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THE LINNAEITE GROUP OF COBALT-NICKEL-IRON-COPPER SULFIDES

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The linnaeite group of sulfides as given by various mineralogists includes several different minerals. Dana[1] includes linnaeite (siegenite), daubréelite, cubanite, and carrollite. He does not include polydymite. In the 1932 edition of Dana-Ford's *Textbook of Mineralogy* (pp. 430–431), sychnodymite is included with linnaeite, and polydymite is called "nickel-linnaeite." Violarite and badenite are also placed in this group. It may be possible that later studies will place badenite, $(Co,Ni,Fe)_3$ $(As,Bi)_4$?, and daubréelite, $FeS \cdot Cr_2S_3$, definitely in this group, but cubanite, $Cu_2S \cdot Fe_4S_5$, does not belong here as it is orthorhombic in crystallization. Doelter[2] uses the term "Polydymite-Carrollite-group" for the linnaeite minerals. Linnaeite (siegenite), polydymite, carrollite, and sychnodymite are included in his list. Daubréelite is placed in this group, but not because Doelter is satisfied that it belongs there; he merely follows the grouping of other mineralogists. Hintze[3] includes carrollite, daubréelite, linnaeite (siegenite), sychnodymite, polydymite, and also hauchecornite, which, however, as it crystallizes in the tetragonal system is not a member of this group. Violarite, $(Ni,Fe)_3S_4$, was described and named by Lindgren[4] (who without an analysis tentatively assigned it the formula, NiS_2), and is undoubtedly a member of the linnaeite group. The formula, $(Ni,Fe)_3S_4$, was determined by Short and Shannon (Ref. 31) in 1930. The following minerals are included in this discussion: linnaeite, carrollite, sychnodymite, siegenite, violarite, and polydymite. Daubréelite, the iron-chromium sulfide, included in the linnaeite group by some mineralogists, will not be discussed

[1] Dana, E. S., *System of Mineralogy*, 6th Edit., **1909**, p. 78.
[2] Doelter, C., *Handbuch der Mineralchemie*, Band **iv**, pt. I, 1926, pp. 645–657.
[3] Hintze, Carl, *Handbuch der Mineralogie*, Band I, pt. I, 1904, pp. 957–968.
[4] Lindgren, W., *Econ. Geol.*, vol. **19**, 1924, p. 309.

in this article because it has not been definitely shown that it belongs in the isometric system. The proximity in the periodic table of chromium to cobalt, nickel, copper, and iron would favor the possibility that daubréelite would be found to be a member of the group; but *x*-ray studies are needed to determine its structure.

The marked range in composition shown by the minerals within this group was brought to the writer's attention while he was comparing a new analysis of siegenite with the earlier analyses of the mineral. The new analysis was made in 1932 by Lix[5] of a siegenite from the well known Mine La Motte locality in Madison County, Missouri. The analysis was made on crystals carefully selected so as to be practically free from chalcopyrite, the commonest and most intimately associated mineral. This analysis is number 28 in the list given below. Mr. Lix after studying a group of analyses placed his new one among those of the siegenites. He concluded that the cobalt, nickel, iron, and copper determined in his analysis were isomorphous, a conclusion in accord with that made by some others who have studied the group. This study has been made by the writer in an effort to determine whether these four elements are actually isomorphous, and whether dividing lines actually exist between the minerals within the group.

Each mineral of the group is fairly well represented by analyses, which, however, as would be expected, vary in their completeness and accuracy. After eliminating those of manifestly little value, there remained 37 analyses (one of them a recalculated analysis). These are tabulated in the order of their decreasing cobalt content, and under their common mineral names in the following table:

LINNAEITE (Haidinger, 1845)

Number	Locality	S	Co	Ni	Fe	Cu	R_3S_4 ratio
1	Müsen	42.25	53.35	—	2.30	0.97	$R_3S_{4.09}$
2	Carroll Co., Md.	41.70	48.70	4.75	2.36	2.40	$R_3S_{3.96}$
3	Sykesville, Md.	43.56	48.63	Trace	3.55	4.43	$R_3S_{4.27}$
4	Bastnäs	41.83	44.92	0.19	4.19	8.22	$R_3S_{4.04}$
5	Gladhammar	41.43	40.71	7.35	1.30	8.79	$R_3S_{4.19}$
6	Müsen	42.76	39.35	14.09	1.06	1.61	$R_3S_{4.19}$
7	Gladhammar	42.19	39.33	12.33	4.29	2.28	$R_3S_{3.96}$

[5] Lix, Henry W., The Composition and Occurrence of Siegenite. M.A. Thesis, *Univ. of Mo.*, **1932**.

