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A POSSIBLE UNIT CELL FOR GLAUKOSPHAERITE

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ABSTRACT

The powder X-ray diffraction pattern of glaukosphaerite from Kasompi, Zaire, has been re-indexed using a cell of a 9.368, b 11.99, c 3.387Å, β 92.12°. The new cell volume of 380Å^3 for Ni/Cu=0.58 yields D_{calc}=3.77 for the analytical formula and D_{calc}=3.80 for the stoichiometric formula as compared to D_{meas}=3.83 g/cm^3. Measured and calculated densities of members of the glaukosphaerite series correlate well provided that Ni/Cu obtained by chemical analysis is assumed to be present in the stoichiometric formula $(Cu,Ni)_2(CO_3)(OH)_2$.

SOMMAIRE

Le diagramme de poudre aux rayons X de la glaucosphaérite provenant de Kasompi, au Zaïre, est ré-interprété à l'aide d'une maille aux dimensions suivantes: a 9.368, b 11.99, c 3.387Å, β 92.12°. Le volume de la nouvelle maille, V=380Å^3 pour Ni/Cu=0.58, donne D_{calc}=3.77 pour la formule analytique et D_{calc}=3.80 pour la formule stoechiométrique contre D_{mes}=3.83. Les densités calculées et mesurées des membres de la série de la glaucosphaérite concordent à condition d'introduire dans la formule stoechiométrique $(Cu,Ni)_2(CO_3)(OH)_2$ le rapport Ni/Cu déterminé par l'analyse chimique.

INTRODUCTION

Glaukosphaerite, $(Cu,Ni)_2(CO_3)(OH)_2$, was named by Pryce & Just (1974). The type locality is Kambalda, Western Australia. The mineral gives X-ray powder diffraction patterns similar to those of rosasite, $(Cu,Zn)_2(CO_3)(OH)_2$, and its cobalt analogue (Deliens *et al.* 1973). Single-crystal data for rosasite and glaukosphaerite have not been obtainable because of their fine-grained character, and unit-cell dimensions reported by Pryce & Just (1974) were calculated principally from powder patterns.

POWDER X-RAY DATA

Indexed powder data for glaukosphaerite are given in Table 1. Although the indexing by Pryce & Just (1974) is based on an orthogonal cell, they also pointed out that better results are obtained with a monoclinic cell of similar dimensions and β ~91°. The problem is that several lines of the powder pattern cannot be indexed with either of their cells.

Powder patterns of malachite, rosasite, and their nickel and cobalt analogues have similarities from which it can be deduced that a and b do not vary radically, and several $hk0$ diffraction lines can be indexed without ambiguity. Thus the principal unknown in these minerals is the value of c sin β. According to Pryce & Just (1974), rotation X-ray photographs of rosasite fibres (Cu/Zn not stated) and bundles of glaukosphaerite fibres from Widgiemooltha, Australia (Cu:Ni=3:1) indicate that their c is "≈3.1Å". Rotation and precession photographs done by the present writer on rosasite fibres from Hayden, Arizona, indicate that their a^*b^* net is dimensionally similar to that of malachite, with $h00$ and $0k0$=$2n$ as in malachite. Although these same fibres do not yield precession photographs of a quality adequate for a satisfactory interpretation of c^*, rotation films

TABLE 1. X-RAY DIFFRACTION DATA FOR GLAUKOSPHAERITE

Pryce & Just (1974)				This Study		Deliens (1975)		This Study	
I	d_{obs}	d_{calc}	hkl	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl
1	7.40	7.36	110	7.36	110	20	7.39	7.38	110
2	5.96	5.96	020	5.97	020	90	5.99	6.00	020
3	5.04	5.03	120	5.03	120	90	5.04	5.05	120
1	4.68	4.67	200	4.68	200	50	4.70	4.68	200
7B	3.68	3.68	220	3.68	220	100	3.688	3.689	220
1	3.65	3.66	130	3.66	130				
2	3.02	{3.03	230	{3.03	230	30	3.000	2.998	040
		{3.02	310	{3.02	310				
1	2.987	{2.982	040	2.983	040				
		{2.980	011						
2B	2.954	-	-	2.961	021	40	2.936	2.947	021
2B	2.928	2.923	101	-	-				
1	2.840	{2.841	140	2.842	140	50	2.844	2.838	$\bar{1}21$
		{2.839	111						
1	2.765	2.762	320	2.764	320	30	2.772	2.768	320
10B	2.587	2.570	201	2.589	031	60	2.584	2.583	031
4	2.516	{2.514	240	2.515	240	70	2.520	2.524	240
		{2.513	211	2.514	$\bar{1}31$				
2	2.482	-	-	2.476	131	30B	2.477	2.472	131
2	2.454	2.453	330	2.454	330				
2	2.340	2.337	400	2.339	400	25	2.328	2.323	150
2B	2.314	-	-	2.312	$\bar{1}50$				
2B	2.310	2.311	150	2.304	$\bar{3}11$				
1B	2.294	2.294	410	2.296	410	5	2.293	{2.297	410
								{2.295	$\bar{3}11$
2B	2.198	2.190	301	2.196	$\bar{1}41$				
2	2.178	2.176	420	2.178	420	10	2.184	2.180	420
1B	2.133	2.141	041	2.126	250				

