

**On the presence of minerals of the linnaeite series  
in some copper ores  
from the Raipas formation of Northern Norway**

BY

F. M. VOKES

With 1 plate.

**Abstract.**

Two minerals of the linnaeite series,  $A_3S_4$ , have been identified and examined in ores from two localities in the Alta district of Finnmark.

Their compositions show them to be siegenite and carrollite, respectively. Associated minerals in each case are bornite, chalcopyrite, neodigenite, and a little covellite. Tennantite is also found in the siegenite-bearing ore.

The properties, chemical compositions and modes of occurrence of the minerals are discussed in this short note which appears to be the first published record of their occurrence in Norwegian ores.

**Introduction.**

During an examination of polished sections of ore from Raipas mine, Alta, the cobalt-nickel sulphide *siegenite* was identified. In some specimens the mineral was a prominent constituent. Later samples were received, from the Bergmester of the Finnmark mining district, of ore from the unworked deposit of Borrås, some few kilometres east of Raipas. One specimen from this locality proved to be very rich in *carrollite*, the Co-Cu member of the linnaeite series. Both the Raipas and the Borrås deposits lie in the tectonic window of Raipas formation surrounding the head of Altefjord. A more

general account of the copper mineralization in this formation has been given in the paper preceding this one.

There is no published record of siegenite or carrollite having been previously discovered in a Norwegian mineral deposit; they do not occur in the list of Norwegian minerals published by Oftedal (1948).

The present short paper, therefore, puts on record the minerals' occurrence at the two above-mentioned localities and describes their properties, chemical composition and paragenesis.

### **Optical properties.**

In polished section both the minerals appear well-polished, smooth, and without any detectable internal texture. Their colour is creamy white, with a slight pinkish tinge. They exhibit no pleochroism or anisotropism.

### **Identification.**

The above optical properties, coupled with the paragenesis, suggested strongly minerals of the linnaeite series. X-ray powder patterns taken in the X-ray laboratory of the Mineralogisk-Geologisk Museum of the University of Oslo showed that the minerals did belong to this series. Their definite identification was the result of the chemical analyses which are described below.

The unit cells of the two minerals were calculated from measurements of their powder patterns. The values for both minerals lay just over 9.4Å, but the interpolation was not reliable enough for the second decimal place to be given. However the values confirm that the two minerals belong to the linnaeite series. Palache, Berman and Frondel (1944) give the following unit cell dimensions:

Siegenite .....	9.41Å
Carrollite .....	9.458Å

### **Chemical composition.**

A sample of the linnaeite-mineral, weighing 0.14 gm, was obtained from one of the Raipas specimens by crushing, sieving and separation in heavy liquids and on the Frantz Isodynamic separator.



The sample was analysed for Co, Ni and Fe in the laboratory of NGU (Analyst, B. Bruun). The following figures were obtained:

Co .....	20.6 %
Ni .....	31.6 %
Fe .....	0.8 %

This analysis compares very well with analyses of *siegenites* given by Palache, Berman and Frondel:

	(Co, Ni) <sub>3</sub> S <sub>4</sub> with Co : Ni, 1 : 1	Siegenite Littfeld, Germany.	Siegenite Mine la Motte, Missouri.	Siegenite Raipas mine.
Ni .....	28.89	31.18	31.24	31.6
Co .....	29.02	26.02	20.36	20.6
S .....	42.09	42.63	42.43	
Fe .....		0.62	3.22	0.8
Cu .....			3.16	

The mineral's chemistry plus its X-ray data seem to identify the mineral definitely as *siegenite*. The analysis figures indicate that there is probably some Cu in the mineral too, but the quantity available was not sufficient for its determination.

The linnaeite-mineral in the specimen from Borrás was much more abundant (see below), so that a more complete analysis could be made. However, the separation of the accompanying minerals proved much less easy. The specimen of powder first analysed contained several per cent of barite, which could not be separated from the carrollite, by either gravity or magnetic methods. Also there were considerable amounts of neodigenite in the analysed sample.