Number	Locality	S	Co	Ni	Fe	Cu	R_3S_4 ratio
	CARROLLITE (Faber, 1852)						
8	Carroll Co., Md.	41.34	42.42	Trace	0.28	15.43	R_3S_4
9	Carroll Co., Md.	41.71	38.70	1.70	0.46	17.55	$R_3S_{4.03}$
10	Carroll Co., Md.	40.94	38.21	1.54	1.55	17.79	$R_3S_{3.97}$
11	Carroll Co., Md.	40.99	37.65	1.54	1.40	19.18	$R_3S_{3.87}$
12	Kantanga	39.40	37.50	Trace	—	19.60	$R_3S_{3.90}$
13	Gladhammar	39.89	37.29	0.78	2.54	19.33	$R_3S_{3.80}$
14	Carroll Co., Md.	41.93	37.25	1.54	1.26	17.48	$R_3S_{4.11}$
15	Carroll Co., Md.	41.89	36.08	7.65	2.25	9.98	$R_3S_{4.18}$
16	Gladhammar	39.47	35.30	1.76	2.33	20.42	$R_3S_{3.72}$
17	Gladhammar	40.74	35.15	7.01	2.18	13.90	$R_3S_{3.90}$
	SYCHNODYMITE (Laspeyres, 1891)						
18	Siegen I.	40.64	35.79	3.66	0.93	18.98	$R_3S_{3.65}$
19	Siegen I.	40.33	35.64	5.74	0.82	17.23	$R_3S_{3.83}$
20	Siegen I.	39.28	26.80	5.70	3.86	23.46	$R_3S_{3.72}$
	SIEGENITE (Dana, 1850)						
21	Müsen	42.63	26.08	31.18	0.62		$R_3S_{4.03}$
22	Mineral Hill, Md.	39.70	25.69	29.56	1.96	2.23	$R_3S_{3.70}$
23	Müsen	40.40	23.39	27.78	2.98		$R_3S_{4.04}$
24	Müsen	41.98	22.09	33.64	2.29		$R_3S_{3.98}$
25	Mine La Motte, Mo.	42.13	21.67	31.00	3.42		$R_3S_{4.12}$
26	Mine La Motte, Mo.	41.54	21.34	30.53	3.37	Trace	$R_3S_{4.17}$
27	Müsen	40.61	20.44	38.16	0.57		$R_3S_{3.77}$
28	Mine La Motte, Mo.	42.43	20.36	31.24	3.22	3.16	$R_3S_{4.05}$
29	Hilgenroth	37.66	16.47	26.55	9.02	0.57	$R_3S_{3.92}$
30	Müsen	42.30	11.00	42.64	4.69		R_3S_4
	VIOLARITE (Lindgren, 1924)						
31	Julian, Calif.	42.17	2.50	33.94	19.33	1.05	
32	Sudbury, Ont.	41.68	1.05	38.68	17.01	1.12	
33	Sudbury, Ont.	41.35		43.18	15.47		
	POLYDYMITE (Laspeyres, 1876)						
34	Grüneau Mine, Siegen	41.08	3.95	49.24	4.76		$R_3S_{3.91}$
35	Grüneau Mine, Siegen	39.20	0.53	13.00	4.12		$R_3S_{4.03}$
36	Grüneau Mine, Siegen	40.27	0.61	53.51	3.84		$R_3S_{3.92}$
37	Grüneau Mine, Siegen	41.09	0.63	54.30	3.98		$R_3S_{3.83}$

