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THE IDENTITY OF PENROSEITE AND BLOCKITE

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Penroseite (Gordon, 1926) was the first native nickel selenide to be discovered; and until so-called blockite was described (Herzenberg and Ahlfeld, 1935) penroseite also possessed the distinction of carrying more selenium than any other known mineral. Gordon found that penroseite possesses three perfect cleavages mutually at right angles and a fourth distinct prismatic cleavage (110) for which he gave no angular measurements. He concluded that the mineral possesses orthorhombic symmetry, but it is obvious that he might equally well have considered the symmetry to be tetragonal or cubic. Herzenberg and Ahlfeld gave no crystallographic data for blockite but found from chemical analysis that the mineral is accurately represented by a formula of the type RSe_2, the predominant metals being nickel and copper. They based their distinction of blockite from penroseite on the much higher lead content of the latter (17.13% for penroseite, 0.35% for blockite) and on the higher selenium content of blockite. Cubic nickel diselenide possessing the pyrite type of crystal structure has been prepared by de Jong and Willems (1928).

It is obviously desirable to study further the relationship between penroseite and blockite, and at the same time to determine whether the symmetry and crystal structure of the two minerals is identical with that of artificial nickel diselenide. The supposed difference in composition of penroseite and blockite also calls for new chemical analyses accompanied by *x*-ray and specific gravity data. For this study the following specimens from the mineral collections of the British Museum (Natural History) were available:

(1) Penroseite: a massive lead-grey fragment ($3\frac{1}{2}\times3\times1$ cm.) showing bladed cleavages, labelled Colquechaca, Bolivia (broken from type specimen). Cavities in this specimen are lined with pseudomorphs of limonite after chalybite, and a portion of the surface is stained green due to nickel and carries a thin brick-red incrustation, presumably of "ahlfeldite" [B.M. 1926, 1].

(2) Blockite: a nodule 3 cm. diameter, compact massive in the centre, shelly-concentric towards the exterior; coated with limonite. Locality, Hiaco mine, 30 Km. E.N.E. of Colquechaca, dep. Potosi, Bolivia [B.M. 1936, 126].

(3) Blockite: a compact matrix of chalybite and quartzite (8×6×3 cm.) enclosing lead-grey nodules up to 2 cm. across showing radiating curved segments and "ahlfeldite." Locality, Hiaco mine, Colquechaca, dep. Potosi, Bolivia [B.M. 1935, 1186].

X-ray photographs of small cubic cleavage fragments detached from specimens 1, 2 and 3 were taken and proved to be identical in pattern and intensity, conforming to cubic symmetry and revealing the pyrite type of crystal structure (figs. 1, 2). Small but appreciable differences in unit-cell size were, however, discovered. With a view primarily to assist the chemical analyses, small quantities of each specimen were also examined with a quartz spectrograph using the electric arc. No difference in the lead content could be detected, but the lines due to silver increase in intensity in the order A, B, C (fig. 3). In order to test the sensitivity of the lead lines comparison photographs, under the same conditions, were also made of mixtures of powdered arc carbon and litharge containing 1% and 10% lead. These preliminary results show quite definitely that penroseite and blockite have the same symmetry and crystal structure and that, whilst the lead content is almost constant, there is some

TABLE 1. CHEMICAL ANALYSES OF PENROSEITE.

	1	2	3	4	5	6
Se	67.01	66.59	67.31	59.80	69.72	72.90
S	0.39	0.52	tr.	—	—	—
Ni	8.89	9.88	10.30	11.14	14.09	27.10
Co	1.10	0.71	0.52	1.34	2.45	—
Fe	tr.	0.72	0.72	1.08[1]	1.29	—
Cu	4.50	3.72	3.55	7.84	6.70	—
Hg	1.45	4.12	1.41	—	1.95	—
Pb	13.72	10.88	8.27	17.13	0.35	—
Ag	2.13	5.00	7.78	2.04	1.73	—
Pt metals	—	—	—	—	0.022	—
Insol.	—	—	—	—	1.28	—
	99.19	102.14	99.86	100.37	99.58	100.00
Unit cell edge	6.017	6.001	6.001	—	—	6.022 Å
Sp. Gr.[2] $D^{18^\circ}_{4^\circ}$	6.87	6.71	7.0	6.93	6.05	6.69[3]

1. Penroseite [B.M. 1926, 1]. Microanalysis by M. H. H.
2. Blockite [B.M. 1936, 126]. Microanalysis by M. H. H.
3. Blockite [B.M. 1935, 1186]. Microanalysis by M. H. H.
4. Penroseite, Bolivia; analyst Whitfield (Gordon, 1926).
5. Blockite, Bolivia; analyst Herzenberg (Herzenberg and Ahlfeld, 1935).
6. $NiSe_2$.

[1] Fe_2O_3.

[2] Determined on portions of about 10 mg. by a micromethod shortly to be described.

[3] Specific gravity calculated from the *X*-ray data and the ideal composition $NiSe_2$ is 6.54.

variation in silver content. Microchemical analyses (table 1) confirm these conclusions.

