

REFINEMENT OF THE CRYSTAL STRUCTURE OF DYSCRASITE, AND ITS IMPLICATIONS FOR THE STRUCTURE OF ALLARGENTUM

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ABSTRACT

The structure of dyscrasite, $\text{Ag}_{3.15}\text{Sb}_{0.85}$, has been refined using $\text{AgK}\alpha$ radiation data to $R = 0.042$ for 246 observed reflections. The space group is $Pmm2$ with a 3.008(1), b 4.828(1), c 5.214(3) Å, and $Z = 1$. The structure proposed by Peacock (1940) has been confirmed.

It is proposed that the structure of allargentum, $\text{Ag}_{1-2}\text{Sb}_x$, is a disordered version of that of dyscrasite, having the space group $P6_3$, with partial random replacement of the antimony of the dyscrasite half-cell by silver in the allargentum cell. Stability of the dyscrasite structure is maintained by having its thermal ellipsoids oriented in a direction at 90° to the required direction of motion towards the hexagonal close-packed allargentum sites.

SOMMAIRE

La structure de la dyscrasite, $\text{Ag}_{3.15}\text{Sb}_{0.85}$, a été raffinée à l'aide des données obtenues en rayonnement $K\alpha\text{Ag}$ jusqu'au résidu $R = 0.042$ pour les 246 réflexions observées. Le groupe spatial est $Pmm2$ avec a 3.008(1), b 4.828(1), c 5.214(3) Å et $Z = 1$. La structure proposée par Peacock (1940) est confirmée.

La structure de l'allargentum, $\text{Ag}_{1-2}\text{Sb}_x$, serait celle d'une dyscrasite désordonnée, dans le groupe spatial $P6_3$, ou une partie de l'antimoine de la demi-maille de la dyscrasite serait remplacée au hasard par de l'argent dans la maille de l'allargentum. La structure de la dyscrasite maintient sa stabilité du fait que les ellipsoïdes thermiques sont allongés perpendiculairement à la direction du mouvement requis vers les sites de l'assemblage hexagonal compact de l'allargentum.

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INTRODUCTION

A good single crystal of dyscrasite, in the form of a tiny orthorhombic tablet, was found attached to the side of a large, deeply striated, elongate orthorhombic dyscrasite prism in siderite from the Consols mine, Broken Hill, Australia (USNM R-419). Microprobe analyses (Table 1) were provided by Dr. L. J. Cabri on

TABLE 1. MICROPROBE ANALYSES OF DYSCRASITE¹

	Sample Current 0.025 m _z		Sample Current 0.035 m _z		SC = 0.025 m _z expanded beam	
	Wt %	Atoms ²	Wt %	Atoms ²	Wt %	Atoms ²
Grain 1						
Ag	74.33	3.104	74.38	3.118	74.66	3.113
Sb	23.86	0.883	23.42	0.870	23.72	0.876
Hg	<u>0.57</u>	0.013	<u>0.55</u>	0.012	<u>0.50</u>	0.011
	98.76		98.35		98.88	
Grain 2						
Ag	75.40	3.152	74.89	3.137	73.78	3.130
Sb	22.48	0.833	22.86	0.849	23.75	0.855
Hg	<u>0.68</u>	0.015	<u>0.62</u>	0.014	<u>0.68</u>	0.016
	98.56		98.37		98.21	

¹Synthetic stoichiometric Ag_3Sb used as standard.

²Calculated on the basis of 4 atoms per cell.

two grains of dyscrasite taken from the larger crystal, immediately below the point of attachment of the crystal studied. These showed that the mineral was very close in composition to the boundary of its stability field. This boundary occurs at about 0.82 antimony atoms per dyscrasite cell, and is of the order-disorder type from orthorhombic $\text{Ag}_{3+2x}\text{Sb}_{1-x}$ (dyscrasite) to a statistical arrangement of $\text{Ag}_{1-2}\text{Sb}_x$ in the hexagonal allargentum cell.

A Weissenberg data set was collected for the purpose of refining the positional parameters proposed for dyscrasite by Peacock (1940), using silver radiation in order to take advantage of its very much smaller linear absorption coefficient. In addition, the nearness of the compound to one of its stability-field boundaries could be expected to have an effect on the direction of its anisotropic thermal ellipsoids, which would be masked by the uncertainties in the absorption correction if either Cu or Mo radiation were used. An averaged formula of $\text{Ag}_{3.14}\text{Sb}_{0.86}$ was assumed for the initial stages of the refinement.