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14. Smith, L., and Brush, G. J., same as No. 9.
15. Shannon, Earl V., same as No. 2.
16. Johannson, K., same as No. 5.
17. Johannson, K., same as No. 5.
18. Laspeyres, H., *Zeits. Kryst.*, vol. **19** (1891), p. 19.
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28. Lix, Henry W., *Thesis.*, *Univ. Mo.*, **1932**.
29. Wolf, G., *Beschr. Bergrev. Hamm* (**1885**), p. 34.
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31. Short, M. N., and Shannon, Earl V., *Am. Mineral.*, vol. **15** (1930), pp. 1–22. For name see Lindgren, W., *Econ. Geol.*, vol. **19** (1924), p. 318.
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34. Laspeyres, H., *Jour. Prak. Chem.*, vol. **14** (1876), p. 397.
35. Laspeyres, H., *Jour. Prak. Chem.*, vol. **14** (1876), p. 397.
36. Laspeyres, H., *Jour. Prak. Chem.*, vol. **14** (1876), p. 397.
37. Laspeyres, H., *Jour. Prak. Chem.*, vol. **14** (1876), p. 397.

Most of the above analyses are more readily accessible in one of the following:

Doelter, C., *Handbuch der Mineral chemie*, vol. **4**, pt. 1 (1926), pp. 645–657, 702 (violarite).

Hintze, C., *Handbuch der Mineralogie*, vol. **1**, pt. 1 (1904), pp. 957–966.

Dana, E. S., *System of Mineralogy*, 6th Ed. (**1909**), pp. 75–79.

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For the most part, the analyses of the minerals are fairly similar, allowing, of course, for the steady decrease in the content of the cobalt and its replacement by the other three metals: nickel, iron, and copper. The quantity of these three metals that replaces the cobalt varies rather widely, and in the past (with some exceptions) they have been regarded as impurities. The various formulae (in which R = Co,Ni,Fe,Cu) suggested for each of the different minerals are as follows:

linnaeite—R_3S_4, $CoS \cdot Co_2S_3$, or $CoCo_2S_4$.
carrollite—R_3S_4, $CuS \cdot Co_2S_3$, or $CuCo_2S_4$.
sychnodymite—R_3S_4, R_4S_5, usually $(Co, Cu, Ni)_4S_5$.
siegenite—R_3S_4, usually $(Ni, Co)_3S_4$.
violarite—R_3S_4, usually $(Ni, Fe)_3S_4$.
polydymite—R_3S_4, also Ni_4S_5, $(Ni, Fe, Co)_4S_5$.

These various formulae were tested by recalculating all the analyses for each mineral, and it was found that the formula R_3S_4 was the best. However, *x*-ray studies of the members of the group (save violarite) show that they have the typical spinel structure; therefore, their formula should be written $R''R_2'''S_4$ (R'' = divalent Co,Ni,Cu,Fe; and R''' = trivalent Co,Ni,Fe). The simpler formula might be used, but it seems better to use the one indicating the molecular structure of the mineral as revealed by *x*-rays. In the above table, the R_3S_4 was used because it indicates briefly how closely each analysis approaches the exact 3:4 ratio. It should be noted that only Co, Ni, and Fe are assigned places in the trivalent group. This is in keeping with the chemistry of these elements as the compound R_3S_4 is known for all of them. No similar salt exists for copper; therefore, when it occurs in the linnaeite group it appears only with the R'' elements.

An inspection of the table reveals five well defined groups of analyses, with a doubtful sixth if sychnodymite is recognized as a separate mineral because of its nickel content. At one end are the dominantly cobalt analyses representing linnaeite, and at the other end the nickel-rich analyses representing polydymite. The copper-rich analyses without nickel are grouped as "carrollite"; for those having some nickel, the name "sychnodymite" has been used. The latter name would seem to be of doubtful value even as a variety name, as the three analyses of it closely resemble those of carrollite, with which it probably belongs. Where both nickel and cobalt are present in somewhat similar amounts, the name "siegenite" is used, and as the cobalt decreases and iron appears with the nickel the mineral is called "violarite." It is conceivable that there should be a mineral having the composition Fe_3S_4, corresponding to the similar salts of cobalt and nickel, but none is known.

