

## SOME OBSERVATIONS ON MINERALS IN THE SYSTEM $\text{CoAsS-FeAsS}$

By

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**Abstract.** An X-ray and optical investigation of the minerals cobaltite ( $\text{CoAsS}$ ), glaucodot ( $((\text{Co,Fe})\text{AsS})$ ), and arsenopyrite ( $\text{FeAsS}$ ) from the Modum district, Norway, has disclosed that naturally occurring cobaltites have either ordered or disordered crystal structures. The presence of ordered cobaltite may be a useful indicator of metamorphism in ore deposits. It is predicted that a similarly disordered structure is possible in arsenopyrite. By means of an X-ray method for the determination of cobalt content of arsenopyrite, it is shown that when cobalt is present in excess of 9%, glaucodot may appear as a separate mineral phase. High cobaltian glaucodot could be considered a polymorphic form of cobaltite. The varietal names 'danaite' and 'allocasite' are thought to be unnecessary and should be replaced by 'cobaltian arsenopyrite' and 'high-cobaltian glaucodot', respectively.

### Introduction

The cobalt deposits of Modum, Norway, worked between 1772 and 1898, have recently been investigated by the author (GAMMON 1964). The Skuterud group of mines in this area is of mineralogical interest as the type locality for the mineral skutterudite ( $\text{CoAs}_3$ ). The deposits were worked mainly for cobaltite ( $\text{CoAsS}$ ) and the arsenopyrite ( $\text{FeAsS}$ ) which contained a recoverable content of cobalt. The presence of these two minerals and of species intermediate in composition makes the Modum deposits useful for studying the interrelationships within this group of sulfarsenide minerals.

The mineralization is of very low grade; the ore minerals are disseminated in metasedimentary rocks and amphibolites of Precambrian age. Metamorphism of amphibolite facies conditions has affected the area, and the rocks have been isoclinally folded and plastically deformed by more than one tectonic event.

Table 1. Powder diffraction data for cobaltite from Modum, Norway, and Cobalt, Ontario

Cobalt Material (PEACOCK and HENRY 1948)			Modum Material (This study)		
I	d(meas)	h k l	I	d(meas)	h k l
			m	5.575	100
			wm	3.91	110
$\frac{1}{2}$	3.27	111	wm	3.19	111
6	2.82	002	s	2.875	002
			w	2.815	
			vvs	2.497	
10	2.53	012	w	2.470	012
			vs	2.275	
8	2.29	112	w	2.263	112
2	1.984	022	m	1.960	022
			wm	1.853	300,221
			vww	1.757	310
9	1.687	113	vs	1.671	113
$\frac{1}{2}$	1.616	222	wm	1.603	222
3	1.556	023	m	1.54	023
4	1.493	123	ms	1.483	123
$\frac{1}{2}$	1.400	004	w	1.386	004
			w	1.3599	410,322
			vww	1.3271	114,330
			vww	1.276	133
$\frac{1}{2}$	1.250	024	wm	1.244	024
1	1.220	124	m	1.218	124
$\frac{1}{2}$	1.196	332	wm	1.190	332
			wm	1.139	
$\frac{1}{2}$	1.146	224	vw	1.138	224
			vww	1.121	005,034
			vw	1.094	015,134
4	1.078	511,333	ms	1.0775	511,333
2	1.040	025,234	m	1.0365	025,234
1	1.022	125	m	1.022	125
3	0.989	044	ms	0.987	044
			vvw	0.9715	522,441
			vvw	0.9550	530,433
			vvw	0.9415	531
			m	0.9315	
$\frac{1}{2}$	0.933	006,244	wm	0.9298	006,244
$\frac{1}{2}$	0.920	061	wm	0.9175	061
			m	0.906	
2	0.908	116,235	wm	0.903	116,235
$\frac{1}{2}$	0.853	335			
1	0.833	063,245			
1	0.825	136			

### Cobaltite

The cobaltite occurs as well-developed euhedral crystals showing cubic morphology, combinations of the cube (100) and pyritohedron (210) being particularly common. However, in polished section, the mineral is strongly anisotropic and twinned. These observations are inconsistent and suggest that either the cobaltite is of a lower symmetry pseudomorphing a cubic habit or else that the observed anisotropism is spurious. Some powder was drilled from a large pyritohedral crystal of anisotropic and twinned cobaltite and was used to prepare a powder photograph with Fe-filtered CoK  $\alpha$  radiation. Following the standard procedure for indexing a cubic substance, it was found possible to assign (hkl) values to all the lines on the film (Table 1). The unit cell parameter ( $a_0$ ) of  $5.575 \pm 0.005$  compares well with previously reported values, but the d-spacing values of the Modum cobaltite differ significantly from the material from Cobalt, Ontario (PEACOCK and HENRY 1948), suggesting that these two types have different structures. These results were confirmed by the use of the diffractometer technique using Cu K $\alpha$  radiation.

Peacock and Henry compared the observed intensity of their lines with uniformly reduced calculated intensities for space groups Pa3 and P $2_1$ 3, concluding that their data indicated the space-group Pa3. However, the Modum cobaltite cannot be assigned to this space-group because good reflections were obtained for (100), (110), (310), (114), and (033), forbidden by space-group Pa3. In addition, the presence of the (100) reflection excludes the possibility of space-group P $2_1$ 3.

The optical properties of the Modum cobaltite were measured using the methods described by CAMERON (1961). The color is silvery-white with slight tints of pink, brown, or violet. In contact with arsenopyrite, it is noticeably pinker, but against pyrite it is a very bright white. Under oil immersion, the pinkish tint against arsenopyrite is accentuated, and the mineral shows slight reflection pleochroism from white to pinkish white.

Quantitative determinations of the apparent uniaxial reflectivities of randomly oriented grains of cobaltite were made in monochromatic light of wavelength  $549 \text{ m}\mu$  (CAMERON 1963). The values obtained for  $R_1$  and  $R_2$  are shown in Table 2.

The data demonstrate that neither  $R_1$  nor  $R_2$  has a constant value,

Table 2. *Apparent uniradial reflectivities of Modum cobaltite* (measured at  $\lambda = 559 \text{ m}\mu$ )

$R_1$ (%) . . . .	48.5	51.6	49.2	52.4	48.6	50.1	51.3	49.6	48.7	52.1	50.8
$R_2$ (%) . . . .	52.8	54.5	53.2	54.3	52.9	53.5	53.3	53.9	52.9	54.1	53.4

indicating biaxial symmetry. All values of  $R_1$  are equal to or less than 52.4%, while all values of  $R_2$  are equal to or greater than 52.8%. The intermediate value of the reflectivity ( $R_m$ ) has been taken as approximately 52.6%. Similarly  $R_p$ , the minimum value, is equal to or less than 48.5%, and  $R_g$ , the maximum value, is equal to or greater than 54.5%. As  $R_m$  is closer in value to  $R_g$  than to  $R_p$ , the mineral is considered to be biaxial negative at  $\lambda = 549 \text{ m}\mu$ .

