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## Glaukosphaerite: A new nickel analogue of rosasite

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**SUMMARY.** Glaukosphaerite, a new secondary basic copper-nickel carbonate was first determined and described from Widgiemooltha ( $31^{\circ} 30' S.$ ,  $121^{\circ} 34' E.$ ), Western Australia, by R. C. Morris at the W.A. Government Chemical Laboratories in 1967. The mineral has since been found at the nickel mines at Kambalda, Windarra, Scotia, Carr Boyd Rocks, and St. Ives, Western Australia, and is apparently an indicator of copper-nickel sulphide mineralization. The name is derived from the colour and spherulitic formation. Associated minerals are goethite, secondary quartz, paratacamite, gypsum, nickeloan varieties of magnesite and malachite, and clays. Glaukosphaerite also fills joints in fresh basic rocks.

The type material is from Hampton East Location 48, 3 km N. of the Durkin Shaft, Kambalda. Glaukosphaerite is monoclinic,  $a$  9.34 Å,  $b$  11.93 Å,  $c$  3.07 Å,  $\beta$  90–1°, space group indeterminate,  $c$  axis disordered, six strongest X-ray powder lines are 2.587 (10b) 201, 3.68(7b) 220, 2.516(4) 240, 2.11, 5.04(3) 120, 2.124(3b), 1.473(3). The mineral occurs in green spherules of fibres cleaved and elongated along  $c$ ,  $D = 3.78$  to  $3.96$  increasing with Cu, is brittle,  $H.$  3 to 4, and has dull to subvitreous to silky lustre.

$\alpha$  1.69–1.71 green,  $\beta \approx \gamma$  1.83–1.85 yellow-green,  $\alpha: [001] 7^{\circ}$ .

Chemical analysis on the type material,  $D$  3.78, containing 0.5% goethite impurity and minimal inseparable malachite, gave CuO 41.57, NiO 25.22, CoO 0.07, ZnO 0.02,  $Fe_2O_3$  0.47, MgO 1.23,  $SiO_2 < 0.01$ ,  $CO_2$  21.70,  $H_2O^+$  9.85,  $H_2O^- < 0.01$ , sum 100.13%. After deduction of goethite the unit cell contains  $4[(Cu,Ni,Mg,Co)_{1.74}C_{0.96}H_{2.12}O_{4.73}]$ . This unit-cell content is deficient in metal ions and oxygen and contains excess H, when compared to  $4[(Cu,Ni)_2(OH)_2CO_3]$ . Two analyses of malachite-bearing glaukosphaerite from Widgiemooltha and Carr Boyd Rocks show the same deficiencies and excess not previously recorded in malachite, rosasite, or aurichalcite analyses. Glaukosphaerite,  $4[(Cu,Ni)_2(OH)_2CO_3]$  is the nickel analogue of rosasite  $4[(Cu,Zn)_2(OH)_2CO_3]$ .

From results based on X-ray rotation patterns of oriented rosasite fibres from Sardinia and Durango with supplementary electron-microprobe studies and Guinier powder-film data, the authors consider glaukosphaerite and rosasite to be separate mineral species from the related malachite,  $4[Cu_2(OH)_2CO_3]$ .

Type material is preserved in the government collection at the Government Chemical Laboratories, Perth, Western Australia.

IN May 1967 Anaconda Australia Inc. submitted a secondary nickel mineral for identification at the Western Australian Government Chemical Laboratories. The specimen, Laboratory Number 7951/1967, was from a costean 3 km south-east of Widgiemooltha ( $31^{\circ} 30' S.$ ,  $121^{\circ} 34' E.$ ). R. C. Morris<sup>1</sup> (1967) determined the mineral as the undescribed copper-nickel analogue of rosasite, measured its unique properties

<sup>1</sup> Now of Delta Petrological Services, Claremont, Western Australia.

