

Linnaeite series minerals from the Kalgoorlie district, Western Australia

J. OSTWALD

The Broken Hill Proprietary Company Limited, Central Research Laboratories,
Shortland, N.S.W. 2307, Australia

SUMMARY. Five members of the linnaeite series of sulphides linnaeite Co_3S_4 , siegenite $(\text{Co}, \text{Ni})_3\text{S}_4$, carrollite Co_2CuS_4 , violarite Ni_2FeS_4 , and polydymite Ni_3S_4 occur in nickel-sulphide-mineralized rocks in areas adjacent to the Kambalda and Scotia deposits of the Kalgoorlie district, Western Australia. Linnaeite, siegenite, carrollite, and polydymite occur in trace amounts as disseminated grains and veinlets. Violarite is also found as disseminations but its major occurrence is in the supergene enriched zones of the ore deposits. Aspects of their mineralogy, including mode of occurrence, general mineragraphy, reflectance at 546 nm, 589 nm and 644 nm, microhardness, and electron probe microanalyses are described.

MINERAGRAPHIC and electron-probe micro-analysis studies carried out on specimens of nickel-sulphide-mineralized rocks from areas adjacent to the Kambalda and Scotia nickel deposits of the Kalgoorlie district, Western Australia (Ostwald, 1973), have shown the presence of five members of the linnaeite series. The minerals identified were linnaeite Co_3S_4 , siegenite $(\text{Co}, \text{Ni})_3\text{S}_4$, carrollite Co_2CuS_4 , violarite Ni_2FeS_4 , and polydymite Ni_3S_4 . Although the linnaeite series minerals are of worldwide occurrence, especially in cobalt and nickel ore bodies, the Kalgoorlie nickel belt may be unique in containing such a variety of these minerals.

The linnaeite series minerals are unevenly developed in the areas. Supergene enriched ore at both Kambalda and Scotia is composed essentially of violarite and gel pyrite, and Woodall and Travis (1969) estimated that in the Durkin shoot, at Kambalda, the normally rare violarite makes up over 50% by weight of the estimated one million tons of supergene ore. In addition to these massive developments, disseminated violarite in the country rocks of the deposits is of widespread occurrence.

In contrast, linnaeite, siegenite, carrollite, and polydymite occur typically in trace amounts, in the form of disseminated grains and veinlets in serpentinized ultrabasics and greenschist level meta-

morphics, which form the country rocks of the deposits. The extent to which these minerals occur within the nickel sulphide ore bodies is not known, though none was detected in ore samples investigated by the writer. At the time of writing, the only member of the linnaeite-siegenite-carrollite-polydymite assemblage known to exist in the ores is polydymite, identified by Keele and Nickel (1974) from the Otter shoot, Kambalda.

Some aspects of the mineralogy of the Kalgoorlie district linnaeite series minerals are described in this paper. A detailed discussion of the genesis of the linnaeite minerals will be published separately.

Determinative techniques

All samples investigated in this study were prepared both as thin sections (for determination of general mode of occurrence) and as polished mineragraphic specimens. The latter were mounted in Araldite epoxy resin, faced on a diamond saw, ground on rotating laps using P360, P600, and P1200 SiC papers, and finally polished on Buehler polishers using $1 \mu\text{m}$ α -alumina (on nylon cloth) and $0.5 \mu\text{m}$ γ -alumina (on silk cloth).

Reflectance was measured using a standard Leitz MPV microscope photometer attached to an Orthoplan microscope with EMI photomultiplier with S10 cathode, standard Knott stabilized power supply, and galvanometer readout. The measurements were carried out using interference-band filters transmitting light of 546 nm, 589 nm, and 644 nm. In the absence of NPL calibrated reflectance standards polished surfaces of basal colourless synthetic sapphire set in black wax, blue-black synthetic silicon carbide, Elba pyrite, and silver film on glass were used. The reflectance of these substances at the wavelengths chosen were taken from the papers of Leow (1966), Bowie (1967), and Nayak (1969). Calibration curves were prepared for the three wavelengths and measurements and corrections were carried out following the outline given by Leow (1966).