The mean uniradial reflectivity was measured in white light in air, using Elba pyrite ( $R = 54.5\%$ ) as a standard. The value obtained was 53.1% with a range from 52.5% to 53.6%. In oil immersion, the corresponding values were: mean, 44.5%; range, 44.1–45.3%. The spectral reflectivity was measured in air, on a face polished parallel to the (100) direction, using a contrast interference filter. The data (Table 3) were measured with a bandwidth of  $\pm 5 \text{ m}\mu$ ; the individual reflectivity values are the mean of four readings.

Table 3. *Spectral reflectivity of Modum cobaltite*

Wavelength ( $\text{m}\mu$ )	400	450	475	500	525	550	575	600	650	700	740
Reflectivity (%)	42.5	47.6	48.1	50.8	52.8	56.2	57.8	58.1	57.6	54.9	52.5

In observing the anisotropism, the position of the analyzer was found by using a Nakamura plate and an anisotropic section of ilmenite and checked by observing the polarization figure of galena. On rotation of the stage, pale blues and browns of varying intensity are observed in sections of different orientation of cobaltite. Four positions of even illumination are observed (the 'extinction' positions) alternating with four positions of maximum illumination (the '45°' positions). When the stage is rotated to place the mineral in a 45° position, the strongest brown or blue hues are observed; on rotation of the analyzer in a clockwise direction, the polarization color becomes slightly more intense before fading out completely; on rotating the analyzer in a counterclockwise direction, the mineral changes color (i.e. from blue to brown or vice versa) before fading out.

Polarization figures obtained from many grains of diverse orientation showed only a slight separation of the isogyres on rotation of the stage. Color fringes, due to dispersion, are distinct and indicate that DRr is violet  $>$  red. With the analyzer and polarizer exactly crossed, the dispersion of the apparent angle of rotation (DAr) was observed by rotating the mineral on the stage, the color fringes were very indistinct but appeared opposite in sense to DRr. This indicates that both DRr and DAr are  $v > r$  (CAMERON 1961 p. 119). A qualitative determination of the sign of the phase differences  $\Delta x, y$  using the gypsum plate (CAMERON 1961 p. 139) indicated that  $\Delta x, y$  is negative.

Values of the Vickers hardness, obtained with a G.K.N. hardness tester with a 100 gm load, range from 957 to 1,180 with a mean of 1,112, but the quality of the indentation was poor.

To confirm the presence of twins, single crystals of cobaltite were etched in dilute  $H_2SO_4$  solution following the electrolytic method described by SUZUKI (1962). The etched surfaces revealed irregularly shaped lamellae, and, by studying polished surfaces of such previously etched specimens, it was confirmed that these represent twinned individuals within the larger crystal.

#### DISCUSSION

The conclusion drawn from this study is that, despite the external crystal morphology, the Modum cobaltite is not now cubic. X-ray determinations have eliminated the only two likely cubic space-groups (Pa3 and P2<sub>1</sub>3), and the optical properties indicate that the mineral has either orthorhombic, monoclinic, or triclinic symmetry.

If this second form is inverted cobaltite, it may be useful to consider what structures are developed if one is dealing only with the ordering of arsenic and sulfur atoms. R. Phillips (personal communication) has determined four possible ways in which this ordering could take place if the original structure was of the pyrite type. Only one of these possibilities retains cubic symmetry, the structure proposed by MECHLING (1921) for the 'Cobaltite Group' and shown by TAKÉUCHI (1957) to be the structure possessed by ullmannite. This arrangement can be eliminated from further consideration of the Modum cobaltite as the diffraction data contains reflections forbidden by this space-group.

Calculations of expected d-spacings and intensities for these various arrangements by Phillips indicate that an orthorhombic ( $Pca2_1$ ) structure compares favorably with the observed X-ray pattern. ONORATO (1957) concluded from the use of Weissenberg techniques that there were five possible space-groups consistent with his results, these included  $Pca2_1$  and  $P2_1/c$ , of which he considered the latter to be the most likely. LE DAMANY (1962) has shown that on Weissenberg photographs of cobaltite reflections are limited by the following conditions:

$$h\ 0\ l - h\ \text{even}$$

$$0\ k\ l - l\ \text{even}$$

This observation led him to the consideration of only two possible space-groups:  $Pca2_1$  and  $Pbcm$ . The latter space-group does not permit a structure similar to that of pyrite, and hence he concluded that  $Pca2_1$  is the more likely space-group.

Very slight splitting of high angle reflections has been observed on some of the films and diffractometer traces during this present study. Similar splitting has been observed by Sæbø (personal communication) and WINTENBERGER (1962), who estimates the difference in cell parameters as being on the order of  $2 \times 10^{-3} \text{\AA}$ .

Thus, it is concluded that the Modum cobaltite is a complexly twinned intergrowth of orthorhombic individuals. Despite the ordering of the As and S atoms, the distortion of the lattice is slight and the cell parameters vary insignificantly from the cubic form. The Modum cobaltite probably originated, in its present form, from the inversion of a disordered (cubic) structure.

#### CANADIAN COBALTITE

The descriptions of the cobaltite from Cobalt, Ontario, are compatible with this material's having the disordered, cubic structure. Some crystals of cobaltite from the Columbus Mine, Cobalt, Ontario, were kindly made available by the Royal Ontario Museum, Toronto, for a comparison with the Modum material.

Polished specimens of these crystals have the same reflectivity (mean uniaxial reflectivity: 52.9%) and hardness ( $V_{100}$ : 1,090) as the Modum material. However, no reflection pleochroism was observed,

and under crossed nicols the mineral was evenly illuminated during a 360° rotation of the stage, the polarization figure being a black cross showing no separation of the isogyres on rotation of the stage. Diffractometer traces, using Cu K $\alpha$  radiation gave a pattern differing only in intensity values from that reported by PEACOCK and HENRY (1948). The (100), (110), (310), (114), and (033) reflections were absent. Electrolytic etching, under the same conditions as those employed in studying the Modum cobaltite, revealed a zonal structure very similar to that observed commonly in hydrothermal pyrite.

These observations strongly suggest that the Canadian cobaltite has a disordered structure, with a statistical distribution of As and S atoms in the lattice producing cubic symmetry with space-group Pa3.

