Roxbyite, a new copper sulphide mineral from the Olympic Dam deposit, Roxby Downs, South Australia

W. G. Mumme, G. J. Sparrow

CSIRO Division of Mineral Chemistry, P.O. Box 124, Port Melbourne, Victoria 3207, Australia

AND

G. S. Walker

CSIRO, Division of Minerals and Geochemistry, Curtin University of Technology, Hayman Road, Bentley, W.A. 6102, Australia

Abstract

Roxbyite ($Cu_{1.74-1.82}S$), a new mineral, was isolated from drill core from the Olympic Dam deposit, from copper flotation concentrates from the Olympic Dam pilot plant, and from reaction residues obtained by treating certain concentrates with sulphuric acid. Powder X-ray diffraction data and the composition of the mineral are similar to results reported previously for the unnamed mineral of composition $Cu_{1.83}S$ (with a trace of iron) from the El Teniente deposit in Chile, and to copper sulphides of composition Cu_xS, $1.75 \leqslant x \leqslant 1.86$, prepared electrochemically by several workers. A Weissenberg single-crystal study shows roxbyite to be monoclinic with $a = 53.79$, $b = 30.90$, $c = 13.36$ Å, $\beta = 90.0°$ and space group alternatives $C2/m$, Cm or $C2$. Some iron in the structure may stabilize the mineral.

KEYWORDS: roxbyite, copper sulphide, new mineral, Roxby Downs, South Australia.

Introduction

THE Olympic Dam deposit on Roxby Downs Pastoral Station, South Australia, has an unusual combination of copper, uranium and rare-earth minerals, and precious metals in a hematite matrix. The copper is present as stratabound bornite-chalcopyrite-pyrite mineralization and as chalcocite-bornite lenses and cross cutting veins (Roberts and Hudson, 1983).

Ragozzini et al. (1986) showed that the mineral described as chalcocite in the deposit was actually a mixture of djurleite and a copper sulphide mineral which had been reported previously but remained un-named. A sulphide with similar properties was also isolated from residues resulting from the reaction of copper flotation concentrates with sulphuric acid (Ragozzini et al., 1986; Ragozzini and Sparrow, 1987).

The X-ray powder diffraction (XRD) pattern of the mineral corresponds with that reported by Clark (1972) for the blue-black powdery material found associated with djurleite in the large El Teniente prophyry copper deposit in Chile. Clark determined its composition as $Cu_{1.83}S$. Cavalotti and Salvago (1969) and Koch and McIntyre (1976) have electrochemically generated copper sulphides with similar XRD patterns by means of anodic oxidation of chalcocite. Their estimated compositions for the phase were $Cu_{1.75}S$ and $Cu_{1.80-1.86}S$ respectively.

We have isolated small single crystals of the unnamed mineral with dimensions up to 0.01 mm from a sample of copper flotation concentrate (PP18-5) and drill cores supplied by Roxby Management Services (RMS). The unit cell and space group alternatives have been determined using Weissenberg methods. These results (which have been lacking in the previous studies), together with the composition (determined by electron probe microanalysis, EPMA) and the powder XRD data for the mineral, are reported here and compared with the previously published data.

It is now possible to characterize the mineral and distinguish it from other copper sulphides in the

CuS–Cu$_2$S system. The mineral has been named roxbyite; the name and status were approved by the Commission of New Minerals and Mineral Names in December 1986. A sample of the mineral has been deposited with The Museum of Victoria, Melbourne.

Physical data

Roxbyite was identified in several flotation concentrates. Its highest concentration was in PP18-5 which contained 60% roxbyite, 15% djurleite, 10% bornite and 10% hematite. Some pyrite, chalcopyrite and a blaubleibender covellite (with the approximate composition Cu$_{1.2}$S) were also identified in PP18-5.

Roxbyite is not easily distinguished from djurleite in polished sections of grain mounts of PP18-5 or in polished sections of drill core specimens. In reflected light its colour is a shade of blue which is intermediate between that of the djurleite (bluish-white) and digenite (a darker greyish-blue) found at Olympic Dam. The synthetic equivalent of roxbyite from reaction residues is more readily recognized and distinguished from (synthetic) djurleite in polished grain mounts of reaction products where the two are frequently intergrown.

The mineral is blue-black with poor (100) cleavage. In reflected light it is white to off white, with a blue tinge, and without discernible pleochroism. Between crossed polars, anisotropism is very weak. The reflectance value at 546 nm is 24.5–29.8 (Zeiss glass standard, $R = 17.5$) and VHN$_{50} = 83$ kg/mm^2.