Chemical Methods. Owing to the rather short time at our disposal it was not possible to make a really adequate study of the possible methods for the microanalysis of penroseite; the methods adopted are thus not ideal, but since partial repeats by other methods have given good agreement it is felt that the analyses are reasonably accurate.

The method adopted was to dissolve the mineral (20 mg.) in hydrochloric acid (1:1) with small additions of potassium chlorate in the cold; solution took about three days.[4] The residue of silver chloride and insoluble matter was filtered off, dried, and weighed, then the silver chloride dissolved out with sodium thiosulphate and the residue of insolubles weighed. In the filtrate excess chlorine was destroyed by the dropwise addition of concentrated solution of hydrazine hydrochloride, then selenium precipitated by the addition of a solution of hydrazine hydrochloride in hydrochloric acid (1:1) saturated with sulphur dioxide. After standing over night the precipitate was filtered off, washed, dried and weighed. Subsequent examination showed that in addition to selenium it contained the whole of the mercury as calomel.

The filtrate from this precipitate was evaporated to dryness, the hydrazine present being destroyed by occasional additions of nitric acid. The residue was dissolved in a little water, 0.1 cc. of strong sulphuric acid added to the mixture, evaporated in the water bath, diluted and filtered ($PbSO_4$). The filtrate from the lead sulphate was precipitated with salicylaldoxime in acetic acid solution and the precipitate filtered off, dried, and weighed. This proved to be an unfortunate step as contrary to the experience of Ephraim (1928) a large proportion of the nickel was carried down (no detailed study of this separation was made, and it is possible that under suitable conditions it might prove to be an efficient one). It was therefore, necessary to re-dissolve this precipitate in hot hydrochloric acid, and precipitate the nickel with dimethylglyoxime in ammoniacal solution; after filtering off and weighing this (a part of the nickel present) the copper was precipitated with pyridine and thiocyanate. In the filtrate from the salicylaldoxime precipitate the remaining nickel was precipitated with dimethylglyoxime, then the iron with cupferron and the cobalt with α-nitroso-β-naphthol. Mercury was determined in a separate portion by a titration with diphenylthiocarbazone according to the method of Fischer and Leopoldi (1935). The aqueous layer after this titration was used for the determination of sulphur as $BaSO_4$.

TABLE 2. ATOMIC RATIOS OF PENROSEITE ON THE BASIS OF $(R, Ag_2)=1$
(Numbers refer to Table 1)

	1	2	3	4	5
Se	2.617	2.425	2.539	1.175	2.055
S	0.038	0.047	—	—	—
Ni	0.467	0.484	0.523	0.430	0.559
Co	0.058	0.035	0.026	0.052	0.097
Fe	—	0.036	0.038	0.031	0.054
Cu	0.218	0.168	0.166	0.279	0.245
Hg	0.022	0.059	0.021	—	0.023
Pb	0.204	0.151	0.119	0.187	0.004
Ag	0.061	0.133	0.215	0.043	0.037

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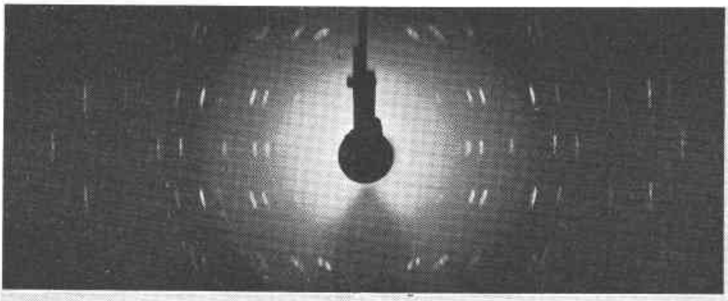
[4] Solution in bromine water was rather quicker, but left some doubts as to the state of combination of the mercury in the selenium—calomel precipitate.

As was to be expected in view of the heterogeneous nature of the material, the atomic ratios yield little information except that the new analyses show selenium very markedly in excess of the formula $(R, Ag_2)Se_2$.

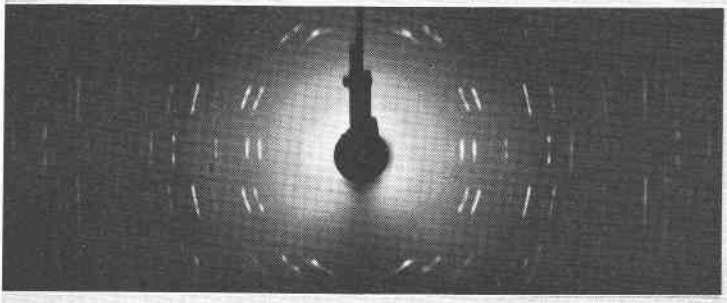
The question immediately arises: are specimens of penroseite and blockite intergrown with small variable amounts of other minerals similar in appearance but different in chemical composition? There are two distinct methods available for testing this possibility: The optical examination of polished sections and *x*-ray examination.