#### HEATING EXPERIMENTS

If the structures of cobaltite from Cobalt and Modum are polymorphs, then it should prove feasible to convert the ordered to the disordered form by heating. Preliminary attempts at achieving this transformation were hampered by the strong oxidation of the cobaltite at temperatures above 450°C. Through the courtesy of Dr. Hayhurst, a sample of the Modum cobaltite was heated in a nitrogen atmosphere in the research laboratory of Messrs. Pickford, Holland, and Co. Ltd. One run was successful when the specimen had been heated slowly, over a period of 4 hours, to 900°C. After 25 minutes at this temperature, the specimen began to fume, so the sample was removed quickly and quenched in air. The sample showed slight signs of cracking and oxidation.

This particular sample was one-half of a single crystal of cobaltite from the Mineralogisk-Geologisk Museum, Oslo, labelled 'Kobaltglanz, Skutterudgruben'. The crystal measured 1 cm in width and showed equal development of (100) and (210) faces. Fragments of each half of the crystal, heated and unheated, were used for preparing smear mounts for the diffractometer; the remaining parts were mounted and polished.

The polished specimen of the unheated half showed the typical development of the anisotropism and lamellar twinning, while the heated half, within a 0.5 mm oxidized zone, was completely homogeneous and isotropic. The diffractometer trace of the unheated

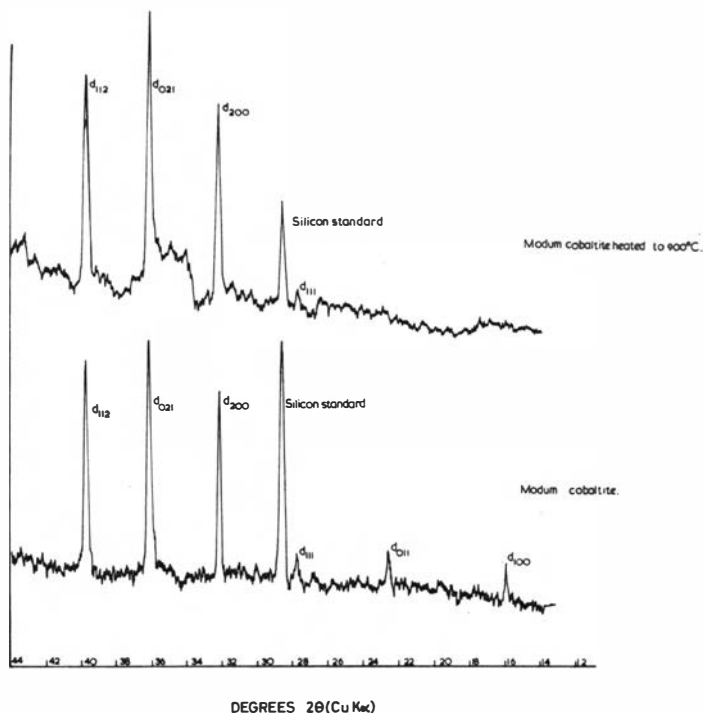


Fig. 1. Diffractometer traces of Modum cobaltite showing changes produced on disordering the structure by heating followed by rapid quenching.

portion of the crystal gave the normal pattern for Modum cobaltite. The heated portions have a pattern similar in all respects to that obtained from the Canadian cobaltite. Fig. 1 shows part of the diffractometer traces and illustrates this difference in the two patterns.

It is concluded that the previous deductions are valid, i.e. the Canadian and Modum cobaltites are polymorphic forms having a cubic (disordered) and orthorhombic (ordered) structure, respectively.

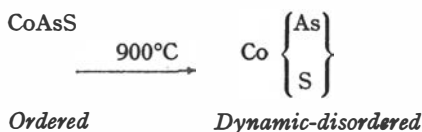
Since this work was completed, GIESE and KERR (1965) have published an interesting paper on the structure of cobaltite in which they confirm the existence of ordered and disordered forms of the structure and conclude, on the basis of Weissenberg techniques, that  $Pca2_1$  is the space-group of the ordered form. It is reassuring to find this confirmation of the present structural determination, which was based



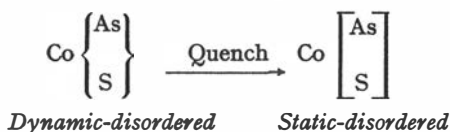
on powder diffraction data only. However, they found some evidence for partial ordering in natural cobaltite from Cobalt, Ontario, thereby differing in their findings from that reported in this paper and by PEACOCK and HENRY (1948).

#### THE CUBIC-ORTHORHOMBIC TRANSFORMATION OF COBALTITE

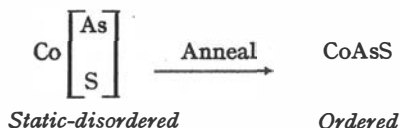
The heating experiment described above can be written thus:



If this disordered form is cooled rapidly, it will retain its structure:



Annealing at elevated temperatures below the critical point (i.e. as in metamorphism) can cause the following reaction:



The cubic-orthorhombic transformation of cobaltite is probably an example of substitutional transformation of disorder (BUERGER 1951). The transformation can be envisaged as a flow of As and S atoms among fixed Co atoms. From the point of view of symmetry, the random flow of the As and S atoms is equivalent to causing the two species to behave, statistically, as one. For this reason, the structure statistically assumes the symmetry that it would have if all the As and S atoms were of one species. It follows that this could be the equivalent structure to pure  $\text{CoS}_2$  (cattierite) which has the pyrite-type ( $\text{Pa}3$ ) structure. Thus the dynamic-disordered  $\text{Co} \left\{ \begin{array}{c} \text{As} \\ \text{S} \end{array} \right\}$  and static-disordered

Co  $\left[ \begin{smallmatrix} \text{As} \\ \text{S} \end{smallmatrix} \right]$  forms of cobaltite have statistically assumed the pyrite-type symmetry.

In the ordered structure, the As and S atoms alternate in a regular way. This reduced the free energy of the structure as it reduces repulsive interactions between identical neighboring atoms. The orthorhombic form of cobaltite has a symmetry which is related to the symmetry of the cubic form. In the high-low inversion, the general structure remains the same, but some of its symmetry operations become suppressed, in such a way that the orthorhombic form has more than one orientation with respect to the cubic form.

Under conditions of slow cooling, or annealing, and unless the crystal is very small, the high-low transformation should start with the spontaneous appearance of transformation nuclei in various parts of the crystal, particularly at the edge. The transformation would then proceed from these centers. The nuclei can have different orientations with respect to each other, depending on the difference in symmetry between the high and low forms. They grow until they make contact with one another, forming irregular twin boundaries. They are in specific twinned orientation with respect to each other and could be brought into coincidence by the operation of one of the symmetry operations of the cubic form which vanished in the transformation to the orthorhombic form. This is considered to be the fundamental cause of the twins frequently seen in the polished specimens of the Modum cobaltite.