TABLE I. Reflectance and Vickers microhardness of linnaeite series minerals from the Kalgoorlie district

	VHN kg/mm ²	Reflectance	
		λ nm	Range %
Linnaeite	432-580	546	46.2-46.8
	510 (ave.)	589	46.6-47.1
	sf*	644	46.8-48.2
Siegenite	450-95	546	45.0-45.4
	475 (ave.)	589	45.8-46.5
	P	644	47.2-48.5
Carrollite	370-520	546	43.5-44.2
	450 (ave.)	589	43.6-44.5
	sf	644	44.1-45.4
Violarite	195-408	546	44.2-45.0
	304 (ave.)	589	45.5-46.7
	f	644	48.6-49.4
Polydymite	380-440	546	48.5-49.0
	410 (ave.)	589	49.6-50.0
	sf	644	51.8-52.2

* Quality of indentation. p = perfect.
sf = slightly fractured. f = fractured.

Microhardness determinations were carried out on a Leitz Miniload hardness tester using a Vickers diamond indenter, a standard load of 100 grams, and an indentation time of 15 seconds. Ten measurements were made on each specimen. The ranges quoted in Table I are minimum and maximum measurements of a number of grains deduced by electron-probe analyses to belong to the same linnaeite mineral. Quality of indentation is indicated in Table I for each mineral.

Electron probe microanalysis (EPMA) determinations were carried out on an ARL instrument with take-off angle of 52.5°. Standards used for the determinations were pure metals and oxides, and chemically analysed pyrite for sulphur. Linnaeite mineral samples for various type localities were analysed under similar instrumental conditions as an aid in the determination of the Kalgoorlie district minerals. Counting data for each determination were corrected for absorption (Duncumb and Shields, 1966), atomic number effect (Duncumb and Reed, 1968), and fluorescence (Reed, 1965). Analytical accuracy is probably $\pm 2\%$ for major elements and $\pm 10\%$ for minor elements.

Linnaeite series mineralogy

Data on the reflectance and Vickers microhardness of the Kalgoorlie district linnaeite minerals are given in Table I, and electron probe microanalyses

in Table II. Brief notes on the individual mineral occurrences are given below.

Linnaeite. The type mineral of the linnaeite M_3S_4 series occurs in the Scotia area as disseminations in graphitic slates and biotite schists probably equivalent to those of the footwall of the ore body, as described by Christie (1975). The mineral occurs as irregular veinlets often 0.1 mm to 0.2 mm in thickness filling fractures and shears in graphitic slate and as isolated grains in the schists. The specimens examined also contained nickeliferous mackinawite, valleriite, chalcopyrite, covellite, nickeliferous gel pyrite, and violarite. The presence of these latter minerals indicated supergene alteration. The linnaeite is creamy-white in colour in contrast to adjacent golden-brown mackinawite. In the slates the parallel-sided veinlet often shows a single cleavage direction. The mineral is always isotropic. Its paragenetic relationship to the accompanying sulphides is not definite but it appears to be contemporaneous with mackinawite and earlier than violarite and gel pyrite.

Siegenite was identified by mineragraphy and EPMA in the form of disseminated grains in serpentinites of the Kambalda area. The siegenite grains are either monomineralic or, more commonly, occur as composite grains associated with millerite or carrollite. A sample of siegenite from

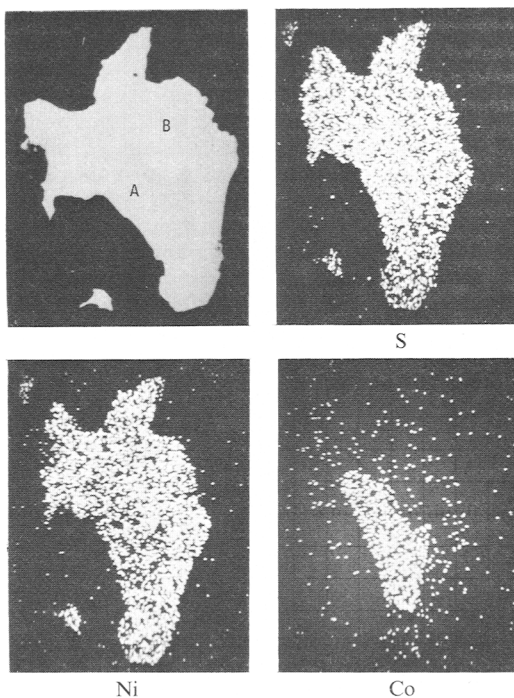


FIG. 1. Optical micrograph of composite siegenite (A) millerite (B) grain and EPMA area scans for S, Ni, and Co.