Figure 1 presents graphically, and in the same sequence, the composition of the analyses given in the table. The curves for each

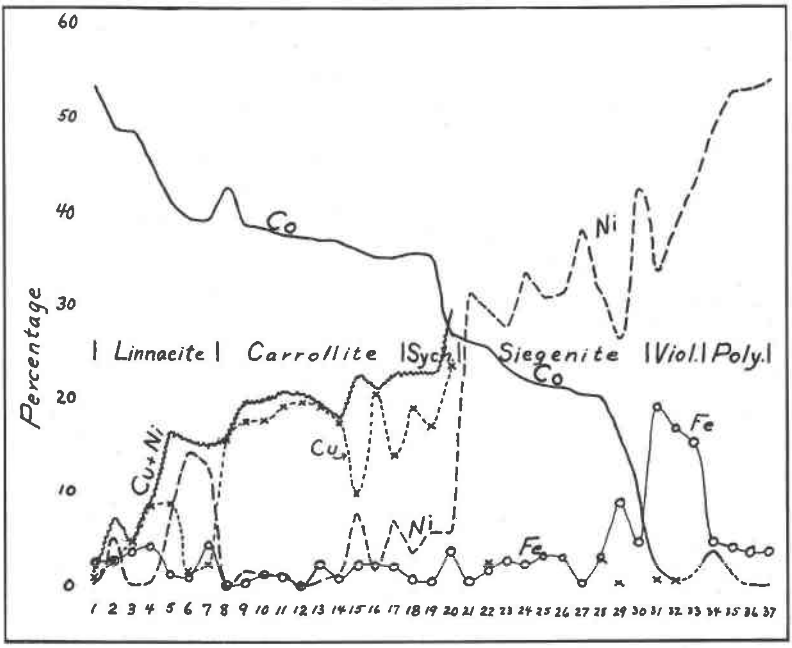

FIG. 1. Curves showing the composition of the linnaeite group by elements. Numbers are those of the analyses in the table.

element (assuming that cobalt is the dominant element) bring out the relationship of the copper to the cobalt and nickel, and the nickel to the cobalt and iron. That the copper is isomorphous with the cobalt is shown by the increase in its content as the cobalt content decreases, the two curves approaching each other steadily. Also, that some nickel replaces the copper is shown by the increase in the nickel content with the copper-content decrease. Where the total amount of copper and nickel are plotted together, as in figure 1, the character of the resulting curve matches nicely with the changes in the cobalt curve. Where nickel entirely replaces copper and equals or exceeds cobalt in amount, as it does in siegenite, the nickel curve mounts steadily as the cobalt content decreases. Near the end of the series, iron enters and replaces a part of the nickel (Fig. 2), forming violarite; but at the end the iron has decreased until only nickel is left. Cobalt and iron appear to have little in common, as iron does not appear in any quantity