Optical Examination. Gordon states that polished sections of penroseite show thin veins of silver selenide but no optical study of blockite has yet been published. The minerals most likely to be intergrown with penroseite and blockite are cubic in symmetry, such as clausthalite, PbSe, naumannite (Ag, Pb)Se, and argentiferous galena (Pb, Ag)S. The sulphur content as shown by chemical analysis is so small that the galena content must be less than 3% .We should expect polished sections of all these to be optically isotropic, hence differentiation is only possible if we can detect differences of colour and reflectivity. A further restriction to optical methods is inherent in the formation of penroseite and blockite. The innermost portion of the nodules is compact, massive and lacks the cleavage boundaries which are so conspicuous nearer the surface. An examination of polished sections of penroseite and blockite nos. 1 and 2 both showed clearly thin veins of a pale mineral which Gordon thought to be silver selenide. The veins of no. 1 are numerous but very thin whereas in no. 2 the veins attain a width of $\frac{1}{2}$ mm. in one or two places. They are most readily seen by oblique illumination under a binocular microscope when their tin-white colour contrasts well with the darker slightly yellowish grey of the penroseite or blockite. Using a vertical illuminator and polarised light it was found that both minerals are isotropic; no third metallic component could be detected.

X-ray examination. A fine steel needle was used to excavate some of the white mineral discovered in the polished sections of 1 and 2. A stationary *x*-ray photograph of the fragments obtained proves to be a powder photograph of a mineral with cubic symmetry and face-centred lattice with *a* 6.12 Å. On the same photograph flecks due to a little adherent penroseite yield unit cell dimensions 6.00 Å. The photograph except for the flecks due to penroseite is identical with one of naumannite from Tilkerode, Harz [B.M. 95201]. Hence it is now certain that both the specimens of penroseite and blockite are intergrown with naumannite and that the variation in silver and lead content is at least partly due to admixture with that mineral. Analyses 1, 2 and 3 suggest, however that penroseite contains both combined lead and silver. Penroseite and



1



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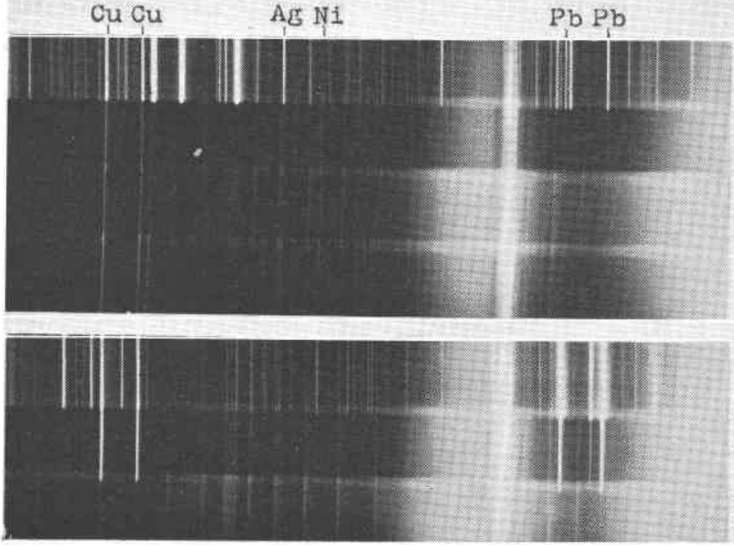

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blockite may therefore be regarded as identical minerals and the latter name may be discarded. Owing to varying proportions of naumannite, specimens yield chemical analyses varying in lead and silver content; and the true composition of penroseite still remains uncertain. It has already been noted that a fragment of the naumannite gives a powder not a single crystal photograph. Thence it is probable that the naumannite is an infilling of the cracks and fissures of the more coarsely crystalline penroseite.

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EXPLANATION OF THE FIGURES

The *x*-ray photographs were taken with unfiltered copper radiation, $\lambda = 1.539$ Å, and with a cylindrical camera, diameter 6.04 cm. A length of 11.85 cm. on the original films is equivalent to 10 cm. on the reproduced figures.

FIG. 1. Rotation photograph of a cleavage of fragment of penroseite [B.M. 1926, 1] about the axis [100].

FIG. 2. Rotation photograph of a cleavage fragment of blockite [B.M. 1935, 1186] about this axis [100].

FIG. 3. A portion of the spectrographic record extending from about 3200 to 3700 Å.

R. U. Powder which is composed of a base of Mg, Ca, and Zn oxides and small, varying amounts of 51 elements in such proportions that only a few of the most sensitive lines (raies ultimes) appear in the emission spectra.

A. Penroseite [B.M. 1926, 1].
B. Blockite [B.M. 1936, 126].
C. Blockite [B.M. 1935, 1186].
D. 10% Pb.
E. 1% Pb.
Arc. Carbon arc alone.

The marked lines have the following wave-lengths: Cu 3247 Å, Cu 3274, Ag 3383, Ni 3415, Pb 3640, Pb 3683.