Using a heating stage attachment to a Philips PW 1050 goniometer with a PW 1710 diffraction controller and PW 1730 X-ray generator, the conversion of roxbyite to a digenite phase was observed to commence at 65–70 °C. Cavalotti and Salvago (1969) observed the same conversion at 70 °C.

Crystallographic data

X-ray single-crystal studies of small crystals of roxbyite obtained from PP18-5 copper flotation concentrate showed an orthogonal lattice $a = 53.79$, $b = 30.90$, $c = 13.36$ Å, with strong pseudo-hexagonal symmetry. Two crystals were aligned, one about b and one about c. Systematic absences for hkl reflections of $h + k \neq 2n$; $h0l$, $h \neq 2n$ and $0k0$, $k \neq 2n$ and intensity variations in what appear to be equivalent reflections indicate monoclinic symmetry $C2/m$, Cm or $C2$ with $\beta = 90.0°$. The cell data and their metric similarities with those of high-chalcocite, low-chalcocite, djurleite, digenite and anilite are recorded in Table 1. Evans (1979) has shown that the monoclinic structures of low-chalcocite and djurleite are based on hexagonal close-packed sulphur atom frameworks, with copper atoms occupying mainly triangular interstices. It is apparent that roxbyite has a similar type of structure, but with a repeat axis normal to the layers of eight times that of high-chalcocite, which itself contains two such layers (Table 1).

Composition of roxbyite

Grain mounts of PP18-5 concentrate were prepared in carbon-doped, cold-setting epoxy mounts, polished and carbon-coated for EPMA using a Cameca Camebax microprobe. Fifteen probe analyses (Table 2) were obtained giving a mean value of

TABLE 1. Unit cell parameters (in Å) for roxbyite and other copper sulphides.

Parameter	High chalcocite*	Low chalcocite		Djurleite	Roxbyite	Digenite	Anilite
		Pseudo-orthorhombic	Mono-clinic				
Space group	P6$_3$/mmc	A2$_1$/c11	P2$_1$/c	P2$_1$/n	C2/m	R$\bar{3}$m	Pnma
a	3.961	11.884	15.246	26.897[†]	53.79[†]	3.92	7.89
b	6.861	27.324	11.884	15.745	30.90	–	7.84
c	6.722[†]	13.494[†]	13.494[†]	13.565	13.36	48.0	11.01
β	–	90.08	116.35	90.13	90.0	120.0	90.0
V	183	4382	2190	5744	22205	639	681
Cell contents	4Cu$_2$S	96Cu$_2$S	48Cu$_2$S	4Cu$_{62}$S$_{32}$	8Cu$_{112}$Fe$_{1.3}$S$_{64}$ (estimated)	3Cu$_9$S$_5$	4Cu$_7$S$_4$

*Orthohexagonal cell at 152°C.

[†]Axis normal to sulphur layers. Value is c_{cch} for high chalcocite; ~2c_{cch} for low chalcocite; ~4c_{cch} for djurleite; ~8c_{cch} for roxbyite.

TABLE 2. Analyses for roxbyite.

| Cu | | Fe | | S | | Total | X in |
wt.%	at.%	wt.%	at.%	wt.%	at.%	wt.%	M_xS
Roxbyite in PP18-5 (EPMA)[1]							
76.15	62.31	0.94	0.87	22.70	36.81	99.79	1.72
76.51	62.82	0.86	0.80	22.36	36.38	99.72	1.75
76.28	62.78	1.54	1.44	21.94	35.78	99.76	1.79
77.98	64.21	0.36	0.34	21.73	35.45	100.07	1.82
77.81	63.93	0.35	0.33	21.95	35.74	100.12	1.80
78.77	64.44	0.62	0.57	21.58	34.99	100.97	1.86
77.99	63.15	0.68	0.63	22.58	36.23	101.25	1.76
77.59	62.92	0.80	0.74	22.61	36.34	101.00	1.74
78.56	63.77	0.82	0.75	22.06	35.48	101.43	1.82
77.42	62.97	0.85	0.79	22.48	36.24	100.75	1.76
77.52	62.81	0.98	0.90	22.60	36.29	101.10	1.76
77.45	62.92	0.71	0.65	22.63	36.43	100.79	1.74
76.51	62.44	0.82	0.76	22.76	36.80	100.09	1.72
77.83	63.22	0.81	0.74	22.39	35.04	101.02	1.77
77.25	63.27	0.77	0.72	22.19	36.01	100.21	1.78
Roxbyite in PP18-5 (SEM-LINK non-dispersive system)[2]							
78.53	63.49	0.56	0.55	22.46	35.99	101.55	1.78
78.19	63.45	0.59	0.55	22.39	36.00	101.18	1.78
78.22	63.80	0.21	0.20	22.27	36.00	100.70	1.78
74.82	62.68	0.86	0.82	21.98	36.49	97.66	1.74
76.11	63.44	1.00	0.95	21.56	35.61	98.67	1.81
75.43	63.44	0.49	0.47	21.65	36.09	97.57	1.77
76.00	62.77	0.63	0.59	22.38	36.64	99.01	1.73
77.06	63.75	0.67	0.63	21.72	35.62	99.45	1.81
Roxbyite in RX 583 (EPMA)[1]							
79.36	64.33	0.36	0.33	22.01	35.35	101.72	1.83
79.68	64.40	0.14	0.13	22.15	35.47	101.97	1.82
79.83	64.77	0.10	0.09	21.85	35.14	101.78	1.84
79.47	64.59	0.07	0.06	21.94	35.34	101.47	1.83
79.13	64.28	0.15	0.14	22.11	35.59	101.39	1.81
78.77	64.21	0.67	0.62	21.77	35.17	101.22	1.85
79.44	64.67	0.12	0.11	21.83	35.22	101.38	1.84
78.46	64.30	0.02	0.02	21.97	35.68	100.46	1.80

