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Ferroan carrollites, cobaltian violarites, and other members of the linnaeite group: $(Co,Ni,Fe,Cu)_3S_4$

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SUMMARY. Electron microprobe analyses and X-ray data are given for iron-rich carrollites, cobaltian violarites, and other members of the linnaeite group. The iron-rich carrollites (8.5 wt% Fe) occur as an unmixed phase in a copper linnaeite host from the Zambian Copperbelt. Primary and secondary cobaltian violarites are reported from Rhodesia and Australia respectively with the latter recording up to 19.2 wt% Co. A diagrammatic review is given of the extremes of composition reported within the group together with the more reliable cell sizes.

THE term linnaeite group is here restricted to include the following species:

Carrollite $(Co_2Cu)_3S_4$	Polydymite Ni_3S_4
Linnaeite Co_3S_4	Violarite $(Ni, Fe)_3S_4$
Siegenite $(Co\ Ni)_3S_4$	*Greigite Fe_3S_4

In addition cobalt-bearing violarites $(Co,Ni,Fe)_3S_4$ are common and copper-bearing siegenites $(Cu,Ni,Co)_3S_4$ have been termed fletcherites (Craig and Carpenter, 1977). Although carrollite and violarite (usually secondary after pentlandite) and, to a lesser extent, siegenite are the most common members of the series, the term linnaeite group is preserved for historical reasons. Linnaeite *sensu stricto* Co_3S_4 in fact appears to be the least positively reported of all the varieties within the group.

A phase more copper-rich than carrollite $(Co_2Cu)_3S_4$ on the Cu_3S_4-Co_3S_4 join would imply a Cu^{3+} oxidation state (Vaughan and Craig, 1978), so that a Cu_3S_4 end member is unlikely. Greigite is somewhat anomalous within the group both in terms of the nature of its occurrence and its structure. It is generally of a low-temperature sedimentary, metastable origin although Radusinovic (1966) and Gruzdev *et al.* (1970) have reported hydrothermal occurrences. It also has a considerably larger cell size than any of the other members. Because of its distinctly different electronic structure, solid solution between the iron and cobalt end members is virtually non-existent (Vaughan and Craig, 1978). Ostwald (1978), however, has recently reported iron linnaeites with up to 10.2 wt% Fe, as well as cupriferous violarites with a recorded maximum of 16.2 wt% Cu. Members in all four ternary systems therefore in the Co_3S_4-Ni_3S_4-Fe_3S_4-Cu_3S_4 tetrahedron have been reported. Previous distributions of various compositions are illustrated in Vokes (1967), Vaughan *et al.* (1971), Moeskops (1975), and Vaughan and Craig (1978).

Materials and techniques. Except where acknowledged all samples were collected by the author. Determinations of the cubic cell size were carried out on a 114.5 mm diameter Gandolfi or Debye-Scherrer camera with silicon as an internal standard. A two-hour exposure using an iron-filtered cobalt tube rated at 30 kV and 60 mA proved adequate to give well-resolved doublets in the back reflection region, except in the case of the secondary violarites and polydymites. The corrected values were extrapolated according to the method of Nelson and Riley (1945) to give the lattice parameter.

Electron microprobe analysis determinations were carried out on a JEOL instrument using a beam diameter of 2-3 μm diameter generated by an accelerating voltage of 25 kV, giving a specimen current of about 80 nA. Pyrite was used for sulphur standard and pure metals for Co, Ni, Cu, and Fe. Mass absorption, atomic number, and secondary fluorescence corrections were applied to all raw data.

Results

Ferroan carrollites. Iron-rich carrollites are reported exsolving from a copper linnaeite host (fig. 1) found in the Rhokana south orebody of the

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* Fe_3S_4 was originally described by Doss (1911, 1912*a*, 1912*b*) as melnikovite and confirmed by Polushkina and Sidorenko (1963, 1968) as a cubic Fe_3S_4, identical with material described as greigite by Skinner *et al.* (1964). In 1968, because the name melnikovite from 1912 to 1963 was commonly used to designate a wide variety of poorly crystallized iron sulphides, the Commission of New Mineral and Mineral Names decided to retain the name greigite (Fleischer, 1969).