and prepared a small sample for analysis by R. S. Pepper, Table I, analysis 3. The possible new nickel mineral stimulated considerable interest amongst nickel prospectors and further occurrences were eventually reported. In April 1969 a second specimen was donated from the gossan of the Otter Shoot at Kambalda (lat.  $31^{\circ} 10' S.$ , long.  $121^{\circ} 37' E.$ ) by W. R. Moriarty. Another occurrence was found later in 1969 by J. Just on Hampton East Location 48 at a point 3 km north of the Durkin Shaft, Kambalda. This material, received from J. Just at the Laboratories in 1971 and numbered 16803/1971 also yielded sufficient mineral to the present authors for full holotype description including various electron-microprobe studies.

The results showed a close relationship with rosasite but with nickel instead of zinc substitution for copper in the malachite-type structure. The name glaukosphaerite and the full data from the high-nickel material of 16803/1971 were accepted by the Commission on New Minerals and Mineral Names, I.M.A., in 1972. The name is derived from the colour and spherulitic mode of occurrence. A further five localities for glaukosphaerite have been recorded in Western Australia since 1969. At all eight localities there has been significant copper–nickel mineralization in the vicinity. Experience thus far indicates that, unlike malachite, which looks similar and is widespread in non-nickeliferous terrains, glaukosphaerite could be useful for nickel prospecting and its recognition in the field is of importance.

*Occurrence.* The nickel mineralization at Hampton East Location 48 occurs in Archean rocks of the Kalgoorlie–Yilgarn succession of the W. A. Shield (Prider, 1965). This succession is represented in the area by NNW trending belts of basic volcanics with lesser acid volcanics and sediments known as greenstone belts. These belts have been invaded by basic to ultrabasic intrusives, also by later porphyries and granites. The whole assemblage has undergone metamorphism of greenschist-facies grade (McCall, 1973).

Disseminated and massive mineralization occurs towards the base of a serpentinized dunite unit in a zone of extreme talc–carbonate alteration. Pyrrhotine, pentlandite, chalcopyrite, sphalerite, chromite, and traces of galena represent the primary assemblage while violarite, secondary pyrite, and magnetite are characteristic of the zone of supergene enrichment. In the zone of oxidation glaukosphaerite, nickeloan malachite, goethite, quartz, wad, and nickeloan chrysotile occur in a weathered talcose outcrop. The 'Discovery Gossan', 11 km south of Windarra ( $28^{\circ} 29' S.$ ,  $122^{\circ} 14' E.$ ), scene of the celebrated Poseidon nickel strike in August 1969, has also yielded glaukosphaerite specimens. The mineral occurs there as thin veinlets in a goethite–quartz–chalcedony rock, specimens of which were donated to the Laboratories by W. R. Jones.

Glaukosphaerite was also collected by P. J. Bridge, of these Laboratories, in July 1971 in the Widgiemooltha area, this time 11 km south-east, at the Dordie North nickel prospect. The mineral was intergrown with nickeloan celadonite in veinlets in a goethite–quartz–tremolite rock. On the same trip he also found glaukosphaerite as films overgrown with quartz crystals on an antigorite–talc–goethite rock at the Scotia nickel mine ( $30^{\circ} 13' S.$ ,  $121^{\circ} 16' E.$ ).

In the following November, J. Just collected glaukosphaerite from the Carr Boyd

Rocks nickel mine (30° 04' S., 121° 37' E.). The mineral was associated with gypsum on an actinolite rock. Further specimen collecting at Carr Boyd Rocks has revealed that the 'glory hole' and surface dumps are an abundant source of glaukosphaerite in multi-hued green specimens of paratacamite, gypsum, and nickel-bearing varieties of magnesite, malachite, and clay.

In March 1973 Dr. E. H. Nickel donated glaukosphaerite material he collected in September 1972 at the bottom of the glory hole. The specimen, 4625/1973, was composed of green fibres up to 3 mm long on a joint face of a weathered basic rock. An electron-microprobe study (J. J.) showed the fibres to be glaukosphaerite with cores of malachite. A small sample, 0.2 gm, was purified to 99 % of glaukosphaerite plus included malachite for complete analysis, Table I, analysis 4.