EXPERIMENTAL

Crystal data for dyscrasite are given in Table 2. The lattice parameters were obtained from a least-squares refinement of 18 high-angle α_1 reflections, using Cu radiation and calibrated by mounting the crystal on a thin silver wire ($a = 4.0862\text{Å}$). These parameters are in good agreement with those reported by Peacock if his cell

TABLE 2. CRYSTAL DATA FOR DYSCRASITE

Formula	Ag _{3.15} Sb _{0.85}	D_{meas}	9.712(8) g/cm ³
Unit Cell	$a = 3.008(1) \text{ \AA}$ $b = 4.828(1) \text{ \AA}$ $c = 5.214(3) \text{ \AA}$	D_{calc}	9.720 g/cm ³
Space Group	$Fm\bar{m}2 (C_{2v}^1)$	$\lambda(\text{AgK}\alpha)$	0.56083 \AA
Z	1	$\nu_{\lambda}(\text{AgK}\alpha)$	137.3 cm ⁻¹
		$\nu_{\lambda}(\text{CuK}\alpha)$	2235 cm ⁻¹

TABLE 3. CRYSTAL DIMENSIONS USED FOR ABSORPTION CORRECTION

Face	Distance from Common Origin (cm)
100	0.0088
$\bar{1}00$	0.0088
001	0.0050
0 $\bar{1}$ 1	0.0034
00 $\bar{1}$	0.0050
010	0.0084
Crystal Volume = 0.002294 mm ³	

is transformed into the conventional setting (100/001/010).

Weissenberg photographs of levels $0kl$ through $5kl$ were taken on a Stoe integrating camera using Pd-filtered $\text{AgK}\alpha$ radiation. The crystal was then remounted about the c axis and inter-scale levels $hk0$ through $hk3$ were collected. The various films were read on a split-beam densitometer and the raw intensities corrected for Lorentz and polarization effects. Absorption corrections were calculated using the crystal dimensions given in Table 3 and an $8 \times 12 \times 12$ Gaussian grid. Maximum and minimum values of this correction with Ag radiation were 0.37 and 0.18, as opposed to a range spanning four orders of magnitude for Cu radiation. Equivalent reflections on all films were averaged ($R = 0.023(5)$ for all levels) and the data set was placed on an approximate absolute scale by Wilson's method. Unobserved reflections were given an arbitrary intensity value of half the local transmittance of the film at the reflecting position and were included in all correction procedures, but were coded as less-than and not included in the refinement.

REFINEMENT

A Patterson synthesis clearly showed that the structure proposed by Peacock (1940) was es-

entially correct. Since it was known from the microprobe analysis that the Sb site was partially occupied by Ag , the origin was fixed by placing a fully-occupied $\text{Ag}(1)$ at $\frac{1}{2}, 0, \frac{1}{2}$ rather than using Peacock's proposed origin of Sb at $0, 0, 0$. The neutral-atom scattering factors for Ag and Sb (Cromer & Mann 1968), corrected for anomalous dispersion, were used in the full-matrix program RFINE (Finger 1969).

The z parameters of all atoms except $\text{Ag}(1)$ were refined with isotropic temperature factors, and converged in four cycles to an R of 0.079. Four further cycles with anisotropic temperature factors reduced R to 0.048. After all other parameters had converged, three further cycles were run, in which the occupancy parameters were allowed to vary. The final value for the Sb site was 0.849(6) Sb and 0.151 Ag ; the three Ag sites all gave values in the range 1.000(8) and are assumed to be fully occupied by silver. No significant peaks were observed in the final difference map; thus the small amount of mercury shown in the analysis could not be assigned to a particular site. The final R value for all observed reflections was 0.042 and the standard deviation of an observation of unit weight was 0.25. Fractional atomic coordinates and anisotropic temperature factors are given in Table 4, and the interatomic distances in Table 5. The table containing observed and calculated structure factors has been deposited with the National Science Library.*

DISCUSSION

The structure proposed for dyscrasite by Burkhardt & Schubert (1959) is in fact incorrect, as has already been suggested by the electron diffraction work of Seng-jung & Pinsker (1960). It is now clear that dyscrasite is not isostructural with $\beta\text{Cu}_3\text{Ti}$, as the doubled a axis required for this structure was not found on long-structure proposed by Peacock (1940) is there-

*This table has been deposited with the Depository of Unpublished Data. Copies may be obtained on request to: Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ontario, Canada.