TABLE I. *Electron microprobe analyses and cell parameters for exsolved iron-carrollites and cupriferous linnaeite hosts from the Rhokana South orebody*

	Iron-rich Carrollites							Cupriferous Linnaeite						
	Wt%													
Sample	Co	Cu	Fe	Ni	S	Total	*a* Å	Co	Cu	Fe	Ni	S	Total	*a* Å
2730	39.9	10.2	8.4	—	41.5	100.0*	9.519	47.9	7.5	2.3	0.4	41.5	99.6*	9.439
2731	40.2	9.9	8.6	0.1	41.0	99.8	9.514	49.0	6.8	1.8	1.1	40.6	99.3	9.433
2732	40.2	10.2	8.2	—	41.7	100.3*	9.516	47.9	7.6	2.2	0.7	41.9	100.3*	9.437
2733	41.4	10.1	8.3	0.1	40.4	100.3	9.508	49.9	7.0	1.6	0.6	40.8	99.9	9.440

* Average of six analyses.

Average stoichiometry for fourteen analyses:

$(Cu_{0.5}Fe_{0.5})_{1.0}Co_{2.1}S_{4.0}$ $(Cu_{0.4}Fe_{0.1})_{0.5}Co_{2.5}S_{4.0}$

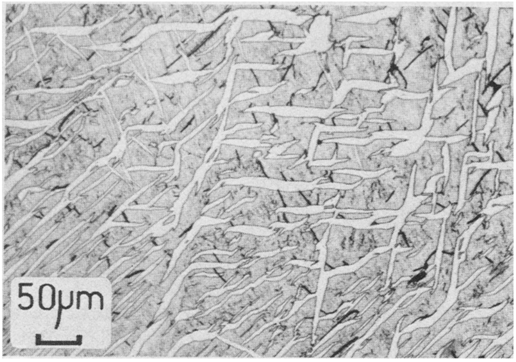

FIG. 1. Ferroan carrollites unmixing from a cupriferous linnaeite host. Sample from Rhokana south orebody—etched 1:1 HNO_3, 40 secs.

Zambian Copperbelt. They are associated with chalcopyrite. These exsolution textures were observed by Hills (1970) in ore from the near-by Chibuluma deposit, but their identity was inferred from a partial wet chemical analysis of the total intergrowth and X-ray diffraction data. Electron microprobe analysis was not conclusive and only the iron values were given. Unless this material is etched the texture can easily be misinterpreted as a homogeneous 'carrollite', but etching with 1:1 HNO_3 for 30–60 seconds distinguishes the two phases. The host (cuprian linnaeite) is more prone to etching and the exsolved iron-rich carrollite is slightly anisotropic.

Electron microprobe analyses (Table I) were restricted to areas showing the coarser intergrowths as the exsolved (smaller) phase can reach 35 μm in width, but only average 5 μm. The host measures at least twice this size. The X-ray powder diffraction data for both phases is given in Table II, with both patterns being well separated on the same film, but with the intensities for the cuprian linnaeite reflections being proportionately stronger.

Cobaltian violarites. Secondary cobaltian violarites (after cobaltian pentlandite) are present in ore samples from Mount Colin and Mount Calcite in North West Queensland as well as from Hømse and Feøy in Norway. Primary cobalt violarite is

TABLE II. *X-ray diffraction data for exsolved ferroan carrollite and cupriferous linnaeite host. Sample* 2732, *Rhokana South orebody*

Ferroan carrollite		Cupriferous linnaeite	
hkl	d_{obs}	*I*	d_{obs}
111	5.51	20	5.50
220	3.35	60	3.34
311	2.862	100	2.850
400	2.373	80	2.363
422	1.931	20	1.921
511,333	1.830	70	1.815
440	1.681	90	1.668
620	—	10	1.491
533	1.448	20	1.438
444	1.370	20	1.362
711,551	—	5	1.321
731,553	—	30	1.228
800	1.189	30	1.179
751,555	1.098	30	1.089
840	1.063	30	1.055
931	0.9976	20	0.9892
844	0.9714	50	0.9634
951,773	0.9201	40	0.9126

Extrapolated cell size
9.516 Å ± 0.003 9.437 Å ± 0.003
Intensities estimated visually

TABLE III. *Cobaltian violarites: Electron microprobe analyses and cell parameters*

