
	7.9	8.0	11.2	0.2	71.6	0.2	99.1	9.9	9.6	13.3	0.4	66.7	0.1
	9.0	7.9	11.0	0.2	71.4	0.1	99.6	11.2	9.4	12.9	0.5	66.0	0.0_4

Compositional data obtained through spot analyses of pararammelsbergite, rammelsbergite, cobaltite and safflorite across randomly-chosen rosettes, recomputed on the basis of assumed stoichiometric M:X ratio of 1:2 (M = Fe+Co+Ni; X = S+As+Sb) are presented in an atomic per cent Fe-Ni-Co triangular plot (Fig. 7). The plot shows a restricted compositional field for rammelsbergite, but a wide variation in the Ni:Co ratios for cobaltite, the compositions with high Ni:Co ratio being characteristic of the cobaltite zone near its contact with rammelsbergite and those with low Ni:Co ratios, in general, being characteristic of the cobaltite zone near its contact with the safflorite zone. Pararammelsbergite occurring as axial blades has a slightly higher Ni:Co ratio than that occurring as interlocking prismatic crystals in cores of rosettes (Table 1), though each of these two groups is fairly homogeneous in composition. For simplicity of representation no distinction between the two has been made in this plot. The safflorite compositions fall into two distinct groups, corresponding to the two optically distinguishable subzones discussed earlier — the Co-rich group corresponding to the inner subzone (IVA) adjacent to the cobaltite zone, and the relatively Co-impoverished group to the outer subzone (IVB). Although both of the safflorite subzones show a significant spread in metal ratios, the compositional variation between them seems to be abrupt rather than one of continuous gradation (also see Fig. 8). The over-all trends of the chemical gradients across the rosettes consist of a continuous decrease in the Ni:Co ratio (with a concomitant, although much smaller, increase in the Fe:(Ni+Co) ratio) outward from the pararammelsbergite core, an increase in the Co:(Ni+Fe) ratio inward from the inner safflorite subzone (IVA), and a convergence of the two gradients in the cobaltite zone.

A plot of the compositional data obtained through analysis of spots at measured intervals across a typical zoned rosette (about 1.1 mm in diameter) illustrates the nature of the compositional variation in each of the mineral zones (Fig. 8). The following points about the distribution may be noted:

(i) Relative to cobaltite and safflorite, rammelsbergite and pararammelsbergite are fairly homogeneous in composition. The

Fe solid solution is uniformly low in both, but there is a preferential concentration of S in pararammelsbergite and of Co in rammelsbergite (also see Table 1).

(ii) As discussed earlier, the safflorite zone consists of two compositionally distinct