Indexed (Pryce & Just) with a = 9.34Å, b = 11.93, c = 3.07, β = 90°

Indexed with a = 9.364Å, b = 11.93, c = 3.413, β = 92.254°

Indexed with a = 9.368Å, b = 11.99, c = 3.387, β = 92.123°

indicate that c is 3.2±0.3Å. The broadness of the layer lines is attributable to the presence of multiple fibres and to the fact that the fibres are variable in Zn:Cu as confirmed by microprobe. Thus, if the 3.1Å c-axis obtained for glaukosphaerite by Pryce & Just (1974) is accurate, the problem of the unindexed powder diffraction lines remains; one possible solution is that pronounced line shifts occur because of disorder along c; the alternative discussed here is that c is larger than 3.1Å, but is still within the ±0.3Å broadness range abtained on the rotation films. There is an obvious need for electron-diffraction work to resolve the problem.

The powder data for the type material of Pryce & Just (1974) have been re-indexed as shown in Table 1. The a– and b–dimensions are not significantly different from those proposed in the original description, but c has been increased from ~3.1Å to 3.4Å. The previously unindexed lines at 2.954, 2.482, and 2.314Å, and the poor agreement between d_{obs} and d_{calc} at 2.587Å are satisfied with the new cell; one line (2.928Å) is not indexable. Although this line does not appear in the powder pattern of glaukosphaerite from Kasompi, Zaire (Deliens 1975), its validity is not questioned despite the fact that the Kasompi material has Cu:Ni= 1.73:1 (~7:4), which is comparable to one of the glaukosphaerite analyses reported by Pryce & Just (1974).

Density

In addition to the problem of unindexed powder diffraction lines in the original description of glaukosphaerite, calculated and observed densities did not agree well. If, however, atomic Ni/Cu and the measured densities obtained by Pryce & Just (1974) are plotted as shown in Figure 1, an excellent linear relationship is obtained. Furthermore, the Kasompi glaukosphaerite of Deliens (1975) has atomic Ni/Cu=0.58, which from the graph (Fig. 1) indicates that its density should be approximately 3.83 g/cm³; the measured value obtained by Deliens is 3.83. Thus the measured specific gravities of glaukosphaerites seem to be fairly accurate; they show a linear decline as Ni/Cu increases.

X-ray data for zincian malachites indicate that substitution of zinc for copper decreases a but increases b so that the unit-cell volume is not drastically affected. If, for cell-volume purposes only, glaukosphaerite with a low nickel content is assumed to be nickelian malachite,

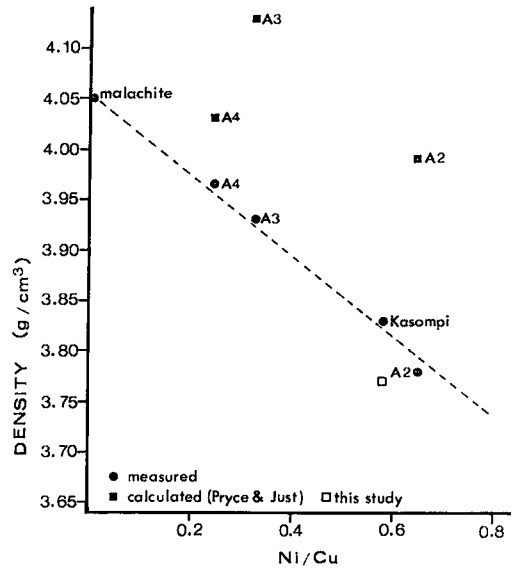

FIG. 1. Measured and calculated densities obtained by Pryce & Just (1974) for Australian glaukosphaerite (A2-A4), and measured density of the Kasompi, Zaire mineral (Deliens 1975) with density calculated (open square) from his chemical analysis and the enlarged cell used in this study.