			Wt %						Ions on basis of four sulphurs		
No.	Location	Grain	Ni	Fe	Co	S	Total	*a* Å	Ni	Fe	Co
2620	Mount Colin N.W. Queensland	1	24.2	23.2	11.2	40.9	99.5	—	1.3	1.3	0.6
		2	24.3	24.0	11.3	40.3	99.9	—	1.3	1.4	0.6
		3	23.9	23.0	11.4	41.3	99.6	—	1.3	1.3	0.6
		4	23.0	19.4	14.2	43.4	100.0	—	1.2	1.0	0.7
		5	22.8	20.4	14.9	41.7	99.8	—	1.2	1.1	0.8
		6	22.4	19.4	15.1	43.1	100.0	—	1.1	1.0	0.8
		7	24.5	16.3	16.5	41.8	99.1	—	1.3	0.9	0.9
		8	22.5	18.6	17.1	41.8	100.0	—	1.2	1.0	0.9
		9	22.6	18.4	17.1	42.6	100.7	—	1.2	1.0	0.9
		10	22.1	17.8	17.6	42.5	100.0	—	1.1	1.0	0.9
		11	22.7	15.8	19.0	41.9	99.4	—	1.2	0.9	1.0
		12	23.8	15.5	19.2	42.0	100.5	9.395	1.2	0.9	1.0
3027	Mount Calcite	1*	25.1	16.5	16.8	41.6	100.0	9.405	1.3	0.9	0.9
3096	Madziwa Mine	1*	31.0	18.1	8.9	42.6	100.6	9.436	1.6	1.0	0.5
3018	Hømse	1**	21.3	31.2	6.4	41.6	100.5	9.461	1.1	1.7	0.3
3295	Madziwa Mine	1**	32.8	19.8	5.3	42.4	100.3	9.438	1.7	1.1	0.3
3017	Feøy	1	28.2	27.3	2.1	42.0	99.6	9.449	1.5	1.4	0.1

* Average of three analyses. ** Average of seven analyses.

described from the Madziwa Mine (formerly the Dry Nickel Mine), Bindura, Rhodesia (Zimbabwe).

At Mount Colin cobaltian violarites showing a replacement texture occur as grains up to 100 μm size within smythite Fe_9S_{11}. Variable cobalt contents were recorded from grain to grain, but not within individual grains. Analyses are listed in Table III and the grain with the highest recorded cobalt value of 19.2 wt % gave a cell size of 9.395 Å. This is somewhat lower than either previously recorded violarites or cobaltian violarites with lesser cobalt values. A decrease in cell size is therefore indicated as Co, Fe, and Ni contents approach similar values. The associated smythite contained nickel and cobalt and average values of 0.5 wt % Ni and 0.2 wt % Co were obtained. The cobalt content of co-existing cobaltian pentlandites (11.0 wt % Co) previously described (Riley, 1977) show a constant value in contrast to the grain to grain variations found in the cobaltian violarites. The lower values reported, however, do correspond to the loose correlation reported by Misra and Fleet (1974) between the cobalt content of genetically related co-existing violarite and pentlandite.

The Mount Calcite, Hømse, and Feøy cobaltian violarites show similar occurrences as irregular-shaped grains up to 200 μm included in hexagonal pyrrhotine from Mount Calcite and Hømse and monoclinic pyrrhotine from Feøy.

The primary cobaltian violarite from the Madziwa Mine occurs as coarse euhedral crystals associated primarily with polydymite and also chalcopyrite, pyrite, and secondary violarite in an ultra-basic host rock (fig. 2). The X-ray diffraction data is listed in Table IV.

TABLE IV. *X-ray powder data for primary cobaltian violarite, Madziwa mine* (8.9 *wt* % Co). Sample 3096

hkl	d_{obs}	*I*	*hkl*	d_{obs}	*I*
111	5.47	20	711 551	1.320	5
220	3.34	60	642	1.256	10
331	2.840	100	731 553	1.227	30
400	2.355	80	800	1.179	30
442	1.920	20	822 660	1.112	5
551 333	1.814	70	751 555	1.089	30
440	1.666	90	840	1.055	30
531	1.596	5	931	0.9890	20
620	1.491	10	844	0.9629	50
533	1.437	20	1020 862	0.9252	10
622	1.420	5	951 773	0.9121	40
444	1.360	20			

Intensities estimated visually.