It is suggested that cobaltites of hydrothermal origin, which show a zonal structure indicative of changing depositional conditions, possess a static-disordered ('open') form in which As and S atoms in the lattice become statistically equivalent leading to a structure with cubic (Pa3) symmetry. On the other hand, cobaltites from high-grade metamorphic terrains have been effectively annealed at less than the critical temperature (ca. 850°C), permitting the high-low substitutional transformation to the twinned orthorhombic (Pca2<sub>1</sub>) structure to take place.

Thus, the crystal structure and type of twinning in cobaltite can be used in elucidating the geological history of cobalt ore deposits. For example, the ordered crystal structure and transformation twinning of the ordered Modum cobaltite strongly suggest that the mineral

has been affected by prolonged heating at an elevated temperature, less than that at which the transformation to the disordered state would occur. This conclusion is supported by studies of the regional metamorphism which has affected the cobalt ore bodies at Modum and attained the upper amphibolite facies (GAMMON 1964).

### Glaucodot

Arsenopyrites containing 9 weight per cent cobalt, or more, have been placed in a separate mineral species variously referred to as 'kobalt-haltigen arsenikkies' (BREITHAUPT 1823) and glaucodot (DANA 1854). The latter name is in more common usage.

The crystal structure of glaucodot from Håkansboda, Sweden, investigated by FERGUSON (1947) using rotating crystal and Weissenberg methods, showed no significant departure from orthorhombic symmetry. The powder pattern could not be indexed using DE JONG'S (1926) cell dimensions for arsenopyrite, and Ferguson suggested, therefore, that glaucodot has a super-lattice, in which the side *b* is three times that of the rectangular cell of arsenopyrite in the classical orthorhombic setting used by de Jong. 'High cobaltian glaucodot', containing 25 per cent cobalt, has been described by SHISHKIN (1962). This material occurs in association with 'ordinary' glaucodot from disseminated ore lenses, in eruptive rocks of Cambrian age, from Russia.

Fringes of another mineral phase, probably glaucodot on the basis of its optical characteristics, are found surrounding some of the Modum cobaltite crystals (Pl. 1, fig. 1). Where these fringes are better developed, they give a spurious appearance of veining of the cobaltite by a later mineral (Pl. 1, fig. 2). A very similar occurrence from South Dashkesan in Russia (BORISHANSKAYA *et al.* 1965) indicated a very high cobalt : iron ratio and the authors concluded that the mineral was alloclasite, a cobalt-rich variety of glaucodot.

An apparently exsolved phase is present in some of the cobaltian arsenopyrite from the Modum Mines. This phase could not be separated for X-ray analysis, but was suspected to be cobalt-rich, possibly glaucodot, exsolved from arsenopyrite containing too much cobalt for the normal arsenopyrite structure to be stable.

An opportunity to test this hypothesis was presented when Miss P. J. Killingworth of the Microscan advisory service, of the Cambridge

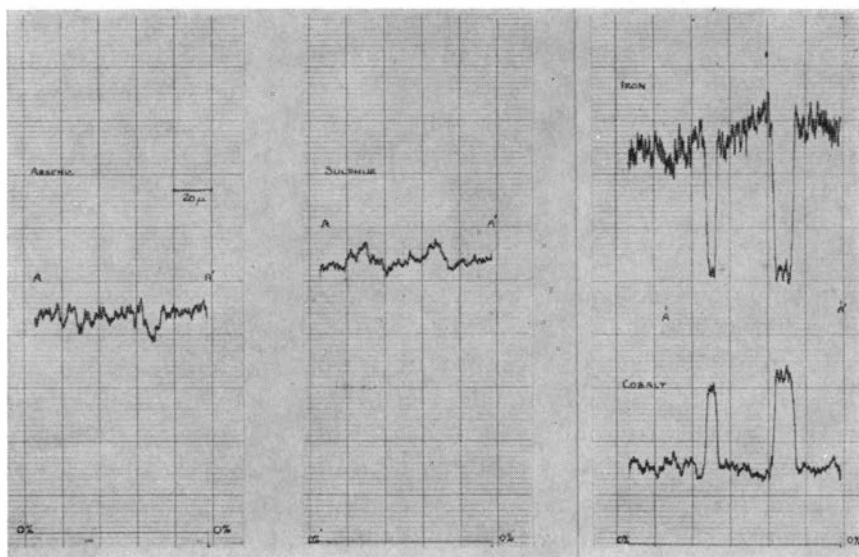


Fig. 2. 'Line-scans' across the lamellae shown in Figs. 4 and 5. Note the minor differences in sulphur and arsenic and major changes in cobalt and nickel contents from the lamellae to the host.

Instrument Co. Ltd., kindly performed an electron probe microanalysis of a sample of Modum arsenopyrite at the Company's laboratories in Cambridge (Report No. M7.3.64). She calculated the compositions of phases 'A' (glauco-dot) and 'B' (cobaltian arsenopyrite) to be the following:

	Fe	Co	As	S
Phase A	18.5% $\pm$ 1%	17% $\pm$ 1%	46%	18.5% $\pm$ 1%
Phase B	28% $\pm$ 1%	7.5% $\pm$ 0.5%	47%	17.5% $\pm$ 1%

The analysis of the lamellar phase A is consistent with 'glauco-dot', and that of the host, phase B, with cobaltian arsenopyrite. Its optical properties, together with the composition, suggest that the lamellar phase is indeed glauco-dot.

### Cobaltian arsenopyrite

Arsenopyrite with varying contents of cobalt is the most common of the ore minerals in the Modum district. It occurs as disseminated grains impregnating the metamorphic rocks and as small concordant

Table 4. *Peak heights for standard iron-cobalt mixtures*

Standard	Admixture	Absolute Peak Height (Scale divisions)		$F_{\text{Co}} : F_{\text{Fe}}$ Ratio
		$F_{\text{Co}}$	$F_{\text{Fe}}$	
Fe 100 Co 0	—	0	66	0
Fe 95 Co 5	—	23.5	64.5	0.364
Fe 95 Co 5	20% As	22.0	62.0	0.354
Fe 95 Co 5	40% As	20.5	53.5	0.383
Fe 95 Co 5	80% As	18.0	50.0	0.360
Fe 95 Co 5	40% As + 50% S	14.2	38.3	0.365
Fe 90 Co 10	—	51.0	59.5	0.857
Fe 80 Co 20	—	98.0	53.0	1.849
Fe 70 Co 30	—	84.0	26.5	3.920
Fe 50 Co 50	—	96.5	11.5	8.391

lenses lying in the foliation and elongated parallel to the prevailing mineral lineation in the surrounding gneisses. It is commonly intergrown with cobaltite and, rarely, with skutterudite. A study was made of the range of arsenopyrite composition.