In the following October, I. Loxton donated further glaukosphaerite material, 18173/1973, exposed during stripping of goethitic overburden from the Jan nickel ore body at St. Ives (31° 25' S., 121° 50' E.). The specimen exhibited a joint coating of green 0.2 mm globules shown by electron-probe microanalysis (J. J.) to be mainly nickeloan malachite with some dolomite layers and a few thin glaukosphaerite zones.

*Mineralogy.* Glaukosphaerite typically occurs as tiny spherules lining cavities and filling joints in the zone of oxidation. The spherules are concentrically zoned and usually solid but the mineral also occurs as radiating aggregates of separate fibres at Carr Boyd Rocks. The colour varies from Ridgway (1912) Bice Green 29' and Winter Green 33' (Cu:Ni  $\approx$  3:2) to Motmot Green 35' (Cu:Ni  $\approx$  3:1) with Light Paris Green 35' streak. The lustre varies from dull to subvitreous to silky, the fibres have a good cleavage parallel to their elongation along *c*, are brittle, and have H 3 to 4.

The three prepared analytical samples had D  $3.78 \pm 0.01$ , D calc. 4.217 (Cu:Ni 3:2), D  $3.92 \pm 0.02$ , D calc. 4.244 (Cu:Ni 3:1) and D  $3.96 \pm 0.02$ , D calc. 4.254 (Cu:Ni 4:1) respectively. D increases with copper content and presumably also with progressive admixture of the less-fibrous malachite grains.

*Optical properties.*  $\alpha \approx 1.69$ , Deep Malachite Green 35',  $\beta \approx \gamma \approx 1.83$ , Apple Green 29', R.I. calc. 1.78 for Cu:Ni 3:2,  $\alpha \approx 1.71$ ,  $\beta \approx \gamma \approx 1.85$ , R.I. calc. 1.79 for Cu:Ni 3:1,  $\alpha$ : [001]  $7^\circ$ .

*Chemistry.* A small sample of glaukosphaerite D  $3.78 \pm 0.01$  from the type material, 16803/1971, was prepared by electromagnetic, Clerici solution, and bromoform separation to 99.5 % purity for analysis by R. S. Pepper, Table I, analysis 2. The impurity was a little inseparable goethite.

The empirical unit cell contents, with corrected D 3.777 and V  $342.1 \text{ \AA}^3$  and assuming  $Z = 4$ , simplify to  $4[(\text{Cu,Ni,Mg,Co})_{1.74}\text{C}_{0.96}\text{H}_{2.12}\text{O}_{4.73}]$ , broadly comparable with malachite  $4[\text{Cu}_2(\text{OH})_2\text{CO}_3]$  but deficient in metal ions and oxygen with excess H. The effect of the deficiency and excess can be gauged from the calculated D 4.217 for  $4[(\text{Cu,Ni})_2(\text{OH})_2\text{CO}_3]$  with Cu:Ni 3:2, compared with D obs.  $3.78 \pm 0.01$  for the type material.

All three analyses, 2, 3, and 4 in Table I show a similar cation and oxygen deficiency and H excess with a significantly larger D calc. than D obs. These characteristics are not previously recorded in published analyses of malachite, rosasite, or aurichalcite.

*Electron-microprobe investigation.* Supplementary study by electron probe was done by J. Just assisted by R. B. W. Vigers on the M.A.C. instrument at the Commonwealth Scientific and Industrial Research Organisation Laboratory, Floreat Park, W.A.

The probe work has shown fine-scale concentric zoning of Cu/Ni in glaukosphaerite and Cu/Zn in rosasite. In a number of samples of each mineral, zones of inseparable nickeloan malachite were found in glaukosphaerite, and zincian malachite in rosasite. The type glaukosphaerite showed the least evidence of intergrown nickelian malachite.