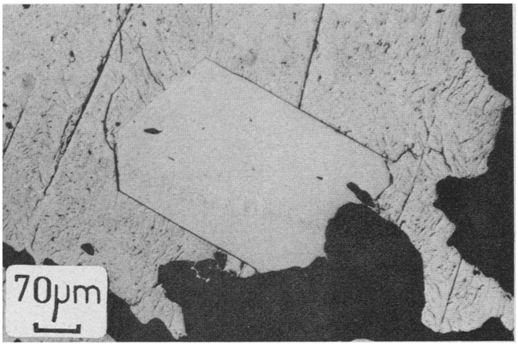

FIG. 2. Euhedral primary cobaltian-violarite crystal within polydymite. Madziwa mine, Rhodesia.

Other linnaeite group members. Electron microprobe analyses and cell sizes are given in Table V for other members of the linnaeite group. Of particular interest is the composition and occurrence of sample 4034 from the Gladhammar Mine, Sweden. This is nickel-rich carrollite showing a graphic intergrowth with chalcopyrite (fig. 3). Sample 4750 from Kilembe, Uganda, is an iron-rich siegenite which may have been previously confused with the classic 'linnaeites' described from that locality in the textbooks. The polydymite from the Madziwa Mine (3295) shows poor polishing characteristics but excellent cleavage (fig. 4).

Apart from the secondary violarites and polydymite, well-resolved X-ray patterns were obtained on all material and data from those showing extreme compositions are listed in Table VI for comparison. Fig. 5 shows the distribution of some reported phases of extreme compositions in the linnaeite system, together with those reported in this paper. Cell sizes are also given where reliable values have been obtained. Tie lines have not been used in the figure and in plotting compositions only the three major cations, or the two major ones and the greater of the minor ones present have been used to place each member in one of the four systems. Up to the present time no phase has been reported with four cations as major components, which would place it wholly within the tetrahedron.

The cell sizes do show some general trends but no attempt has been made to contour the figure while insufficient data is available. This applies particularly to those reported occurrences of extreme composition. Of the values given only the carrollite 'A' of Clark (1974) with a cell size of 9.468 Å and 14.2 wt % Cu and the polydymite of Hoffmann *et al.* (1963) with a cell size of 9.447 Å seem to be at some variance with the general trends reported so far.

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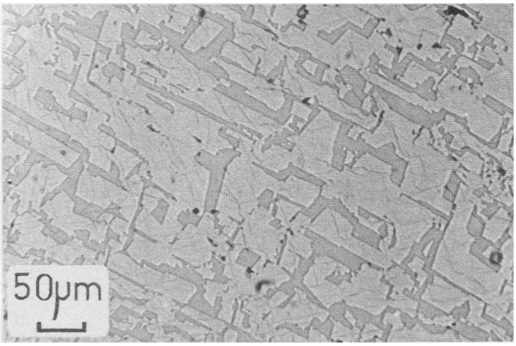

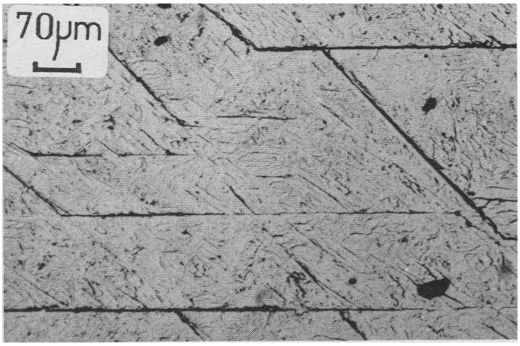

FIGS. 3 and 4. FIG. 3 (*left*). A graphic intergrowth of chalcopyrite (dark grey) and siegenite host. Gladhammar mine, Sweden. FIG. 4 (*right*). Polydymite showing good cleavage and poor polishing characteristics. Madziwa mine, Rhodesia.

TABLE V. *Electron microprobe analyses and cell sizes for linnaeite group members*