#### DETERMINATION OF THE COBALT CONTENT

Standard mixtures of iron and cobalt metal powders were prepared and analyzed on a Norelco X-ray fluorescence spectrograph. Straight-line plots of peak height against concentration for both elements indicate negligible interelement effects. Addition of arsenic at various levels and sulphur, followed by fusion and regrinding, had no effect on the Co:Fe peak height ratio as demonstrated in Table 4 for the sample  $\text{Fe}_{95}\text{Co}_5$ .

These results suggest that the peak height ratio ( $F_{\text{Co}}:F_{\text{Fe}}$ ) can be used to determine the Co:Fe ratio in an unknown sample in the presence of sulphur and arsenic. The data presented in Table 4 were used to prepare the determinative curve shown in Fig. 3.

The Co:Fe ratios for 21 crystals of cobaltian arsenopyrite from the Skuterud Mines were obtained by this method. All published analyses of arsenopyrite support the hypothesis that the sum of the cations is essentially a constant ( $34.8 \pm 0.5$  wt %), suggesting that cobalt enters

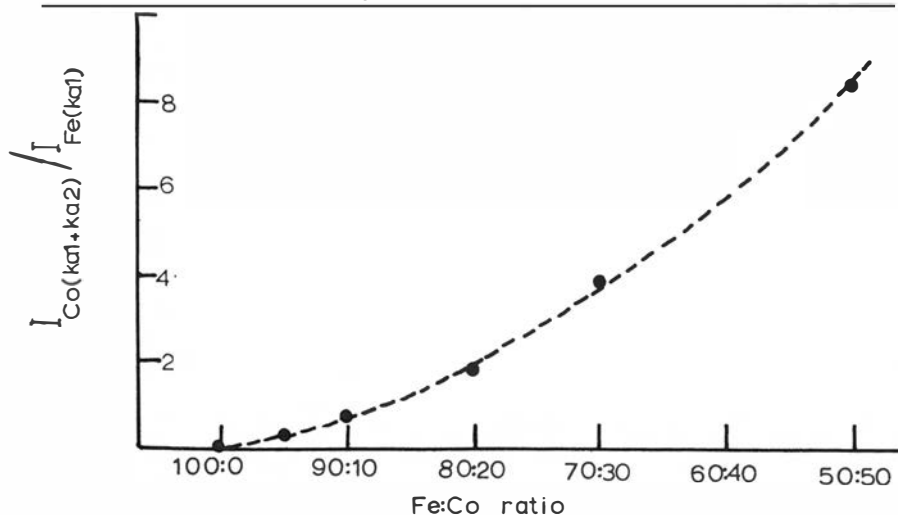


Fig. 3. Determinative curve for obtaining iron:cobalt ratio in an unknown sample based on the relative intensities of X-ray fluorescence peak heights.

the lattice at the expense of iron. Thus, knowing the ratio of iron:cobalt and assuming their sum to be  $34.8 \pm 0.5$  wt %, the cobalt and iron contents of a particular cobaltian arsenopyrite can be calculated. The recalculated analyses of the Skuterud arsenopyrites are shown in Table 5.

The frequency distribution of the cobalt content in the analyzed specimens in Fig. 4 approximates a normal distribution tailing off towards a value of 9 per cent cobalt, the value suggested by FERGUSON (1947) for the boundary between 'danaite' and 'glaucodot'. Two speci-

Table 5. *Modum arsenopyrite analyses recalculated in terms of wt % cobalt*

Sample No.	wt % Co	Sample No.	wt % Co	Sample No.	wt % Co
Bleik.Aspy.	0	1034-8	6.6	1034-16	4.9
1034-1	5.6	1034-9	4.9	1034-17	8.3
1034-2	6.3	1034-10	11.8	1034-18	4.9
1034-3	4.5	1034-11	4.9	1034-19	2.8
1034-4	7.7	1034-12	6.3	1034-20	4.2
1034-5	8.0	1034-13	5.6	1034-21	5.2
1034-6	11.5	1034-14	4.5		
1034-7	7.0	1034-15	4.9		

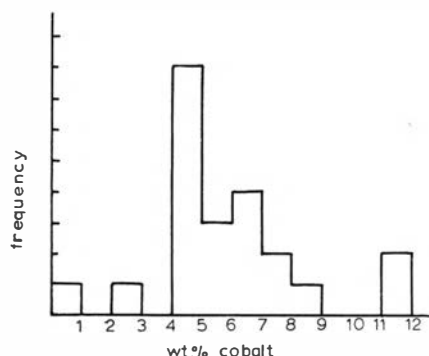


Fig. 4. Frequency distribution of cobalt content in Modum arsenopyrites. Those specimens with greater than 9 wt % cobalt were found to contain lamellae of glaucodot. (These values were obtained on the assumption that nickel is present in negligible proportions, a conclusion based on detailed study of the Modum ores.)

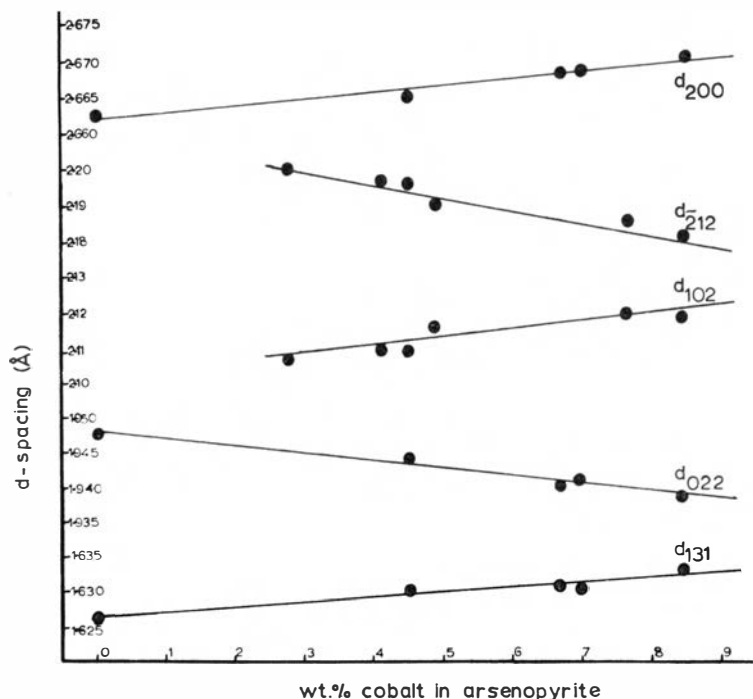


Fig. 5. Variation in lattice spacings as a function of cobalt content in Modum arsenopyrites. The values for  $d_{200}$ ,  $d_{022}$ , and  $d_{131}$  spacings were obtained using a diffractometer; the  $d_{212}$  and  $d_{102}$  spacings were obtained by using the powder method with a Guinier-Nonius quadruple camera.

mens (1034-6 and 1034-10) contained more than 9 wt %; these two are the only samples to contain more than one visible phase in polished specimen. The anisotropism and hardness of the other phase suggest that it is glaucodot rather than cobaltite.