TABLE II. *Electron-probe analyses and atomic ratios to 4 sulphur for linnaeite-series minerals from the Kalgoorlie district and from certain typical localities*

		Ni	Fe	Co	Cu	S	Ni	Fe	Co	Cu	Σ	
Linnaeite	S08	0.2%	10.2%	47.8%	n.f.	41.8%	0.01	0.18	0.81	0.00	3.0	n.f., not found
	S16	0.8	2.9	54.2	n.f.	42.1	0.01	0.06	0.93	0.00	2.9	* Katanga
	S24	0.4	6.5	50.5	n.f.	42.6	0.01	0.12	0.87	0.00	2.9	† Mine La Motte
	S28	0.5	1.2	56.8	n.f.	41.5	0.01	0.02	0.97	0.00	3.0	‡ Kambone
	Kt*	n.f.	2.7	54.4	n.f.	42.9	0.00	0.05	0.95	0.00	2.9	Siegen
Siegenite	K33	31.2	0.7	23.7	n.f.	44.2	0.56	0.02	0.42	0.00	2.8	S, Scotia area
	K39	28.8	2.2	21.9	0.4	46.7	0.54	0.05	0.41	0.01	2.5	K, Kambalda area
	MM†	28.9	2.3	28.7	n.f.	40.2	0.48	0.04	0.48	0.00	3.2	Σ, sum of metal atoms
Carrollite	K33	9.7	2.1	38.8	11.5	40.9	0.17	0.04	0.61	0.18	3.1	
	K76	0.4	0.8	35.9	16.1	46.8	0.02		0.69	0.29	2.4	
	Km‡	0.2	0.6	37.2	20.1	41.7	0.00	0.01	0.66	0.33	3.0	
	Sn	3.6	0.9	35.8	18.8	40.6	0.06	0.02	0.62	0.30	3.1	
Violarite	K05	44.0	15.4	0.9	n.f.	40.1	0.72	0.26	0.02	0.00	3.3	
	K06	35.1	19.4	2.0	n.f.	43.6	0.61	0.35	0.04	0.00	2.9	
	K07	43.8	15.1	1.2	n.f.	40.8	0.72	0.26	0.02	0.00	3.3	
	K08	32.1	25.0	0.5	n.f.	42.4	0.54	0.45	0.01	0.00	3.0	
	K11	27.9	15.0	15.7	n.f.	41.4	0.47	0.27	0.26	0.00	3.1	
	S12	38.2	18.8	0.6	n.f.	42.4	0.65	0.34	0.01	0.00	3.0	
	S23	36.9	19.8	0.1	n.f.	43.1	0.66	0.34	0.00	0.00	2.9	
	S24	12.3	32.7	13.9	n.f.	41.1	0.20	0.57	0.23	0.00	3.2	
Cuprian violarite	S34A	36.5	10.6	0.9	10.8	41.2	0.63	0.19	0.01	0.17	3.0	
	S34B	36.5	14.0	n.f.	8.5	41.0	0.62	0.25	0.00	0.13	3.1	
	S35	34.5	8.7	n.f.	16.2	40.6	0.59	0.16	0.00	0.25	3.1	
Polydymite	S18	47.0	8.3	0.8	1.6	42.1	0.81	0.15	0.02	0.02	3.0	
	K24A	52.9	4.5	0.8	n.f.	41.8	0.91	0.08	0.01	0.00	3.1	
	K24B	52.8	4.5	0.9	n.f.	42.6	0.90	0.08	0.02	0.00	3.1	
	K25A	48.7	5.2	3.4	n.f.	42.7	0.84	0.10	0.06	0.00	3.0	
	K25B	50.4	7.1	n.f.	n.f.	42.5	0.87	0.13	0.00	0.00	3.0	

Specimens collected by the author and described in Ostwald (1973).

Mine La Motte, Madison County, Missouri, U.S.A., was used to assist the mineragraphic identification and was analysed by EPMA for comparison. The Kambalda specimens are similarly optically to specimens described by Wang and Yo (1963) and Petruk *et al.* (1969). The mineral is grey, with a faint pink tint, and is isotropic. Grains up to 0.8 mm in dimension were observed. X-ray area scans for nickel, cobalt, sulphur for a composite grain of millerite and siegenite are shown in fig. 1.

Carrollite occurs with siegenite and millerite as disseminated grains in serpentinites in the Kambalda area. All carrollite grains observed in this study were composite. The carrollite is white, without the definite pink tint of siegenite. Grains up to 0.6 mm were observed. In the investigation type specimens of carrollite (from the Kambone Mine, Congo, and from Siegen, Germany) were used for comparison. The Kambalda mineral is essentially similar in general optical properties to these type locality minerals. The mode of occurrence is ap-

parently unusual, as carrollite usually occurs in a very copper-rich paragenesis associated with chalcopyrite, bornite, and blue copper sulphides (Vokes, 1967).