The analysis figures showed:

	wt %	mol.pptns.	at. %	Recalculated to 4S
Cu .....	47.9	0.753	41.97	3.8
Co .....	13.5	0.229	12.76	1.2
Ni .....	1.2	0.020	1.11	0.1
Fe .....	0.3			
S .....	25.4	0.792	44.15	4.0
SiO <sub>2</sub> .....	0.6			
BaSO <sub>4</sub> .....	7.8			
Insolubles .....	3.2			
	99.9	1.794	99.99	Analyst, B. Bruun.

These figures show a formula  $(\text{Cu}_{3.8}\text{Co}_{1.2}\text{Ni}_{0.1})\text{S}_4$  or of the form  $\text{A}_5\text{S}_4$  where A is mainly Cu and Co. Since the impurities are mainly neodigenite,  $\text{Cu}_2\text{S}$ , we may write

$$\begin{aligned} & \text{X A}_2\text{S} + \text{Y A}_3\text{S}_4 = 100 \text{ A}_5\text{S}_4 && \text{from which we may} \\ \text{obtain} & && \\ & \frac{2}{3} \text{X} + \frac{3}{7} \text{Y} = \frac{5}{9} \cdot 100 && 1) \\ & \frac{1}{3} \text{X} + \frac{4}{7} \text{Y} = \frac{4}{9} \cdot 100 && 2) \end{aligned}$$

Solving 1) and 2) simultaneously we get

$$\text{X} = 53\frac{1}{3} \%$$

$$\text{Y} = 46\frac{2}{3} \%,$$

i.e. the original material consisted of  $53\frac{1}{3}$  atomic %  $\text{Cu}_2\text{S}$  and  $46\frac{2}{3}$  atomic % of the linnaeite-mineral.

From this we may obtain the composition of the linnaeite mineral as:

	mol.pptns.	at. %	wt. % recalculated to 100 %
Cu .....	0.116	13.84	19.81
Co .....	0.229	27.33	36.29
Ni .....	0.020	2.39	3.14
S .....	0.473	56.44	40.75
	<hr/> 0.838	<hr/> 100.00	<hr/> 99.99

A mineral of this composition would have the formula  $(\text{Co}_{1.94}\text{Cu}_{0.98}\text{Ni}_{0.16})\text{S}_4$  or  $\text{A}_{3.08}\text{S}_4$ , which is in keeping with the formula of the linnaeite minerals.

As a check, another much purer specimen of the mineral was later obtained and analysed for Cu, Co and Ni:

Cu .....	18.5 %
Co .....	32.3 %
Ni .....	3.4 %

These figures are in good agreement with those above and the identification of the linnaeite-mineral from Borras as *carrollite* seems quite definite. Below are given published analyses of carrollites for comparison.



	Co <sub>2</sub> CuS <sub>4</sub>	Carrollite, Gladhammar, Sweden		Carrollite, Siegen Germany.	Carrollite Borras Alta.
		1.	2.		
Cu .....	20.53	20.42	13.90	18.92	19.81
Co .....	38.06	35.30	35.15	35.79	36.29
S .....	41.41	39.47	40.74	40.64	40.75
Fe .....		2.33	2.18	0.93	
Ni .....		1.76	7.01	3.56	3.14

The specimen of Borras ore which was used to obtain the carrollite sample was also analysed and showed 25.0 % Cu, 7.0 % Co and 0.7 % Ni. This gives a cobalt : nickel ratio of 10 : 1 which compares well with that in the carrollite of 11.5 : 1. This near agreement is a further indication of the correctness of the analysis given above.

The existence of carrollite as a separate mineral species has been questioned by Earl V. Shannon (1926). He put forward microscopic and chemical evidence that the originally analysed material from Carroll County, Maryland, to which the name was first applied, contained considerable admixtures of copper sulphides. Shannon reanalysed material which had been subjected to careful mineral separation, controlled by microscopic observations. The copper contents of the «carrollites» found during this re-analysis ranged between 2.40 % and 9.98 %. From this evidence Shannon concluded that the so-called «carrollites» were linnaeites in which a limited amount of Cu was substituting for Co and not a separate species within the linnaeite group.