[1] Accelerating voltage 20 kV, specimen current 15 nA;
Standards: chalcopyrite (Cu Kα, S Kα) and hematite (Fe Kα).

[2] Accelerating voltage 15 kV, specimen current 0.8 nA;
Standard: djurleite (Cu Kα, Fe Kα, S Kα).

$Cu_{1.75}Fe_{0.02}S$ ($M_{1.77}S$) with the measured range $M_{1.72-1.86}S$. The mean value obtained for eight analyses of roxbyite found in drill core sample RX 583 was $Cu_{1.80}Fe_{0.03}S$ (Table 2). The preferred range based on the frequency of analytical results is $M_{1.74-1.82}S$.

The accuracy of these results was checked by analysing samples of djurleite coexisting with roxbyite in the Olympic Dam samples, and from the Dianne Mine (Segnit, 1981), under similar analytical conditions. The measured mean value of five analyses for Olympic Dam djurleite was $Cu_{1.94}Fe_{0.02}S$ ($M_{1.96}S$), and seven analyses for the Dianne Mine djurleite gave $Cu_{1.90}Fe_{0.03}S$ ($M_{1.93}S$). Since the

range determined for djurleite is $M_{1.934-1.965}S$ (Evans, 1979), the analytical results for Olympic Dam and Dianne Mine djurleite are quite acceptable, respectively lying towards each end of the reported range.

A further eight analyses of roxbyite were obtained using a Jeol 25-S scanning electron microscope fitted with a Link energy-dispersive analytical system. The standard used in this case was a Cameca-probe-analysed djurleite from the Dianne Mine ($M_{1.93}S$). The mean value (Table 2) obtained for roxbyite using this method was $Cu_{1.76}Fe_{0.02}S$ ($M_{1.78}S$). The results indicate that the higher specimen currents encountered in the probe

TABLE 3. XRD data for roxbyite and roxbyite-like phases.

Cavalotti and Salvago & Cook et al. Combined data JCPDS 23-958		Clark (1972)		CSIRO						
				Diffractometer				Gandolfi		
				Concentrates[†]		Reaction product[‡]				
d	I	d	I	d	I[#]	d	I[#]	d	I	h k ℓ
6.72	10	6.70	12							002, 440
4.75	10	4.75	10	4.78	10	4.78	10			802; 442
4.24	20	4.24	20	4.26	*	4.24	15			10,0,2; 12,2,0
3.88	10	3.89	5	3.90	10	3.90	5			080; 861
3.60	30	3.60	25	3.60	15	3.59	20			37$\bar{2}$; 153
3.35	55	3.36	50	3.34	*	3.35	55			16,0,0
3.16	5	3.15	5	3.16	*	*				604
3.00	45	3.002	40	3.00	30	3.00	30			804
2.864	75	2.866	80	2.862	55	2.862	60	2.86	70	12,8,1; 18,2,1
2.630	65	2.630	65	2.626	40	2.628	45	2.630	50	10,10,1; 20,0,1
2.537	35	2.540	40	2.52	*	2.532	25			0,10,3; 20,4,0
2.452	25	2.452	25	2.45	*	2.451	15			1,5,5; 22,0,0
2.374	90	2.377	85	2.373	85	2.372	85	2.375	90	885
2.300	10	2.300	10	2.29	*	2.299	10			665; 10,10,3
2.238	15	2.240	15	2.23	*	2.239	10			1,13,2; 865
2.178	10	2.178	10	2.176	15	2.174	15			136; 516
2.123	10	2.126	15			2.121	10			6,14,1
2.023	10	2.021	15							
1.979	10	1.978	10							
1.962	5									
1.938	100	1.937	100	1.934	*	*		1.933	100	086; 0,16,0
1.896	10	1.899	10	1.893	10	1.894	10			027; 117
		1.870	10							
1.861	90	1.860	90	1.859	90	1.859	90	1.857	80	886
1.794	10	1.795	10	1.791	10	1.794	10			
1.762	10									
1.705	5									
1.678	40			1.671	30	1.675	30	1.673	25	
1.656	5			1.65	*	1.652	10			
1.628	20			1.628	10	1.628	25	1.626	20	
1.584	5					1.581	5			
1.560	10									
1.540	10									
1.526	5									
1.501	20					1.499	10			
1.482	10									
1.463	10									
1.444	10									
1.431	10									
1.399	10									
1.342										
1.268										
1.246										
1.186										
1.134										