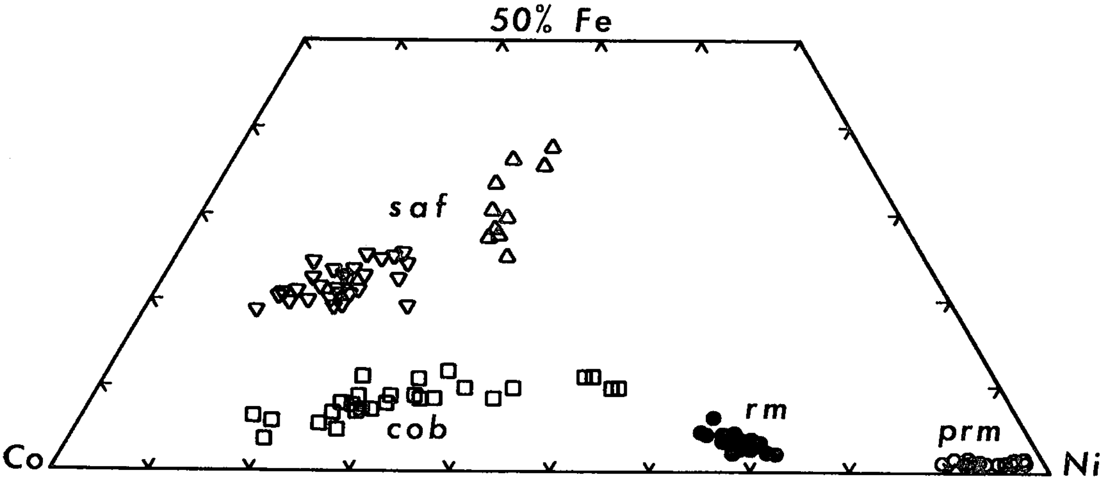


FIG. 7. Composition of pararammelsbergite (open circles, 39 data points, prm), rammelsbergite (solid circles, 27 points, rm), cobaltite (open squares, 27 points, cob), and safflorite (inverted triangles inner subzone, 39 points; upright triangles, outer subzone, 10 points; saf) in the arsenide assemblage under study.

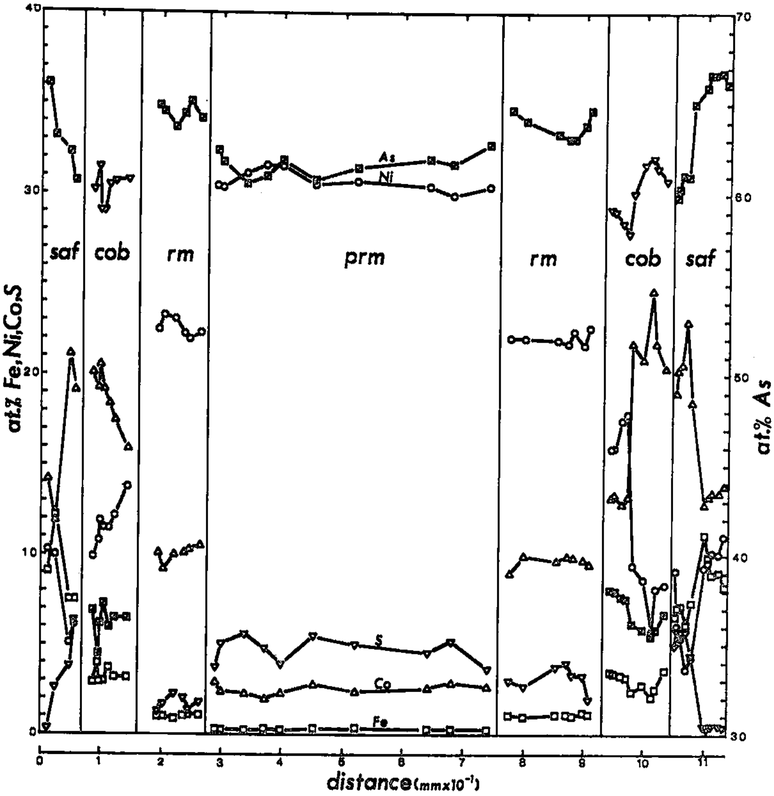


FIG. 8. Compositional variations across a typical zoned rosette about 1.1 mm in diameter. Open squares — Fe; open triangles — Co; open inverted triangles — S; open circles — Ni; and squares with a bar — As.

subzones, a low Co- low S outer subzone and a high Co- high S inner subzone, separated by a sharp compositional discontinuity.

(iii) Element distribution patterns across the cobaltite zone are marked by a significant discontinuity in the middle portion of the zone. Judging from continuous microprobe scans across several rosettes, the type of distribution seems to be a consistent and characteristic feature of the cobaltite zone.

(iv) The over-all gradients of Ni and Co distributions across the rosette are similar to those in Figure 7 compiled for many randomly chosen rosettes. The convergence of the gradients in the cobaltite zone is marked by cobaltite compositions with the lowest S contents.

DISCUSSION

The phase and compositional zoning in similar arsenide assemblages from the Cobalt-Gowganda area have been interpreted to represent sequential crystallization of the phases, outward from the cores, in an open-space environment, reflecting the progressive change in the composition of the precipitating solutions (Petruk 1971a, 1971b). Pararammelsbergite has been interpreted to have been formed variously: as a late mineral in the Ni-As assemblage, cutting across other arsenide phases and formed through inversion of earlier rammelsbergite; as intergrowths, formed contemporaneously with the other arsenide phases in the Ni-Co-As assemblage, at temperatures below that of rammelsbergite-pararammelsbergite inversion.