Obviously, since the linnaeite series is quite isomorphous one can expect to find minerals of very varying compositions depending on the degree of substitution between the various metal atoms. However for the sake of classification there should be names to distinguish the main minerals characterized by a preponderance of certain metals. An analogy may be found in the feldspars where the names change at definitely fixed An-Ab ratios.

The above chemical evidence shows that the linnaeite mineral from Borras has a Co : Cu atomic ratio of nearly 2 : 1. The separation was controlled microscopically, and it is certain that the only sulphide mineral impurities in the analysed samples consisted of neodigenite (or chalcocite). The calculation on p. 115 has shown that in order to satisfy the A<sub>3</sub>S<sub>4</sub> formula, the linnaeite mineral must con-

tain very nearly a whole atom of Cu. Whatever the nature of the material from Carroll County, it seems quite definite that in the Borrás deposit we have a linnaeite mineral of the formula  $\text{Co}_2(\text{Cu Ni})_1\text{S}_4$ . The author therefore is in agreement with Palache, Berman and Frondel in retaining carrollite as a distinct species in the linnaeite series.

### Paragenesis.

The mineralogy of the Raipas ore has been dealt with in some detail in the preceding paper. From the few specimens of Borrás ore available it appears that the mineralogy is almost identical with that of Raipas.

Only the forms exhibited by the siegenite, and its relationships to the other sulphides in the ores will be dealt with here.

Siegenite was present in all the Raipas specimens examined, but in greatly varying proportions. Because of the small number of specimens examined and because their degree of representativeness was not known, no average value for the proportion of siegenite in the ore can be given. Its proportion varied from about 1 % to over 5 % in the polished sections examined.

In the specimen of Borrás ore carrollite was a major constituent, as will be seen from the figures derived from the chemical analysis above. The remarks about «unrepresentativeness of sampling» apply with even more force in this case.

In the Raipas specimens the most usual occurrence of siegenite was as small, often rounded, sometimes subhedral grains of the order of size of 0.05 to 0.1 mm scattered at random in the surrounding copper sulphides, usually either chalcopyrite or bornite. These small grains invariably showed convex boundaries to the copper sulphides and must be considered older than them. They are thought to be replacement residuals of originally larger grains.

Larger grains, up to 0.6 mm in diameter were observed in some specimens. On one beautiful example (Plate 1, Fig. 1) the linnaeite grain had been shattered, and the cracks were invaded by bornite, giving a clear and unmistakable age relationship.

In most cases the copper-sulphides appeared to have replaced the siegenite evenly, from the perimeter inwards giving smoothly embayed junctions, but in two specimens another replacement re-

lationship was seen. Here the mineral had been replaced from the core outwards, leaving in many cases just a thin rim or, rather, shell, surrounded by bornite. This mode of replacement is well recognised in the literature under the term «core replacement» and the resulting texture is known as «atoll texture, (e.g. Edwards, 1954. p. 118).

Various «pairs» of minerals have been described in the literature showing this texture, a very famous example being cobaltite replaced by native silver in an uranium deposit in the Great Bear Lake district of Canada (G. M. Furneal, 1939). In Norway, apparently similar textures between cobalt arsenides and native silver in the Kongsberg ores have been interpreted by H. Neumann (1944) as being due to rim replacement of the silver by the arsenides.

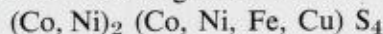
The textures shown in the Raipas specimens are very beautiful examples of «atoll texture» and are illustrated in Plate 1, Figs. 2 and 3. In Fig. 2 the complete history of the replacement can be traced, starting from the «solid» rounded grains of siegenite and ending up with the thinnest, almost hair-like remnant, the very rim of the original grain. In Fig. 3 it can be seen that the bornite which has replaced the core of the siegenite grain has, in its turn, been partly replaced by neodigenite.

This evidence clearly shows that siegenite is the oldest sulphide in the Raipas ore.

In the Borrás specimen the abundant carrollite occurred as a medium-grained allotriomorphic aggregate, and the later copper sulphides «filled-in» between the grains and in cracks in the mineral, so that here the age-relationship is the same as that for the siegenite at Raipas.