	Wt%							Ions based on four sulphurs			
	Co	Cu	Ni	Fe	S	Total	a Å	Co	Cu	Ni	Fe
Carrollite											
2737 Zambian Copperbelt	38.2	20.1	—	0.9	40.6	99.8	9.478	2.1	1.0	—	0.1
2736 Zaire	39.0	20.0	0.1	0.5	39.9	99.5	9.474	2.1	1.0	—	—
4502 Success Mine, N.W. Queensland	39.6	18.9	1.3	0.1	40.8	100.7	9.463	2.1	1.0	—	—
2453 Mt. Gunson, S. Australia	37.0	18.4	3.5	0.2	40.9	100.0	9.466	2.0	0.9	0.2	—
3181 Lady Annie Mine, N.W. Queensland	39.7	18.1	1.5	0.5	40.3	100.1	9.456	2.1	0.9	0.1	—
2734 Nkana Mine, Zambia	42.3	17.5	0.4	—	39.8	100.0	9.461	2.3	0.9	—	—
2456 Mt. Gunson, S. Australia	37.8	16.9	4.3	0.1	41.2	100.3	9.467	2.0	0.8	0.2	—
2367 Nkana Mine, Zambia	42.8	12.7	—	3.3	41.5	100.3	9.467	2.3	0.6	—	0.2
4034 Gladhammar, Sweden	37.7	12.8	8.0	0.2	41.7	100.4	9.440	2.0	0.6	0.4	—
Siegenite											
3299 Mine la Motte, Missouri	23.8	—	31.9	2.4	41.7	99.8	9.408	1.3	—	1.7	0.1
3298 Müsen, Germany	20.7	0.2	35.3	1.4	42.1	99.7	9.421	1.1	—	1.8	0.1
5010 Shinkolobwe, Zaire	19.6	4.0	34.2	0.6	41.7	100.1	9.442	1.0	0.2	1.8	—
5011 Kambowe, Zaire	19.3	3.8	33.9	0.5	42.0	99.5	9.442	1.0	0.2	1.8	—
4750 Kilembe, Uganda	24.2	0.1	27.5	7.0	41.5	100.3	9.410	1.3	—	1.5	0.4
Polydymite											
3295 Madziwa Mine, Rhodesia	0.5	—	54.4	3.0	41.9	99.8	9.471	—	—	2.8	0.1
Violarite											
3177 Agnew Mine, W. Australia	1.0	—	29.0	27.9	42.2	100.1	9.458	—	—	1.5	1.5
3241 Kambalda, W. Australia	—	—	33.6	24.5	42.0	100.1	9.452	—	—	1.8	1.4

TABLE VI. *X-ray diffraction data for linnaeite group members*

	d_{obs}									
hkl	1	2	3	4	5	6	7	8	9	Intensity
111	5.49	5.45	5.48	5.47	5.45	5.48	5.47	5.42	5.45	20
022	3.35	3.33	3.33	3.33	3.33	3.35	3.34	3.33	3.34	60
113	2.858	2.847	2.843	2.838	2.836	2.853	2.849	2.840	2.846	100
004	2.368	2.358	2.358	2.356	2.351	2.367	2.362	2.356	2.357	80
224	1.932	1.919	1.919	1.919	1.918	1.921	1.919	1.920	1.918	20
115,333	1.823	1.814	1.816	1.815	1.810	1.823	1.819	1.811	1.814	70
044	1.674	1.667	1.667	1.666	1.662	1.674	1.671	1.666	1.668	90
135	1.603	1.591	1.596	1.592	1.591	1.601	—	—	—	5
026	1.498	1.490	1.492	1.488	1.487	1.498	1.504	—	—	10
335	1.445	1.438	1.440	1.434	1.433	1.444	1.449	—	—	20
444	1.367	1.360	1.363	1.356	1.357	1.367	—	—	1.359	20
117,155	1.326	1.320	1.323	1.316	1.315	—	—	—	1.225	5
137,355	1.233	1.228	1.228	1.225	1.225	1.233	—	—	—	30
008	1.184	1.179	1.179	1.176	1.176	1.184	1.182	—	1.178	30
006,228	1.116	1.111	1.112	1.108	1.108	—	—	—	1.107	5
157,555	1.094	1.089	1.090	1.087	1.087	1.094	—	—	1.086	30
048	1.059	1.055	1.056	1.052	1.052	1.059	—	—	1.053	30
931	0.9933	0.9893	0.9901	0.9857	0.9863	0.9926	—	—	—	20
844	0.9670	0.9634	0.9636	0.9599	0.9604	0.9666	—	—	0.9576	50
10.2.0; 862	0.9292	0.9258	0.9259	0.9229	0.9229	—	—	—	—	10
951,773	0.9159	0.9125	0.9128	0.9101	0.9097	—	—	—	—	40

Intensities estimated visually.