TABLE I. *Chemical composition of glaukosphaerite samples and unit-cell contents with atomic ratios calculated on a basis of five oxygen atoms and  $V = 342.1 \text{ \AA}^3$*

	1	2	3	4		2a	3a	4a	2b
CuO	43.94	41.57	52.52	53.8	Cu <sup>2+</sup>	1.08	1.43	1.44	1.02
NiO	27.51	25.22	16.82	12.2	Ni <sup>2+</sup>	0.70	0.48	0.35	0.66
CoO	—	0.07	0.08	0.12	—	—	—	—	—
MgO	—	1.23	0.09	1.15	Mg <sup>2+</sup>	0.06	—	0.06	0.06
ZnO	—	0.02	0.01	0.05	—	—	—	—	—
CaO	—	—	—	0.21	Ca <sup>2+</sup>	—	—	0.01	—
Fe <sub>2</sub> O <sub>3</sub>	—	0.47	0.13	0.54	Σ cations	1.84	1.91	1.86	1.74
Sb <sub>2</sub> O <sub>3</sub>	—	—	—	0.38	—	—	—	—	—
SiO <sub>2</sub>	—	<0.01	0.86	0.04	H <sup>+</sup>	0.30	0.20	0.29	0.28
CO <sub>2</sub>	20.26	21.70	19.68	20.7	CO <sub>3</sub> <sup>2-</sup>	1.02	0.96	1.00	0.96
H <sub>2</sub> O <sup>+</sup>	8.29	9.85	9.72	9.75	OH <sup>-</sup>	1.94	2.12	2.00	1.84
H <sub>2</sub> O <sup>-</sup>	—	<0.01	0.07	—					
Insols.	—	—	—	0.88					
Total	100.00	100.13	99.98	99.82					
D calc.	4.217					3.99	4.13	4.03	
D obs.		3.78(1)	3.92(2)	3.96(2)					
D corr.		3.777	3.93	3.964					

1. (Cu,Ni)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>, Cu:Ni 3:2, D calc. 4.217.

2. Holotype sample 16803/1971, Kambalda, goethite impurity; analyst R. S. Pepper.

3. Sample 7951/1967, Widgiemooltha, malachite, goethite, and quartz impurity; analyst R. S. Pepper.

4. Sample 4625/1973, Carr Boyd Rocks, malachite, actinolite, goethite and stibiconite (?) impurity; analyst F. R. W. Lindsey.

2a, 3a, and 4a. Atomic ratios from 2, 3, and 4 calculated on a basis of O = 5, V = 342.1 Å<sup>3</sup>.

2b. 16803/1971 empirical unit-cell contents, D corr. 3.777, V 342.1 Å<sup>3</sup>.

Fig. 1 is a Cu/Ni electron-microprobe profile across a polished section of twin glaukosphaerite spherules from the holotype specimen. The step was 10 microns, approximately the effective diameter of each analysed spot.

The initial data were computer-corrected for atomic number, fluorescence, and matrix effects using the MAGIC-4 Programme, (Colby, 1968). The Cu:Ni ratios plot symmetrically about the junction of the spherules, Cu:Ni ≈ 1.2:1 and also their centres, Cu:Ni ≈ 1:1. Most of the profile shows Cu:Ni < 1.4:1. By comparison the analysis of the prepared chemical sample of the type material shows a bulk composition of Cu:Ni ≈ 1.5:1.

*X-ray data.* The poor quality and disorder of the material available for single crystal work limited the X-ray studies to Weissenberg rotation films and some powder patterns with a Guinier focusing camera. The Guinier work produced the data of Table II. The Guinier X-ray powder patterns of malachite, rosasite, and glaukosphaerite are superficially comparable except that the patterns of the latter two differ less and are both composed of fine *hko* lines and broad *hk1* lines.