#### VARIATION IN LATTICE SPACINGS WITH COBALT CONTENT

Diffraction patterns of the above material were obtained on a Phillips high-angle X-ray diffractometer using silicon as an internal standard. The lattice spacings (200), (022), (131), (212), and (102), indexed on the primitive monoclinic cell of MORIMOTO and CLARK (1961), show a variation with cobalt content. Fig. 5 shows the d-spacings in Ångströms plotted as a function of cobalt content for these samples.

#### VARIATION IN PHYSICAL AND OPTICAL PROPERTIES WITH COBALT CONTENT

Since the variation in lattice spacings recorded above reflects a change in the cell dimension, it was thought that a corresponding change in physical or optical properties might be evident.

Vickers hardness tests were made on four euhedral arsenopyrite crystals of varying cobalt content, polished parallel to (012). The average value for all the indentations was 1014, with a range of 715-1354. This is rather low compared with the value of 1124 quoted by BOWIE and TAYLOR (1958) for 'glaucodot' and of 1094 for 'arsenopyrite' with a range of 1048-1127. The results, shown in Table 6, indicate that there is no correlation with cobalt content.

The following optical data were obtained from specimen 1034-17, which contains about 8.3 per cent cobalt. No significant variations were found in specimens with differing cobalt contents.

The arsenopyrite is white in color with a slight bluish tint against cobaltite. Reflection pleochroism is very weak. In oil immersion, it is white with a slightly brownish tint, the reflection pleochroism being slightly stronger. The mean uniradial reflectivity in air, using white light and Sulitjelma pyrite as a standard, was 64.8 per cent. The corresponding value in oil was 50.7 per cent. The apparent uniradial reflectivity was measured, with monochromatic light ( $\lambda = 549 \text{ m}\mu$ ), for a large number of grains. No constant value was found for  $R_1$  or



Table 6. *Vickers Hardness of Modum arsenopyrites measured on surfaces cut parallel to (012)*

Specimen No.	Co wt %	Mean V.H. (100 gm load)	Range
1034-19	2.8	974	715-1354
1034-11	4.9	1064	974-1168
1034-17	8.3	1167	1048-1246
1034-10	11.8	949	762-1267

$R_2$ , indicating a biaxial nature. The values found indicate that  $R_p$  is equal to or less than 62.3 per cent.  $R_g$  is equal to or greater than 65.7 per cent, and  $R_m$  lies in the range 63.4-63.9 per cent. Thus, the Modum arsenopyrite is optically positive in the sense of CAMERON (1963). The mineral is anisotropic in shades of olive-brown and greenish-blue. The polarization figure shows a separation of the isogyres on rotation of the stage. The magnitude of this separation would indicate a  $2V$  value of ca.  $20^\circ$  with a transmitted light interference figure. The dispersion of the reflection rotation (DRr) and the dispersion of the apparent angle of rotation (DAr) were distinct and opposite in sense, indicating that in both cases the dispersion is  $v > r$  (CAMERON 1961).

The preceding investigations suggest that on the basis of composition and crystal structure most of the arsenopyrite from Modum is more properly referred to cobaltian arsenopyrite than to glaucodot.

## Arsenopyrite

### CRYSTAL STRUCTURE

The unit cell of arsenopyrite was first investigated by DE JONG (1926). Using powder and rotating crystal methods, he assigned arsenopyrite to the orthorhombic group which includes marcasite. BUERGER (1936) showed that no orthorhombic space-group can satisfy the intensity data obtained by the Weissenberg method, but instead that the arsenopyrite structure can be considered as a derivative superstructure based on the marcasite type, and concluded that, ideally, it has monoclinic symmetry with space-group  $B2_1/d$ . He found that the

mineral is also commonly triclinic (space-group B1) and concluded that this was the result of variations from the ideal chemical formula.

MORIMOTO and CLARK (1961) have shown that arsenopyrite, although appearing to be of orthorhombic symmetry, is composed of twinned monoclinic individuals. The following transformations are employed: de Jong (orthorhombic) cell  $\rightarrow$  Buerger (double monoclinic, metrically orthorhombic) cell: 001/100/010; Buerger cell  $\rightarrow$  Morimoto and Clark (primitive monoclinic) cell:  $\frac{1}{2}0\frac{1}{2}/10\bar{1}/\frac{1}{2}0\frac{1}{2}$ . In all subsequent discussion, the latter monoclinic orientation will be retained. The twin planes of the monoclinic individuals (Type I twins) are  $(10\bar{1})$  or  $(101)$  with twin axis  $[10\bar{1}]$  or  $[101]$ . MORIMOTO and CLARK (1961) have shown, on the basis of oscillation, precession, and Weissenberg methods, that splitting of some reflections occurs which can only be accounted for by a second type of twinning (Type II twins). This requires the assumption that arsenopyrite is triclinic; the postulated twin law is twin axis  $[010]$  with twin plane  $(010)^*$ . The deviation of  $\alpha^*$  and  $\gamma^*$  from  $90^\circ$  are less than  $30'$ .

Since  $(10\bar{1})$  reflections were obtained for all samples studied by Morimoto and Clark; none had truly monoclinic symmetry. They consider that the replacement of S by As causes a gradual change in the properties of arsenopyrite, which raises the symmetry of the structure from triclinic to monoclinic, and that this change might also be achieved by the incorporation of Co and Sb in the structure rather than calling on further arsenic substitution.

These researches can be summarized as follows:

- 1) Arsenopyrite is commonly triclinic but has a pseudomonoclinic symmetry resulting from the Type II twinning;
- 2) Arsenopyrite of suitable composition may be truly monoclinic;
- 3) The monoclinic arsenopyrite has a pseudo-orthorhombic symmetry resulting from the Type I twinning.