Violarite. Since the publication of the original paper on the Kambalda deposits by Woodall and Travis (1969) the mineralogy and genesis of violarite, which makes up the bulk of supergene ore in many of the Western Australian deposits, has been examined by a number of authors including Nickel (1973), Nickel *et al.* (1974), Watmuff (1974), and Moeskops (1975). In view of this already extensive literature the present discussion is restricted to a brief compilation of data on a number of aspects of violarite mineralogy, including microhardness, reflectance, cell edge, and chemical composition by EPMA.

Vickers microhardness data for violarite show a wide range of values, probably due to incipient mechanical breaking apart of the coarser violarite along its cleavage. The values shown in Table I were obtained from more compact specimens of

violarite from sulphide veinlets in graphitic slates of the Scotia area. The cell edge (a) of Kambalda violarite was measured by X-ray diffractometry, using silicon as an internal standard. The result obtained, 9.46 ± 0.01 Å, is essentially similar to that published by Nassim (1949) for violarite from St. John's Isle (9.47 Å), and somewhat different from the figure of 9.51 Å obtained from Vermilion Mine violarite by Bannister (1940).

In addition to normal violarite, a cupriferous variety occurs in close association with gel pyrite in some samples of Scotia supergene ore. The violarite has developed as lamellae at interfaces in the gel pyrite and locally has crystallized into larger areas showing its characteristic cleavage traces. Optically, the violarite is indistinguishable from normal violarite but EPMA determinations indicate that it is much higher in Cu and lower in Fe than normal violarite. EPMA analyses and derived formulae for three areas of the Scotia cupriferous violarite are given in Table II, and EPMA X-ray line scans across a grain of the violarite in contact with gel pyrite are shown in fig. 2. The existence of a cupriferous violarite rather than, say, a copper sulphide contaminated normal violarite is demonstrated by the violarite metal/sulphur ratio, and by the close parallelism of Cu and Ni in the line scans, which are 'in phase' rather than alternating. X-ray

diffraction analyses on a sample of the cupriferous violarite gave a general linnaeite group pattern. Cupriferous violarites have previously been described from the Bulong area, some 50 km SE. of Scotia, by Moeskops (1975), though the maximum Cu detected was 3.2% by weight. Moeskops also notes in passing the occurrence of supergene violarites with 'quite a high Cu' content at the Perseverance nickel deposit at Agnew, north of Kalgoorlie. The Cu-Ni minerals described by Watmuff (1975) from the supergene zones of the Mount Windarra deposit are also interesting in this context.

Polydymite occurs as disseminations in ultra-basic rocks in both the Kambalda and Scotia areas. The two occurrences are texturally quite distinct. At Kambalda the polydymite occurs as minute (50 to 100, rarely 200 μm) particles interstitial to antigorite blades. The particles occur alone, or are associated with millerite or pyrrhotine and pentlandite. The Scotia polydymite occurs as contorted and elongate veinlets and smears in talcose serpentinite, in association with chalcopyrite, bornite, chalcosine, and nickeliferous gel pyrite. Optically, the polydymite is yellow without the pinkish tint that appears in the case of violarite and siegenite, and is isotropic.

Discussion

The chemistry of the linnaeite series has been reviewed by Vokes (1967), who noted the existence of three natural groupings, i.e. carrollite-linnaeite, siegenite, and polydymite-violarite, as shown in the diagram in fig. 3. Compositional ranges of violarite, polydymite, siegenite, and linnaeite identified in this study are shown in fig. 4, for comparison.

Of the three groupings, siegenite is the most well defined, occurring half-way between theoretical polydymite (Ni_3S_4) and theoretical linnaeite (Co_3S_4). It is characterized by a limited spread along the Co-Ni join, and by minor content of Cu and Fe, and natural siegenites lie on the Ni-rich side of the 50% Ni, 50% Co point on the Co-Ni join. The Kambalda siegenite analyses (Table II) are consistent with this definition.

Kambalda polydymite also clearly fit Vokes's definition, i.e. an M_3S_4 mineral with no Cu and less than 10% Fe. The Scotia mineral, though it contains more Fe than the Kambalda material and a little Cu, has none of the characteristics of violarite and is here classed as polydymite on the basis of its general mineralogy and high Ni content.