### Conclusions.

The linnaeite series has the general formula



and the following members are recognised,

Linnaeite	$\text{Co}_3\text{S}_4$
Siegenite	$(\text{Co, Ni})_3\text{S}_4$
Carrollite	$\text{Co}_2\text{CuS}_4$
Violarite	$\text{Ni}_2\text{FeS}_4$
Polydymite	$\text{Ni}_3\text{S}_4$



The only one of this series previously identified as occurring in Norway is violarite. According to H. Bjørlykke (1941), there «has been found in several Norwegian nickel ores a nickel-sulphide mineral which, in appearance and mode of occurrence, corresponds exactly with violarite  $(\text{NiFe})_3 \text{S}_4$  . . . ».

T. Gjelsvik (1957) has very recently published the preliminary results of a study of ore types similar to those of Raipas and Borrás which he found in 1955 in the southwest part of Finnmarksvidda. He tentatively identifies one of the accessory sulphides as «linnaeite», without being able as yet to place it more accurately in the series.

The present work indicates that two more minerals of the linnaeite series may be added to violarite as occurring in Norway.

The ore-types shown by the Raipas and Borrás deposits are almost identical. Raipas is virtually exhausted and probably would not yield any further specimens of interest. Borrás, however, has hardly been worked and, apart from the present brief treatment, has not been investigated scientifically. There is good hope that this ore, and, possibly, others not yet discovered in the same area, might yield further linnaeite minerals.

From an economic point of view the presence of these minerals in deposits known already to be very rich in copper, (albeit of small dimensions) is an added incentive to prospecting in the area.

### Sammendrag.

*Om tilstedeværelsen av linneitt-mineraler i noen koppermalmer fra Nord-Norge.*

To mineraler tilhørende linneitt-serien er blitt funnet i prøver av malmer fra Alta-området, Finnmark. Prøvene fra den gamle Raipas gruve viser *siegenitt*,  $(\text{Co}, \text{Ni})_3 \text{S}_4$ , og de fra Borrás forekomsten viser *carrollitt*,  $\text{Co}_2\text{CuS}_4$ .

Så vidt det har kunnet bringes i erfaring er disse mineraler ikke tidligere funnet i norske malmer.

I denne notis beskrives mineralenes egenskaper, kjemiske sammensetninger og relasjoner til de andre sulfider i malmen. Resultatene av analysene gis på side 114 (*siegenitt*) og side 115 (*carrollitt*).