TABLE 4. ATOMIC COORDINATES AND THERMAL PARAMETERS FOR DYSCRASITE*

Atom	X	Y	Z	$B(\text{equiv})(\text{\AA}^2)$	β_{11}^{**}	β_{22}	β_{33}	RMSD $a^{\#}$	RMSD b	RMSD c	$\Delta^{++}(\text{\AA})$
Sb^{\dagger}	0	0	-0.02488(43)	1.09(5)	377(6)	88(3)	99(4)	131(7)	102(3)	117(5)	0.130
$\text{Ag}(1)$	1/2	0	1/2	1.96(7)	836(7)	275(4)	27(5)	196(6)	180(6)	61(4)	0
$\text{Ag}(2)$	0	1/2	0.64808(52)	0.96(5)	168(4)	146(3)	84(9)	88(6)	131(6)	106(3)	0.097
$\text{Ag}(3)$	1/2	1/2	0.16016(52)	1.71(5)	910(7)	63(3)	115(9)	204(4)	126(7)	86(3)	0.034

*Standard deviations (in parentheses) refer to the last decimal places.

**Anisotropic thermal parameters $\times 10^4$, $\beta_{12} = \beta_{13} = \beta_{23} = 0$.

$\#$ Root mean square deviation (\AA) parallel to the cell edge given $\times 10^3$.

\dagger Occupancy = 0.849(6) Sb + 0.151 Ag .

$^{++}\Delta$ = distance an atom would have to move in the $\pm z$ direction to achieve hexagonal closest packing.

TABLE 5. INTERATOMIC DISTANCES FOR DYSCRASITE IN Å*

Sb - Sb	3.008**	Ag(1) - Ag(2)	2.947(2)
- Ag(1) , †	3.123(3)	- Ag(3)	2.995(3)
- Ag(1) , †	2.898(3)		
- Ag(2)	2.956(3)	Ag(2) - Ag(3) , †	2.955(4)
- Ag(3)	3.003(4)	- Ag(3) , †	3.064(4)

*Standard deviations (in parentheses) refer to the last decimal place.

**All atom pairs of the same species have the a -cell translation of 3.008 Å.

† Primed atoms are located in an adjacent cell along a .

fore confirmed; the refined structure is still in approximate hexagonal closest-packing, but the deviations found are somewhat larger than for his model and they are all in the same direction (Table 4 and Fig. 1).

On mineralogical grounds, the dyscrasite structure should be an ordered form of the allargentum structure. It is known from the work of Petruk *et al.* (1970) that natural allargentum from Cobalt, Ontario, is probably hexagonal close-packed, containing two atoms in a cell having $a = 2.952\text{Å}$ and $c = 4.773\text{Å}$, with an average formula of $\text{Ag}_{0.88}\text{Sb}_{0.14}$, but no structural studies have been made. The relationship be-

tween the two unit cells is that $a_a = a_a$ and $b_a = c_a$; two allargentum cells taken together are required to form dyscrasite. If the origin of the first allargentum cell is placed at 0, $-\frac{1}{4}$, $\frac{1}{3}$ in the dyscrasite cell, the conditions for close-packing are fulfilled with Sb at approximately $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$ and Ag(3) at $\frac{2}{3}$, $\frac{1}{3}$, $\frac{3}{4}$. The second allargentum cell thus contains Ag(1) and Ag(2) in analogous positions. In effect, then, the c axis of allargentum is a 6_3 axis and there are 3-fold axes through the $\frac{1}{3}$, $\frac{2}{3}$, z and $\frac{2}{3}$, $\frac{1}{3}$, z points of the cell; since it can be assumed from the powder diffraction studies of Petruk *et al.* that $00l = 2n$, the probable space group for allargentum is thus $P6_3$.

In dyscrasite the same one of the six equivalent sites about the pseudo 6_3 axis is always filled by Sb, whereas in allargentum the occupancy of these sites is distributed randomly between Sb and Ag. A trivial calculation shows that if 50 dyscrasite cells are considered together, the exposure rotation photographs. The original resultant 100 allargentum cells will have the