The chemical nature of violarite is less well defined than that of the other linnaeite series minerals. Recently, Buchan and Blowes (1968) tentatively identified three varieties of violarite from the Marbridge No. 2 Mine, Malartic, Quebec, with differing chemical compositions: grey

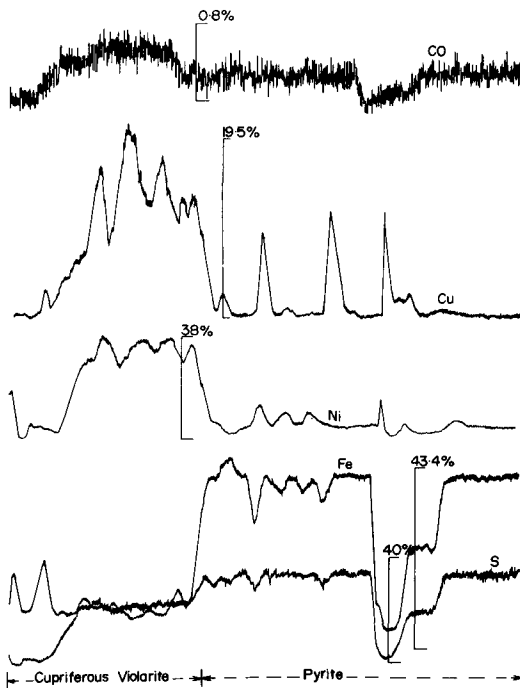
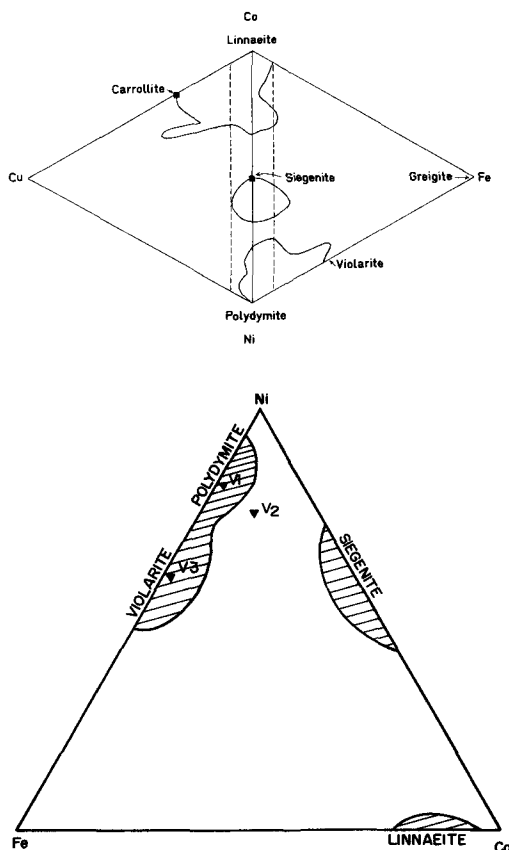


FIG. 2. EPMA line scans for Co, Cu, Ni, Fe, and S across the junction of cupriferous violarite and pyrite.



FIGS. 3 and 4: FIG. 3 (top). Compositional fields of linnaeite series minerals (after Vokes, 1967). FIG. 4 (bottom). Metal proportions of linnaeite series minerals from the Kalgoorlie district, Western Australia.

violarite ($\text{Ni}_{0.84}\text{Fe}_{0.16}$) $_{\Sigma 3.2}\text{S}_4$, pink violarite ($\text{Ni}_{0.62}\text{Fe}_{0.37}\text{Co}_{0.01}$) $_{\Sigma 3.2}\text{S}_4$, and lavender violarite, ($\text{Ni}_{0.76}\text{Fe}_{0.13}\text{Co}_{0.11}$) $_{\Sigma 3.35}\text{S}_4$. For comparison, these values are also plotted in fig. 4. The plot indicates that there is a definite merging in composition between grains with the optical properties of polydymite and those with the properties of violarite. Two of the violarites identified by Buchan and Blowes fall within the Kalgoorlie mineral compositions. The 'pink violarite' (V_3) could be classed as a normal Kalgoorlie violarite. The 'grey violarite' (V_1) is chemically similar to Kalgoorlie polydymite. The lavender violarite (V_2), which is richest in cobalt, is similar in composition to certain sulphides recognized in this study.