then its cell volume should be about 365±5Å³, which is considerably larger than the 342Å³ used for the density calculations by Pryce & Just (1974). On the other hand, the chemical analysis of the Kasompi glaukosphaerite gave Ni/Cu= 0.58, and with the measured density, an assumed stoichiometric formula of $(Cu,Ni)_2(CO_3)(OH)_2$, and the calculated cell volume of 380Å³, D_{calc}=3.80 g/cm³. With the analytically derived formula $(Cu,Ni)_{1.95}C_{1.02}H_{2.04}O_5$ of Deliens (1975), the calculated density of the Kasompi mineral is 3.77 g/cm³ as compared to D_{meas}= 3.83. The latter comparison is shown in Figure 1.

Powder diffraction data for the type Kambalda specimen only were given by Pryce & Just (1974). The new cell dimensions given in Table 1 yield a cell volume of approximately 381Å³ for this material, and the calculated density using the chemical results is 3.58 g/cm³, which is much too low. However, Pryce & Just (1974) drew attention to the fact that their analyses consistently yielded unit-cell contents deficient in metal ions and oxygen. If their analytical ratio of Ni:Cu=1:1.57 for type glaukosphaerite is used in the stoichiometric formula $(Cu,Ni)_2(CO_3)(OH)_2$, the calculated density is 3.78 g/cm³, identical to their measured value.

Volume-Density Extrapolations

The agreement between the measured density and that obtained by calculation using a stoichiometric formula was tested with other members of the glaukosphaerite series. Figure 2 shows the calculated cell volumes of the Kasompi and Kambalda glaukosphaerites relative to that of malachite. If their cell volumes are linearly related, then the analytical Ni:Cu of the two additional glaukosphaerites described by Pryce & Just (1974) should have the volumes shown in the upper part of Figure 2. The resultant calculated densities based on $(Cu,Ni)_2(CO_3)(OH)_2$ are in good agreement with the measured values as shown in the lower part of Figure 2.

Conclusions

Pryce & Just (1974) concluded that the powder diffraction patterns of malachite, rosasite, and glaukosphaerite are each unique and that these minerals represent three distinct monoclinic species. The results of the present study are not at variance with a conclusion that rosasite and glaukosphaerite differ from malachite, and it is suggested that the difference may be partly attributable to a change in the *c*-axes of the minerals from about 3.1Å in malachite to 3.4Å in rosasite and glaukosphaerite. With the larger *c*-axis, indexing of the powder X-ray pattern and the correlation between measured and calculated densities are improved.

Acknowledgment

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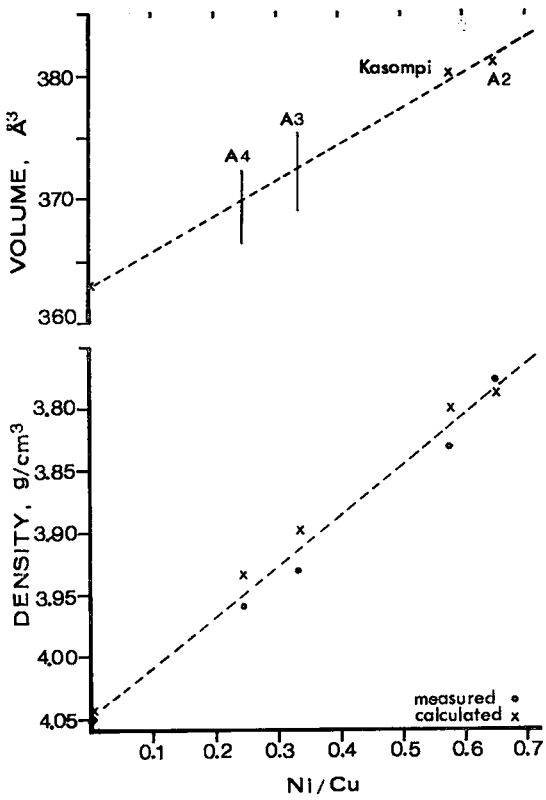

Fig. 2. Upper part shows cell volumes of Kasompi and A2 Australian glaukosphaerite based on new cell dimensions and published atomic Ni/Cu from the analyses of Deliens (1975) and Pryce & Just (1974). Extrapolation to malachite gives the possible cell volumes of Australian glaukosphaerites A3 and A4. Lower part of diagram shows measured and calculated densities of glaukosphaerite based on the new cell with Ni/Cu assumed to be in stoichiometric $(Cu,Ni)_2(CO)_3(OH)_2$.

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