The patterns of all three minerals show slight differences, distinctive enough to define small amounts of admixed malachite in X-rayed samples of either of the other two. The correspondence of the forward region *hko* lines shows that for all three minerals *a* must be similar and *b* very close. However, as demonstrated by Morris (*pers. comm.*), rotation X-ray films (usually composed of layers of short arcs) about *c* of fibre aggregates of rosasite from Durango and glaukosphaerite from Widgiemooltha prove *c* for both minerals to be  $\approx 3.1 \text{ \AA}$ . This *c* length is significantly shorter than the  $3.24 \text{ \AA}$  given for malachite, Powder Diffraction File card 10-399. The substitution in the malachite structure of Zn for Cu to form rosasite and Ni for Cu to form glaukosphaerite has shortened the *c* axis and introduced obvious *c* axis disorder. This disorder, combined with the fact that *a* and *b* are respectively three and four times longer, make *c* difficult to define from the powder X-ray pattern because there are so many available combinations of *h* and *k* to index possible *hk1* lines.

A unit cell refinement of glaukosphaerite parameters was attempted using the CELFIT programme described by Pryce (1970) starting from the *a* and *b* axes of malachite and  $c = 3.1 \text{ \AA}$ . Numerous trial modifications of malachite parameters combined with an indexing programme based on Ito's method failed to satisfactorily index all the glaukosphaerite powder lines. The approximate pseudo-orthorhombic cell, readily available from the powder data and a rotation film, is  $a 9.34 \pm 0.01 \text{ \AA}$ ,  $b 11.93 \pm 0.01 \text{ \AA}$ ,  $c 3.07 \pm 0.02 \text{ \AA}$ ,  $\beta \approx 90^\circ$ ,  $a:b:c; 0.7829:1:0.2573$ ,  $V = 342.1 \text{ \AA}^3$ ; this cell was derived by combining *a* and *b* lengths refined from Guinier powder *hko* line measurements with a semi-refined value of *c*, obtained by adding to the *hko* refinement some measurements of *hk1* lines tentatively indexed using  $c = 3.1 \text{ \AA}$ . This approach yielded an approximate cell volume useful for calculation of unit cell content but left several unindexed powder lines in Table II. A slightly monoclinic cell,

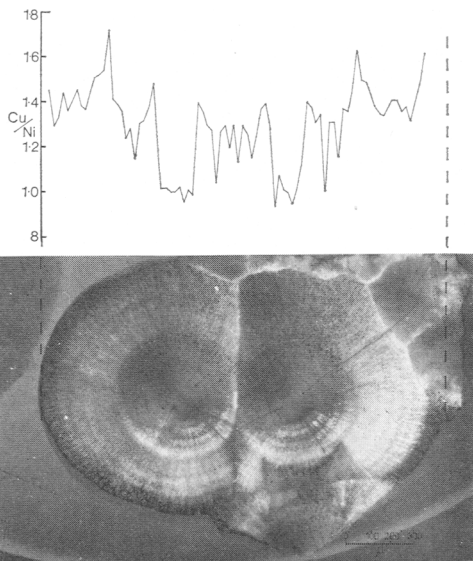


FIG. 1. Photomicrograph of polished section of twin glaukosphaerite spherules 16803/1971 and matching plot of electron-probe microanalyser line scan for Cu/Ni. Length of scan 1.8 mm.

initially proposed by Morris (*pers. comm.*) and giving better but not perfect indexing, was refined by CELFIT to  $a\ 9.36 \pm 0.03\ \text{\AA}$ ,  $b\ 11.92 \pm 0.03\ \text{\AA}$ ,  $c\ 3.08 \pm 0.01\ \text{\AA}$ ,  $\beta\ 91.1 \pm 0.04^\circ$ ,  $V = 343.6\ \text{\AA}^3$ . However, none of the glaukosphaerite material was sufficiently ordered for confirmation of this more logical cell or the space group by  $hk1$  Weissenberg films. It seems certain, however, that glaukosphaerite is monoclinic.