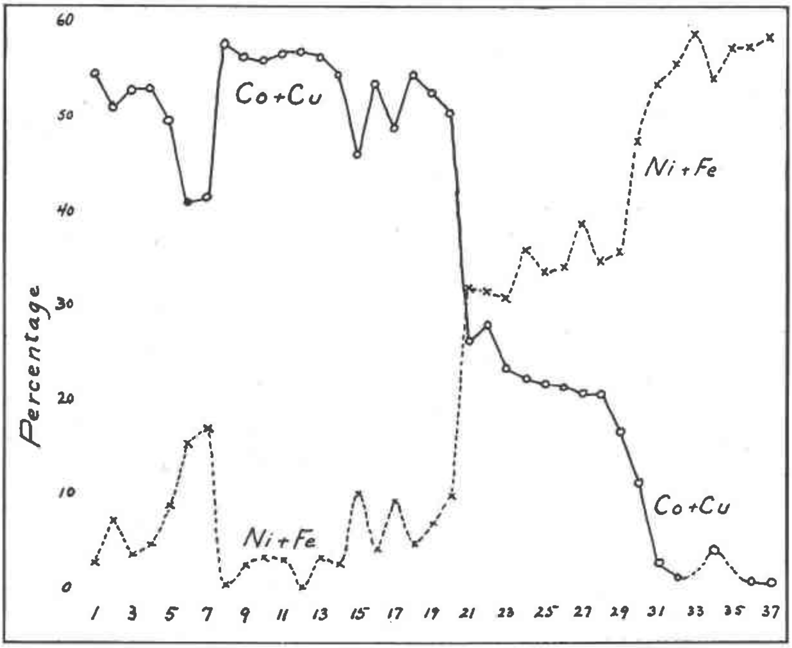

FIG. 2. The paired isomorphous elements: Co+Cu and Ni+Fe, of figure 1. Note the strong similarity of the two curves throughout.

until the cobalt content has fallen below 10 per cent. The appearance of the iron in the nickel-rich members is in perfect keeping with the common association of these two elements in many other minerals. The copper undoubtedly takes the place of the cobalt in the R″ position in the spinel formula. Cobalt is both divalent and trivalent, hence in linnaeite it appears in both forms; but, as the copper enters, it displaces the cobalt as the divalent element. As both nickel and iron are also divalent, varying amounts of both these elements may replace some copper and cobalt. A check of the percentage of copper in carrollite and sychnodymite showed that in only one analysis did the copper content exceed the amount of copper (i.e., 20.52 per cent) that could replace the divalent elements. Johannson (Ref. 5) suggests 15 per cent as the maximum for Cu in linnaeite, and regards carrollite as a mixture (a needless and erroneous deduction). Further evidence that the copper is isomorphous with the cobalt is shown in figure 2, in which total

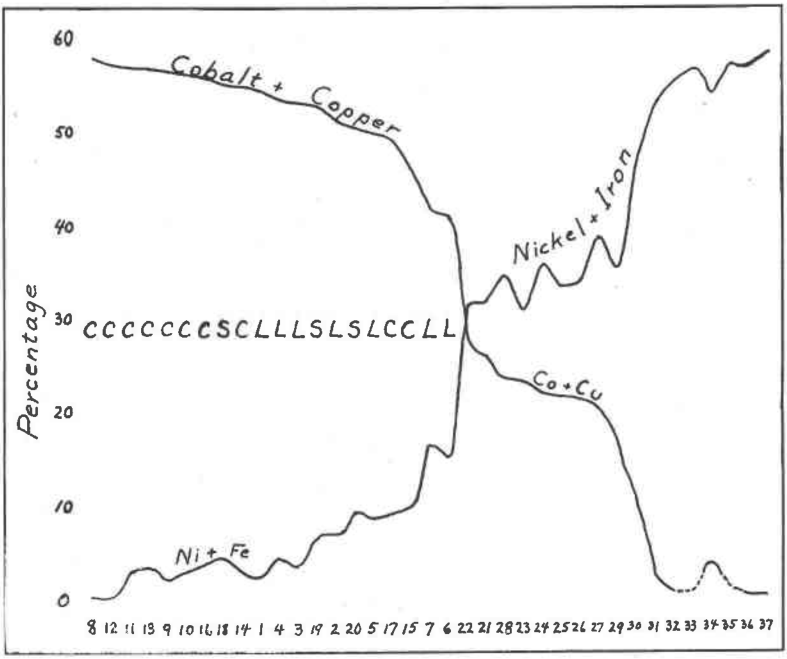

FIG. 3. Curves based upon decreasing Co+Cu content. Note the positions of linnaeite (L) and sychnodymite (S) with reference to the carrollite (C). The Co in polydymite No. 34 is ignored in the arrangement.

cobalt and copper are plotted together as are total nickel and iron. Whenever the first two decrease, the last two increase. As the cobalt content controlled the distribution in the plotting, the matched irregularities in the two curves suggested that the order of plotting in the curves should be according to the sum of the cobalt and copper. This was done for all the analyses, and a curve constructed (figure 3) according to the decrease in cobalt and copper content. This resulted in mixing the position of the first

20 minerals (the first linnaeite analysis appears in position number 11); in short, cobalt and copper are the determining factors in the composition of linnaeite, carrollite, and sychnodymite, which strongly confirms the view that the two elements are isomorphous. The formula would then conform to that of the spinel group and should be written $(Cu,Co)Co_2S_4$. This is in keeping with the chemical studies of Shannon,[6] who showed that carrollite was similar to linnaeite and that copper, nickel, and iron were also doubtless isomorphous with the cobalt.