1. Carrollite (2736), Zaire.
2. Ni-Carrollite (4034), Gladhammar, Sweden.
3. Cu-Siegenite (5010), Shinkolobwe, Zaire.
4. Siegenite (3299), Mine La Motte, Missouri.
5. Fe-Siegenite (4750), Kilembe, Uganda.
6. Polydymite (3295), Madziwa Mine, Rhodesia.
7. Violarite (3177), Agnew Mine, Western Australia.
8. Co-Violarite (3027), Mt. Calcite, N.W. Queensland.
9. Co-Violarite (2620), Mt. Colin, N.W. Queensland.

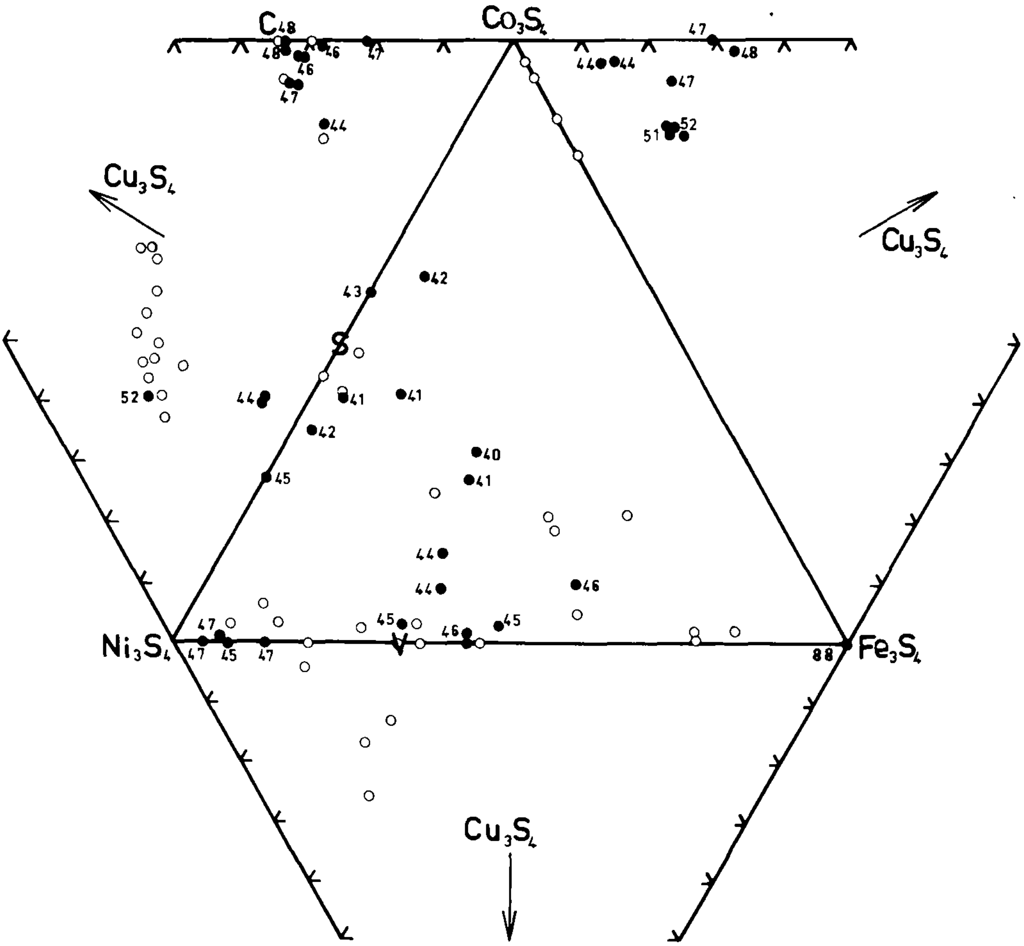

FIG. 5. Distribution and cell size values for members in the tetrahedral system Cu_3S_4-Co_3S_4 (linnaeite)-Ni_3S_4 (polydymite)-Fe_3S_4 (greigite). V = violarite $(Ni_2Fe)_3S_4$, S = siegenite $(Co,Ni)_3S_4$, C = carrollite $(Co_2Cu)_3S_4$. Cell size values are given as 9·—and indicated with solid circles. Open circles represent extreme compositions with no cell size given. Where not mentioned in the text, values were obtained from Craig and Higgins (1975), Imai *et al.* (1973), Petruk *et al.* (1969), Speer and Martin (1974), Stoinova (1975), Stumpfl and Clark (1964), Tatsumai *et al.* (1975), and Williams (1968).

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