**Literature.**

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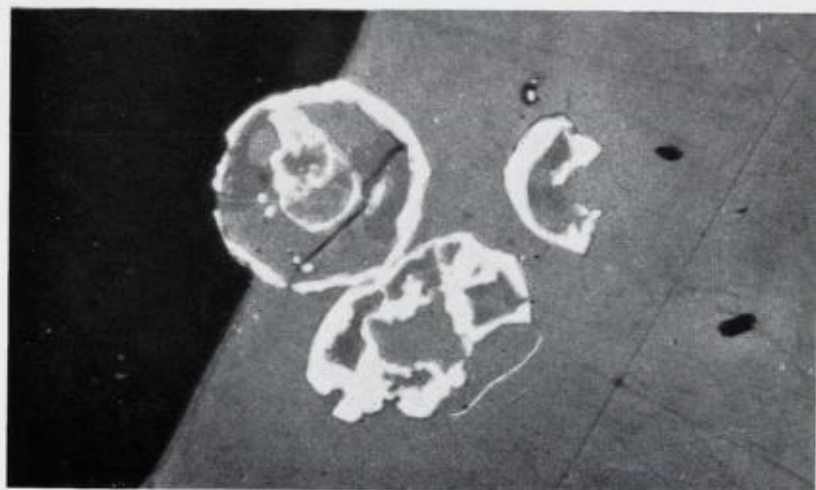
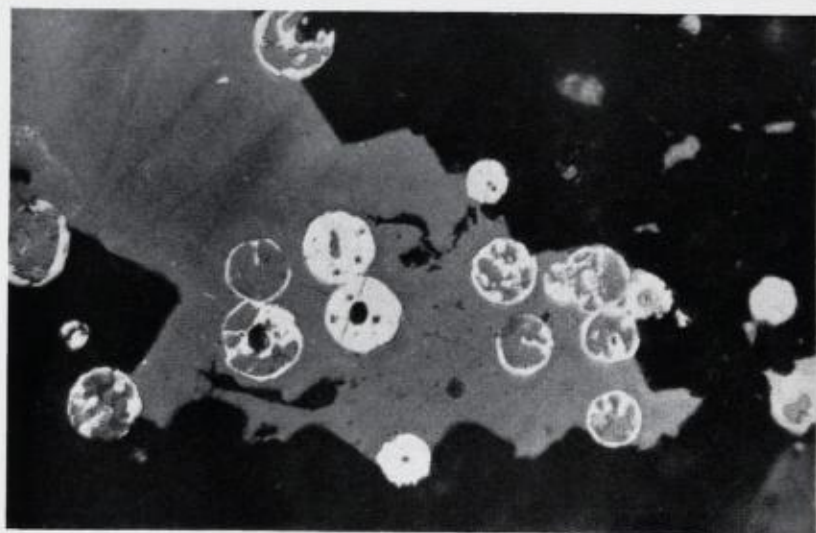
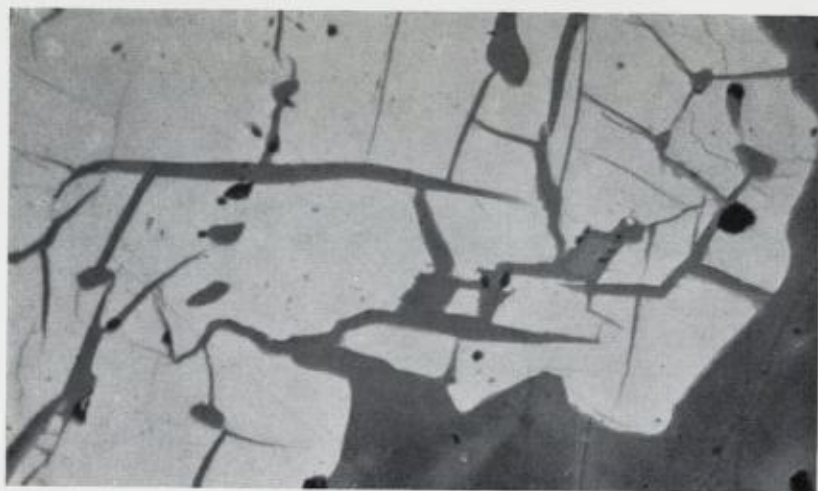


Plate 1, Fig. 1. Part of a large grain of siegenite (light) which has been partly cracked and the cracks infilled by later bornite (dark). The cracks are clearly controlled by the cubic cleavage of the siegenite. Raipas mine. Reflected light. X340.

*Siegenitt (hvit) med sprekker fylt av bornitt (mørk). Oppsprekking har tydeligvis foregått langs siegenittens kubiske spalteretninger. Raipas gruve. Reflektert lys. X340.*

Plate. 1. Fig. 2. Rounded grains of siegenite (white) showing «atoll texture» in bornite (grey). Sulphides are surrounded by a gangue of carbonate or barite (black, with internal reflections). Raipas mine. Reflected light. X250.

*Avrundete siegenitt-korn (hvit) som viser «atoll struktur» i bornitt (grå). Sulfidene omgis av karbonater eller tungspat (sort). Raipas gruve. Reflektert lys. X250.*

Plate 1. Fig. 3. Details of a siegenite «atoll» (white) in bornite (grey). Note replacement of the bornite in the core of the atoll by neodigenite (dark grey). Raipas mine. Reflected light. Oil immersion. X1000.

*En «atoll» av siegenitt (hvit) i bornite (grå) som viser at bornitten har fortrent siegenitten fra kjernen utover. Senere har neodigenitt (mørk grå) fortrent en del av bornitten i kjernen av «atollen». Raipas gruve. Reflektert lys. Olje immersjon. X1000.*