It is interesting to speculate on the origin of the Type I twins. These have the appearance in polished specimen of being transformation twins of the type observed in cobaltite. An analogy may exist between the cubic (pyrite-type) structure of disordered cobaltite and the pseudo-cubic (twinned orthorhombic) structure of ordered cobaltite and an orthorhombic (marcasite-type) structure of disordered

arsenopyrite, so far undescribed, and the pseudo-orthorhombic (twinned monoclinic) structure of the ordered arsenopyrite described by Morimoto and Clark.

MORIMOTO and CLARK (1961 p. 1462) investigated this possibility by heating Freiberg arsenopyrite at 600°C for 30 days in a sealed, evacuated, silica-glass tube followed by rapid cooling in cold water. No difference in Weissenberg or precession photographs was observed between the heated and unheated specimens. However, these conditions would not have been sufficient to achieve the disordering of orthorhombic cobaltite. The possibility still exists that an orthorhombic-monoclinic polymorphic inversion may be possible in arsenopyrite.

#### RELATIONSHIP OF THE ARSENOPYRITE AND COBALTITE STRUCTURAL TYPES

It has been shown that the structure of cobaltite can be derived from the pyrite structure; similarly, the arsenopyrite structure is closely related to the marcasite structure.

For a better understanding of the relationships of these structures, it is useful to consider the polymorphic transformation of pyrite to marcasite. The unit cell of pyrite ( $Pa3$ ,  $a_0$ : 5.417,  $Z$ :4) does not bear any obvious relationship to the marcasite unit cell (orthorhombic,  $Pnmm$ ,  $a$ :4.436,  $b$ :5.414,  $c$ :3.381,  $Z$ :2). However, intergrowths of the two minerals are common which have marcasite (101) parallel to pyrite (001) suggesting that a similar structural environment of Fe and S is present in these respective planes. HUGGINS (1922) postulated that this was achieved if the arrangements of Fe atoms about S-S pairs in the pyrite structure were rearranged to give an orthorhombic lattice. BUERGER (1931) showed more rigorously that this was in fact the marcasite structure. He showed that the relationship of marcasite to other structures could best be visualized by detaching a sulphur pair, with its immediate iron environment, which consists of a capping at each end by iron triads rotated 180° with respect to each other. These same units, in the undistorted, ideally symmetrical condition, are distinguishable in pyrite. The difference in the structures is essentially one of a different linking of these units. BUERGER further compared certain geometrical properties of pyrite with those of the marcasite structure (1931 Table X) to bring out the essential identity of

this common unit. The structure of marcasite projected on (101) is similar to that of pyrite on (001) and probably accounts for the observed mineral intergrowths.

These dimorphs can be considered as being related by a reconstructive transformation (BUERGER 1951), whereby the entire structure is unlinked then relinked again to form a new and different network, yet one having first coordination identical with that of the first structure.

As no examples have yet been described of either cobaltite assuming a marcasite type structure or arsenopyrite assuming a pyrite type structure, it follows that there is some fundamental difference which makes both structures stable under identical geological conditions. However, glaucodots containing as much as 32.93 per cent cobalt with only 3.14 per cent iron have been described (SHISHKIN 1962, BORISHANSKAYA *et al.* 1965). These could well be considered as a polymorphic form of cobaltite.

The similarities of the arsenopyrite and cobaltite structures may be reviewed. In the arsenopyrite lattice, each iron atom has 6 neighbors at the corner of a somewhat distorted octahedron. One face of the octahedron is a triangle of 3 arsenic atoms while the opposite face is a triangle of 3 sulphur atoms. This same arrangement is found in the ordered, orthorhombic cobaltite structure. In the arsenopyrite structure, each sulphur atom is surrounded by 3 iron and 1 arsenic atoms at the corners of a somewhat distorted tetrahedron. Each arsenic atom is similarly surrounded by 3 iron and 1 sulphur atoms. These arrangements are analogous to those found in the ordered cobaltite structure. A similar relationship between the As-S pairs with their immediate metal atom environment is found between the arsenopyrite and cobaltite structures as that found for the S-S pairs in the marcasite and pyrite structures.

### Summary

It has been shown that cobaltite is present as the ordered, orthorhombic form at Modum. A disordered, cubic form may be obtained by heating and rapidly quenching an ordered crystal. The disordered form is also found naturally in deposits at Cobalt, Ontario. It is possible that a similar disordered form of arsenopyrite may be found which will possess orthorhombic symmetry. The crystal structures of arseno-

pyrite and cobaltite are closely related to those of marcasite and pyrite.

The name *danaite* has been used to describe arsenopyrites containing an appreciable amount of cobalt. However, this additional name is unnecessary and should be dropped in favor of cobaltian arsenopyrite.

The presence of glaucodot, probably as exsolution bodies, in cobaltian arsenopyrite, and as fringes to cobaltite crystals, suggests that the arsenopyrite lattice can accommodate cobalt only up to about 9 wt %. When cobalt was present in excess of this value in the specimens studied, the mineral glaucodot appears as a separate phase. The use of the term *alloclasite* to describe high cobaltian glaucodot would seem to be unnecessary. The possibility exists that glaucodot should be regarded as a polymorphic form of cobaltite.

### Acknowledgements

This work was carried out during the tenure of a NATO Science Studentship at the Universities of Durham, England, and Oslo, Norway. Grateful acknowledgements are due to Professor K. C. Dunham, Dr. H. Neumann, Mr. R. Phillips, and Dr. F. M. Vokes for helpful assistance at all stages of the work. Dr. T. K. Ball gave helpful suggestions in the use of X-ray techniques. Drs. A. C. Dunham, D. M. Hirst, and J. O. Kalliokoski critically read portions of the manuscript.