A number of textural and compositional features of the zoned arsenide assemblage under study do not fit a model of sequential precipitation of the phases. These are:

(i) the idiomorphic outlines of cobaltite cutting across grain boundaries of rammelsbergite (and of safflorite), suggesting a later development of cobaltite in the paragenetic sequence;

(ii) outlines of relict rammelsbergite within the cobaltite;

(iii) the presence of cobaltite islands in all the other three zones;

(iv) the compositional variations in the cobaltite zone; and

(v) the relatively homogeneous composition of the rammelsbergite.

In the absence of data on the synthetic Fe-Ni-Co-As-S system and on the chemistry and nature of the precipitating solution, one cannot work out a paragenetic sequence based on stability of coexisting phases. Based on textural features and compositional variations within and between the phases, we suggest the following interpretation.

It is hypothesized that the initial precipitation was in the form of a high temperature (below 800°C, as the experimental data of Roseboom (1963) would suggest) Ni, Co and As-rich metal diarsenide-disulphide solid solution. This precipitate was chemically zoned, with a relatively Ni-rich core [Ni(Co,Fe)(As,S)$_2$] — high-temperature rammelsbergite solid solution — grading into a relatively Co-rich margin [Co(Ni,Fe)(As,S)$_2$] — high temperature safflorite solid solution. The well-defined inclusion-dotted boundary between the two safflorite subzones and the corresponding sharp compositional discontinuity suggest that the outer subzone (IVB) represents a later, separate phase of precipitation. Reequilibration of the solid solution at lower temperatures led to recrystallization and redistribution of the elements, resulting in segregation of the phases in roughly concentric zones. In the Ni-rich core, pararammelsbergite developed by inversion of the high-temperature rammelsbergite solid solution, and the Co-rich rim recrystallized to low-temperature safflorite (subzone IVA). The formation of cobaltite was a "sink" for the excess Co, Fe, and S that could not be accommodated in the recrystallized pararammelsbergite, rammelsbergite and safflorite. The elements migrated within the assemblage by solid state diffusion. The relative homogeneity of the rammelsbergite suggests that this was an effective process within the time-scale of the recrystallization process; for example, there can be little doubt that the pararammelsbergite developed by recrystallization of a high-temperature rammelsbergite solid solution, yet there are no concentration gradients within the rammelsbergite, toward the grain with pararammelsbergite. It is expected that the element redistribution took place in the virtual absence of a fluid phase within the mass of metal diarsenide-disulphide solid solution, so that marked discontinuities in the assemblage, for example, the gangue-filled boundary between the IVA and IVB safflorite subzones, or the cherty gangue between the rosettes, would form effective barriers to such redistribution. The cobaltite developed preferentially between the rammelsbergite and safflorite zones because of the diffusion of excess S and Co from these zones and its probable early nucleation along the margins of the Ni-rich areas which were inverting to pararammelsbergite.

With regard to the stability of the proposed high-temperature solid solution, extensive solid solution between the Fe-Ni-Co diarsenides is known from experimental studies (Roseboom 1963; Radcliffe 1966). The S-solubility of the $FeAs_2$-$NiAs_2$-$CoAs_2$ solid solution has not been determined experimentally, but it may be estimated approximately from the available data on the condensed Fe-As-S and Ni-As-S systems. At 700°C the S-solubility of rammelsbergite is only about 1.1 wt. % (about 2.2 at. %) (Yund 1962) and that of loellingite about 3.4 wt. % (about 7.0 at. %) (Clark 1960). However, the S contents of the pararammelsbergite and rammelsbergite are of the order of 4-5 at. % (2-3 wt. %) and 1-3 at. % (less than 1 to 2 wt. %), respectively, and the data for these two phases reported by Petruk *et al.* (1971) also show in many cases S contents higher than the 1 wt. % limit suggested by Yund (1962) for natural pararammelsbergite and rammelsbergite. The higher S contents may well be due to appreciable solid solution of Co in the natural phases. Further, it seems likely that the S solubility in diarsenides may increase in the sequence $NiAs_2 < CoAs_2 < FeAs_2$, and this may be related to the order of increase of the metal-sulphur bond strength in the disulphides $NiS_2 < CoS_2 < FeS_2$ (Nickel *et al.* 1969). Thus, it is very probable that the primary, high-temperature, diarsenide precipitate would have contained enough S (of the order of 3 wt. % S) in solid solution to account for the small volume (about 10-15%) of cobaltite in the present assemblage.