Scotia linnaeite (Table II), though essentially an $M_3\text{S}_4$ cobalt sulphide, can contain more Fe than the linnaeite minerals considered by Vokes. The carrollite identified in this study fits Vokes's

definition, i.e. an $M_3\text{S}_4$ mineral containing more than 10% Cu.

Physical properties. Vickers microhardness and reflectance values given in Table I are indicative of the range of variation present in each linnaeite mineral species from the Kalgoorlie district. This spread of properties is to be expected in view of the chemical variability that exists within each mineral and further studies are in progress to attempt to document reflectance and microhardness variability with chemistry as determined by EPMA.

Microhardness variation in the Kalgoorlie linnaeite minerals follows the pattern deduced by Vaughan *et al.* (1971) from their studies of geochemistry and bonding in the thiospinel minerals. The only deviation occurs in the case of violarite where incipient cleavages are so abundant as to possibly invalidate many measurements. Vaughan *et al.* postulated that the reflectance would generally decrease along the linnaeite-siegenite-polydymite, linnaeite-carrollite and violarite-polydymite composition series. The results in Table I do not agree entirely with this generalization (Kalgoorlie polydymite has generally higher reflectance than Kalgoorlie linnaeite) but they are not considered to invalidate it as the Kalgoorlie minerals are not simple stoichiometric $M_3\text{S}_4$ compounds. In fact the effects of varying degrees of isomorphous replacement of elements on the electronic structure of a simple stoichiometric sulphide and the resultant relationship between effective number of free electrons and spectral reflectance are matters of current research (Vaughan, 1973, 1975).

Acknowledgements. The linnaeite-series minerals were first identified in nickel sulphide mineralized rocks collected by the writer from the Kambalda and Scotia localities and the investigation followed up by a post-graduate research programme at Macquarie University, Sydney. In particular, the writer would like to thank Mr. Roy Woodall and Mr. Guy Travis of Western Mining Corporation Limited and Mr. Kevin Schultz of Great Boulder Gold Mines Limited for supplying information and ore specimens. Appreciation is expressed to the Management of The Broken Hill Proprietary Company Limited for permission to publish the results of these investigations.

REFERENCES

- Bannister (F. A.), 1941. *Mineral. Mag.* **26**, 16.
 Bowie (S. H. U.), 1967. In *Physical Methods in Determinative Mineralogy* (ed. J. Zussman). Academic Press.
 Buchan (R.) and Blowes (J. H.), 1968. *Can. Min. Met. Bull.* **61**, 529.
 Christie (D.), 1975. *Austr. Inst. Min. Met. Monograph* **5**.
 Duncumb (P.) and Reed (S. J. B.), 1968. *U.S. Nat. Bur. Standards*, Publ. 289.

- Duncumb (P.) and Shields (P. K.), 1966. *The Electron Microprobe*, Wiley.
- Keele (R. A.) and Nickel (E. H.), 1974. *Econ. Geol.* **69**, 1109.
- Leow (J. H.), 1966. *Econ. Geol.* **61**, 598.
- Moeskops (P. G.), 1975. *Amdel Bull.* **20**, 19.
- Nassim (G. L.), 1949. *Econ. Geol.* **64**, 143.
- Nayak (V. K.), 1969. *Metallography*, **2**, 57.
- Nickel (E. H.), 1973. *Austr. Inst. Min. Met. Conference*, Perth, Western Australia.
- Ross (J. R.), and Thornber (M. R.), 1974. *Econ. Geol.* **69**, 93.
- Ostwald (J.), 1973. Thesis, Macquarie University, Sydney.
- Petruk (W.), Harrison (D. C.), and Stewart (J. M.), 1969. *Can. Mineral.* **9**, 597.
- Reed (S. J. B.), 1965. *Brit. J. App. Phys.* **16**, 913.
- Vaughan (D. J.), Burns (R. G.), and Burns (V. M.), 1971. *Geochim. Cosmochim. Acta*, **35**, 365.
- 1973. *Miner. Materials News Bull.* **3**.
- 1975. *Ibid.* **2**.
- Vokes (F. M.), 1967. *Mineral. Deposita*, **2**, 11.
- Wang (C.) and Yo (S.), 1963. *Sci. Sinica (Peking)*, **12**, 617.
- Watmuff (I. G.), 1974. *Mineral. Deposita*, **9**, 199.
- Woodall (R. W.) and Travis (G. N.), 1969. *9th Com. Min. Met. Congr.* London, Paper 26.

[Manuscript received 10 February 1977;
revised 12 September 1977]