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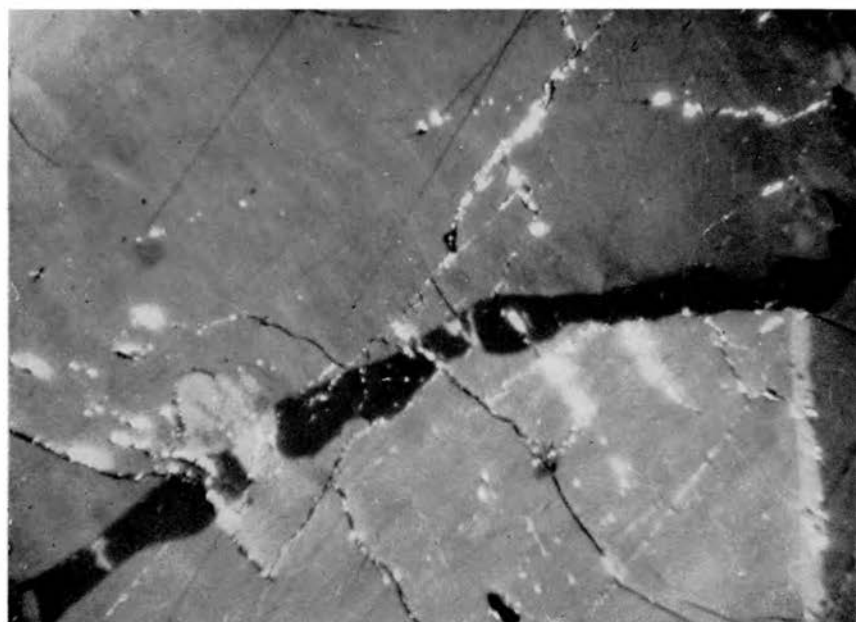
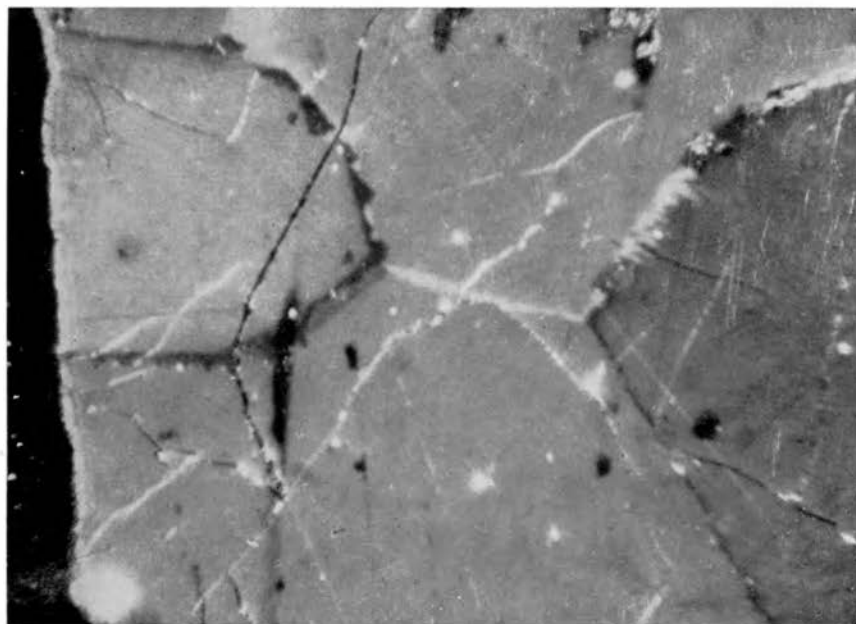
## PLATES

## PLATE 1

**Fig. 1.** Fringes of glaucodot developed at the boundaries of polyhedral crystals of cobaltite (Skuterud Mines, Modum). Reflected, polarized light, crossed nicols, width of field 2.3 mm.

**Fig. 2.** Glaucodot fringing cobaltite giving a spurious appearance of later veining (Skuterud Mines, Modum). Reflected, polarized light, crossed nicols, width of field 1.9 mm.

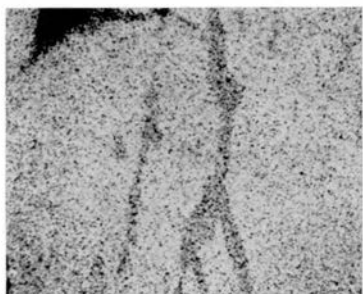
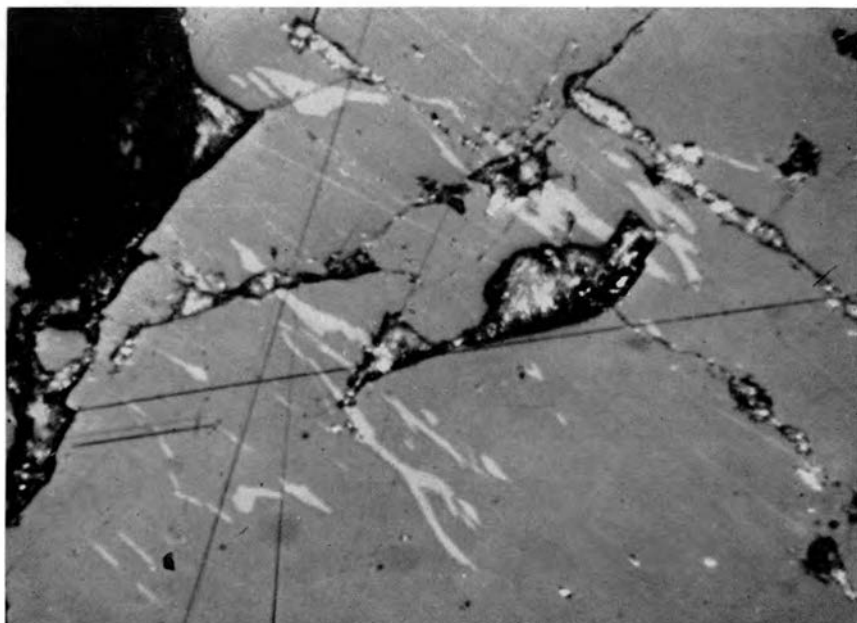




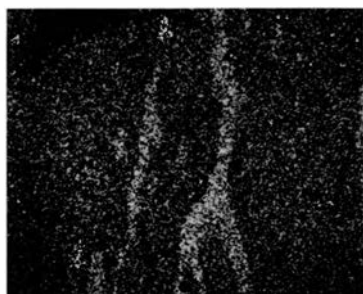
## PLATE 2

Fig. 1. Glauco-dot lamellae in host cobaltian-arsenopyrite (Skuterud Mines, Modum). Reflected, polarized light, crossed nicols, width of field 2.3 mm.

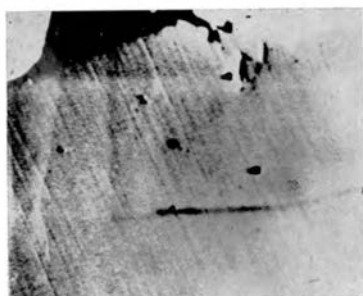
Fig. 2. Photographs of the images produced on the 'Microscan' electron probe by part of the area shown in Fig. 1. No lamellae are visible on the electron image; in the other images, the intensity of the light is proportional to the presence of the element scanned for.



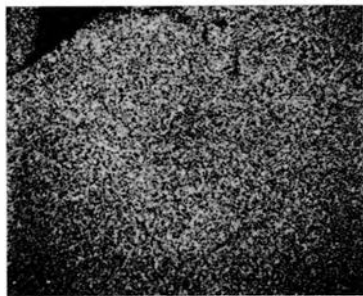
Iron



Cobalt



Electron



Sulphur