Santorio and Sitzia (1964)<sup>1</sup> have reported rosasite from Sardinia to be isotypic with and have a unit cell nearly identical to that of malachite, from a powder diffractometer study with bulk chemical analyses.

TABLE II. X-ray powder data for glaukosphaerite

<i>hkl</i>	<i>I</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>	<i>I</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i>	<i>d</i> <sub>obs</sub>	<i>I</i>	<i>d</i> <sub>obs</sub>
110	1	7.40	7.36	320	1	2.765	2.762	3b	2.124	1b	1.576
020	2	5.96	5.96	201	10b	2.587	2.570	1	2.011	1b	1.558
120	3	5.04	5.03	240	4	2.516	2.514	1b	2.000	1b	1.554
200	1	4.68	4.67	211				2b	1.986	1b	1.528
220	7b*	3.68	3.68	—	2	2.482	—	2b	1.966	1	1.510
130	1	3.65	3.66	330	2	2.454	2.453	2b	1.944	1	1.496
230	2	3.02	3.03	400	2	2.340	2.337	2	1.894	3	1.473
310				—	2b	2.314	—	1	1.846	2b	1.400
040	1	2.987	2.982	150	2b	2.310	2.311	2	1.788	2	1.382
011				—	2b	2.294	2.294	2b	1.744	1	1.325
—	2b	2.954	—	301	2b	2.198	2.190	2b	1.697	1	1.301
101	2b	2.928	2.923	420	2	2.178	2.176	1	1.690	1	1.265
140	1	2.840	2.841	041	1b	2.133	2.141	1	1.678	1	1.260
111				—	2b	1.646	—	—	—	—	—

\* Denotes broad line.

Guinier focusing camera, Cu- $K\alpha_1$  radiation, ThO<sub>2</sub> internal standard, I visual.

Indices and *d* calc. from  $a\ 9.34\ \text{\AA}$ ,  $b\ 11.93\ \text{\AA}$ ,  $c\ 3.07\ \text{\AA}$ ,  $\beta \approx 90^\circ$ .

However, rotation X-ray films prove that the *c* axis of rosasite is approximately  $3.1\ \text{\AA}$  and electron-probe line scans show that rosasite nodules from both Sardinia<sup>2</sup> and Durango contain fine inseparable zones of zincian malachite. Zincian malachite impurity would contribute the necessary extra peaks to make a rosasite record conform to a malachite unit cell. Santorio and Sitzia's data show a strong enhancement (no doubt due to pronounced preferred orientation) of the comparable rosasite-malachite *hko* peaks (between  $7.4\ \text{\AA}$  and  $2.9\ \text{\AA}$ ) against the distinctive rosasite *hk1* peaks, especially the  $2.6\ \text{\AA}$  reflection. Guinier films of rosasite record  $2.6\ \text{\AA}$  as a broad major line. Moreover, the standard diffractometer data of malachite, P.D.F. card 10-399 (U.S. National Bureau of Standards), was measured on artificially prepared material reasonably presumed to be of very fine grain and random orientation. In contrast to the reference malachite data of Santorio and Sitzia, P.D.F. card 10-399 gives the highest peak at  $2.857\ \text{\AA}$ . There is no corresponding line present on the pattern of rosasite either from Bulgaria, Cu:Zn 1:2:1, P.D.F. card 18-1095, or from Sardinia, Guinier pattern of a zone showing Cu:Zn  $\sim 1:2:1$ , BM 1924, 167, or on patterns of glaukosphaerite from Kambalda and Widgiemooltha.

<sup>1</sup> Translation by A. Guzzi, Water Division, W.A. Government Chemical Laboratories.

<sup>2</sup> BM 1924, 167 supplied by P. Embrey, British Museum (Natural History), London; 24,996 and 53,958 supplied by K. Tuček, National Museum, Prague.

The present authors contend that the powder-diffraction records of malachite, rosasite, and glaukosphaerite are each unique and that the minerals represent three distinct monoclinic species.

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