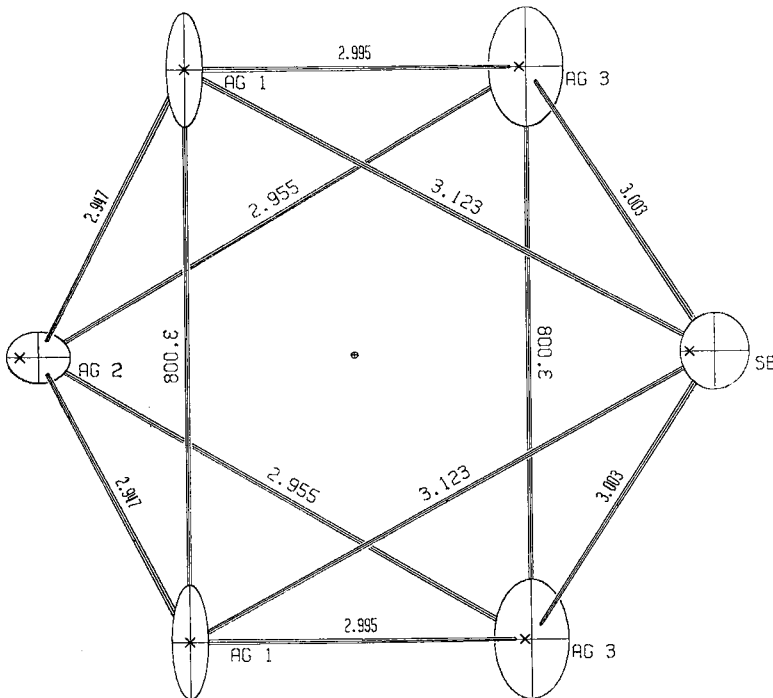


FIG. 1. Projection along the pseudo 6_3 axis of dyscrasite. The small crossed circle in the centre represents this axis, located at 0, $-\frac{1}{4}$, z of the dyscrasite cell. Interatomic distances are shown for dyscrasite in Å, and the positions of the ideal hexagonal close-packed sites in allargentum are indicated by crosses within the thermal ellipsoids.

correct Ag/Sb ratio if 14 of the Sb atoms in dyscrasite are replaced by Ag. Since the Ag sites in the dyscrasite structure are all fully occupied and the Sb site is partially occupied by Ag, it is easy to visualize more extensive replacement in the latter site. The volume change to be expected from such a replacement in a hexagonal close-packed structure is approximately the same as the change observed between the allargentum cell and the dyscrasite half-cell.

The thermal ellipsoids in dyscrasite are constrained by symmetry to vibrate parallel to the cell edges and are in general elongate parallel to the a axis. Thus they extend in a direction at 90° to that in which the atoms would have to move in order to reach the hexagonal close-packed allargentum sites. In view of the relatively minute distances involved (Table 4), it might have been expected that the thermal ellipsoids would elongate parallel to c , that is, towards the allargentum sites. It is interesting to note that the two most spherical ellipsoids are those of Sb and Ag(2), which are the farthest displaced from the allargentum sites, and that the most elongate is Ag(1), which is exactly on its equivalent site in the allargentum cell. Figure 1 shows a projection down the pseudo 6_a axis of dyscrasite; the positions of the ideal hexagonal close-packed sites in allargentum are indicated by crosses.

Since the crystal used has a composition very close to the limit of the dyscrasite stability field, one can postulate that the large observed thermal motions of Ag(1) and Ag(3) are in effect a measure of the resistance of the structure to incipient disorder. The observation that the Sb site, which is farthest from its close-packed equi-

valent, has nearly spherical motion and that the Ag(2) site, which is only slightly closer, has a somewhat more deformed ellipsoid, tends to confirm this. It would be instructive to refine the structure of dyscrasite from the middle of its stability field and observe the effects on the thermal ellipsoids of Ag(1) and Ag(3).

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REFERENCES

- BURKHARDT, W. & SCHUBERT, K. (1959): Über messingartige Phasen mit A3-verwandten Struktur. *Z. Metallkunde* 50, 442-452.
- CROMER, D. T. & MANN, J. B. (1968): X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Cryst.* A24, 321-324.
- FINGER, L. W. (1969): Determination of cation distributions by least-squares refinement of single-crystal x-ray data. *Carnegie Inst. Wash. Year Book* 67, 216-217.
- PEACOCK, M. A. (1940): On dyscrasite and antimonial silver. *Univ. Toronto Studies, Geol. Ser.* 44, 31-46.
- PETRUK, W., CABRI, L. J., HARRIS, D. C., STEWART, J. M. & CLARK, L. A. (1970): Allargentum redefined. *Can. Mineral.* 10, 163-172.
- SENG-JUNG, L. & PINSKER, Z. G. (1960): An electron diffraction study of the Ag-Sb system in thin films. *Kristallografiya* 5, 228-232.
- Manuscript received September 1975, emended December 1975.*