Although the rammelsbergite-pararammelsbergite inversion occurs at 590° ± 10°C for pure $NiAs_2$, the substitution of approximately 1 wt. % S for As lowers the inversion temperature to 475° ± 25°C (Yund 1962) and, since both Co and Fe probably lower the inversion temperature also, the pararammelsbergite in the present assemblage must have formed at less than 500°C. However, according to the phase relations in the FeAsS-CoAsS-NiAsS system reported by Klemm (1965), most of the cobaltite compositions would not be stable at 500°C and, further, many of the cobaltite compositions reported by Petruk *et al.* (1971, Fig. 109) would not be stable even at 600°C. Thus, there is an apparent contradiction between the compositional data of natural cobaltite and the phase relations data of Klemm. A high-temperature origin for cobaltite does not seem consistent with the data from the present study discussed earlier. However, the stability of cobaltite solid solutions might be extended, to lower temperatures, by the substitution of As for S (see Table 1 for some typical cobaltite compositions in the present assemblage), and the Ni-rich and Co-rich subzones we have reported in the cobaltite zone (see Fig. 8) may be a reflection on the supposed instability of intermediate compositions at the temperature of formation of the cobaltite.

Finally, although pararammelsbergite appears to be replacing rammelsbergite in the present assemblage, the two phases may coexist over a range of temperature, since neither is strictly stoichiometric and rammelsbergite, in particular, has about 19 at. % Co.

REFERENCES

CLARK, L. A. (1960): The Fe-As-S system: phase relations and applications. *Econ. Geol.* 55, 1345-1381 and 1631-1652.

FLEET, M. E. (1972): The crystal structure of pararammelsbergite ($NiAs_2$). *Amer. Mineral.* 57, 1-9.

——— (1973): The crystal structure of maucherite ($Ni_{11}As_8$). *Amer. Mineral.* 58, 203-210.

KLEMM, D. D. (1965): Synthesen und Analysen in den Dreieckdiagrammen FeAsS-CoAsS-NiAsS und FeS_2-CoS_2-NiS_2. *Neues Jahrb. Mineral. Abh.* 103, 205-255.

LINDGREN, W. A. (1930): Pseudo-eutectic textures. *Econ. Geol.* 25, 1-13.

MISRA, K. C. & FLEET, M. E. (1973): The chemical compositions of synthetic and natural pentlandite assemblages. *Econ. Geol.* 68, 518-539.

NICKEL, E. H., WEBSTER, A. H. & RIPLEY, L. G. (1969): Bond strengths in the disulphides of iron, cobalt and nickel. *Can. Mineral.* 10, 773-780.

PETRUK, W. (1971a): Mineralogical characteristics of the deposits and textures of the ore minerals. *Can. Mineral.* 11, 108-139.

——— (1971b): Depositional history of the ore minerals. *Can. Mineral.* 11, 396-401.

———, HARRIS, D. C. & STEWART, J. M. (1971): Characteristics of the arsenides, sulpharsenides, and antimonides. *Can. Mineral.* 11, 150-186.

RADCLIFFE, D. (1966): *Mineralogical studies on Safflorite-Loellingite.* Ph.D. thesis, Queen's Univ., Kingston, Ontario, Canada.

ROSEBOOM, E. H. (1963): Co-Fe-Ni diarsenides: compositions and cell dimensions. *Amer. Mineral.* 48, 271-299.

RUCKLIDGE, J. C. & GASPARRINI, E. L. (1969): Specifications of a computer program for processing electron microprobe analytical data, EMPADR VII. *Dept. Geol. Univ. Toronto.*

YUND, R. A. (1962): The system Ni-As-S: phase relations and mineralogical significance. *Amer. J. Sci.* 260, 761-782.

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