The sharp change from the copper-bearing linnaeites to the nickel-rich siegenite indicates that the latter should be ranked as a species instead of being called a variety of linnaeite. The curves indicate a fair uniformity in the composition of siegenite. Passing from siegenite to violarite, cobalt disappears and iron replaces it in the formula. Polydymite is at the end of the series and is a nearly pure nickel sulfide, but still contains some iron and traces of cobalt isomorphous with the nickel.

The relationships of the members of the group are perhaps more clearly shown by figure 4 which is based upon the average analysis of each mineral (sychnodymite is averaged with carrollite). The curves for Co+Cu and for Ni+Fe show that as the quantity of one pair of metals decreases it is accompanied by an increase in the amount of the other two. Linnaeite shows a greater departure from the ideal Co_3S_4 (indicated by X) than any member. The analyses show that all four elements are present. Carrollite closely approaches the ideal copper-cobalt sulfide, and polydymite does likewise for the nickel sulfide. The chemical affinities of the four elements and the dominant isomorphous pairs are clearly shown by the curves.

This interpretation of the members of the linnaeite group as an example of an isomorphous series of the four elements finds further support in the *x*-ray studies which have been made of them. The statement is made in the 1932 edition of Dana-Ford's *Textbook of Mineralogy* (page 430) that "*x*-ray study shows practically identical structure in linnaeite, polydymite and sychnodymite. Structure is face-centered cube." Studies made by de Jong and Hoog[7] show that carrollite has the same spinel structure as

[6] Shannon, Earl V., The Identity of Carrollite with Linnaeite, *Am. Jour. Sc.*, vol. **211**, 1926, p. 488.

[7] de Jong, W. F., and Hoog, A., *Zeits. Krist.*, vol. **66**, 1927, pp. 168–71.

linnaeite and sychnodymite, which definitely correlates it with the other members of the group. Holgersson[8] definitely added siegenite to the group by his x-ray studies in 1929. Thus, the only mineral of the group not definitely shown by x-ray analysis to possess the

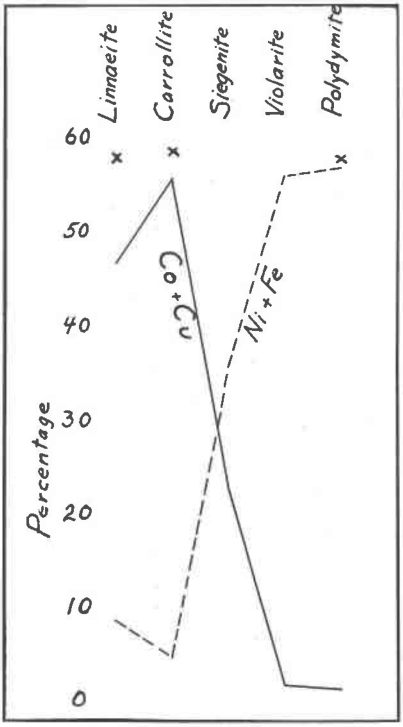

FIG. 4. Average analysis of the five major members of the linnaeite group (sychnodymite is averaged with carrollite, where it belongs).

spinel structure is violarite, and its composition strongly indicates its possessing it.

The atomic radii of these four elements are so close that isomorphism should be expected. According to Neuburger[9] they are, in Ångström units, Fe=1.259, Co=1.256, Ni=1.243, Cu=1.275.

[8] Holgersson, Sven, *Chem. Zentr.*, vol. **1**, 1929, pp. 372–3.

[9] Neuburger, M. C., Gitterkonstanten für 1931, *Zeits. Krist.*, vol. **80**, 1931, pp. 126–127.

Wyckoff, R. W. G. has similar data in the second edition of his *The Structure of Crystals*, **1931**, pp. 192–193.

These values would make it possible for them to replace each other within a crystalline structure. The analyses show, however, that such replacement has been restricted dominantly to certain pairs, with copper and iron the subordinate elements. The door was open for an extremely variable group of replacements, which, for the most part, were restricted to these paired groups, indicating that either the composition of the solution (in which one or two elements predominated) was a controlling factor, or that isomorphism is a last resort in mineral formation. The fact that the mineral members of this group occur alone favors the first interpretation.

However,[10] recent studies of the spinel structure by Barth and Posnjak[11] have revealed the fact that there are two structural arrangements within the true spinel group, one with fixed positions for the ions and the other with variable positions. In the latter (for which Barth and Posnjack suggest the term, "cells with variate atom equipoints"), "different atoms may partly replace one another in structurally equivalent positions of a crystal." The fixed spinel structure corresponds to $XY_2S_4(R''R_2'''S_4)$ in the linnaeite group, and $YXYS_4$ is the arrangement in the variate atom equipoint group. As noted above, the study of the available chemical analyses of the members of this group favored the formula XY_2S_4 as being best suited to the chemical relationships of the four elements (Fe,Co,Ni,Cu). The study showed, also, that the atomic radii would permit any element to isomorphously replace another. It is, of course, perfectly possible to apply the type formula of the variate spinel group to this group of sulfides but there does not appear to be any reason, at present, for doing so. If *x*-ray studies showed that violarite, for example, belonged in the variate group, its formula would be written $NiFeNiS_4$ instead of $FeNi_2S_4$. Nothing seems to be gained by this change. The linnaeite group would seem to offer an excellent opportunity to make an *x*-ray study of the sulfide members of the spinel group, and to determine, if possible, whether the two spinel groups are

[10] The writer is indebted to Dr. George Tunell of the Geophysical Laboratory for calling his attention to the new interpretation of the spinel structure and for suggestions as to its application to the linnaeite group.

[11] Barth, Tom. F. W., and Posnjak, E., The Spinel Structure: An Example of Variate Atom Equipoints: *Jour. Wash. Acad. Science,* vol. **21,** 1931, pp. 255–258.

Barth, Tom. F. W., and Posnjak, E., Spinel Structures: With and Without Variate Atom Equipoints: *Zeits. Krist.* (A) Band **82,** 1932, pp. 325–341.

present. Dr. Tunell[12] expressed himself regarding such a study as follows: "On looking up the scattering powers of copper, nickel, and cobalt I find that they are so nearly alike that it will not be possible to discriminate the two structure types in compounds of these elements."

Dr. Wyckoff of the Rockefeller Institute for Medical Research has also expressed the opinion[13] that the "distinction (of the two classes of spinel structures) would have no bearing on the structure of linnaeite considered basically as Co_3S_4." These two opinions indicate that as far as the minerals included in this study are concerned, the fixed spinel type may be adopted as their structural type.

Summary

This study of the chemical composition of the best analyses available for the various members of the linnaeite group has furnished, it is believed, evidence that all members of the group should be represented by the general formula $R''R_2'''S_4$. The four elements Co, Ni, Fe, and Cu are isomorphous, but copper, only, as a divalent element. The atomic radii of the four elements are so nearly identical that such isomorphism is easily possible. The name "Carrollite" ($CuCo_2S_4$) is preferred for those minerals rich in copper, and "Sychnodymite" might very well be dropped, even as a variety name. *X*-ray studies of all the members, except violarite, show that they have the spinel structure type, and give further proof that the several minerals in the group: linnaeite, carrollite (sychnodymite), siegenite, probably violarite, and polydymite have the same type formula. It appears doubtful whether further *x*-ray studies would contribute any more information regarding the structures of the group.

[12] In a letter to the writer.

[13] In a letter to the writer.