[†] PP18-5 concentrate and chalcocite-bornite concentrate.

[‡] Product from reaction of djurleite-rich "chalcocite" concentrate with sulphuric acid.

[#] Intensities estimated from 1.859 Å peak of intensity 90.

* Peak at this position was due to roxbyite and another mineral (bornite, quartz or hematite). Because of this overlapping, intensities were not estimated.

(approx. × 20) do not produce any significant effect on the analytical results for roxbyite.

Roberts (1983) reported EPMA analytical data for 'chalcocite' minerals in RMS sample 2551. However, in view of our results, it can be concluded that the 'chalcocite' analysed by him was a mixture of djurleite and roxbyite. The djurleite in sample 2551 gave a composition of $M_{1.94}S$, while what is obviously roxbyite gave a composition of $M_{1.78}S$ $(Cu_{1.75}Fe_{0.03}S)$.

X-ray powder diffraction data

X-ray diffraction analysis data for roxbyite are given in Table 3. Positions of the peaks were determined from XRD patterns for samples of a chalcocite–bornite concentrate (Ragozzini et al., 1986) and PP18-5 concentrate. However, due to the presence of other minerals in the sample (djurleite, bornite, hematite and quartz), it was not possible to estimate the relative intensities of the diffraction peaks.

Also reported in Table 3 are the XRD data for the product from the reaction of a djurleite-rich 'chalcocite' concentrate with sulphuric acid. This copper sulphide has similar XRD and chemical properties to roxbyite (Tables 3 and 4). It is the first intermediate in the sequence of phases observed in the oxidation of djurleite to covellite in the concentrate. Since interferences from other unreacted minerals

were not as great as in the original concentrates, intensity values for the peaks could be determined more easily from the pattern of the reaction product and they are given in Table 3. Included in Table 3 for comparison are the combined data of Cavalotti and Salvago (1969) and Cook et al. (1970) for so-called Cu_xS ($1.96 > x > 1.86$) on file in the JCPDS XRD Reference Card 23-958, and that given by Clark (1972) for his $Cu_{1.83}S$. (Note that Cavalotti and Salvago (1969) actually gave the composition in their paper as $Cu_{1.75}S$). The XRD values for roxbyite from Olympic Dam concentrates are in excellent agreement with the previously reported data.

Gandolfi film X-ray data were also determined from the single crystal used to determine the crystallographic data. In Table 3 it can be seen that they are in good agreement with the bulk powder XRD patterns, and also confirm that the single crystal was in fact one of roxbyite.

Discussion

The XRD data obtained for roxbyite and the reaction product of the djurleite-rich 'chalcocite' concentrate with sulphuric acid are the same as the collective data of Cavalotti and Salvago (1969) and Cook et al. (1970) (which have been collated in JCPDS Card 23-958), and the XRD data reported by Clark (1972) for $Cu_{1.83}S$. This suggests the

TABLE 4. Analyses for djurleite, roxbyite and digenite-like phases and blaubleibender covellite in product from reaction of djurleite-rich "chalcocite" concentrate with sulphuric acid (EPMA).

Cu		Fe		S		Total	X in
wt.%	at.%	wt.%	at.%	wt.%	at.%	wt.%	M_xS
Roxbyite-like phase							
77.99	63.15	0.68	0.63	22.58	36.23	101.25	1.76
77.52	62.81	0.98	0.90	22.60	36.29	101.10	1.76
77.25	63.27	0.77	0.72	22.19	36.01	100.21	1.78
77.81	63.93	0.35	0.33	21.95	35.74	100.12	1.80
76.87	63.49	0.51	0.48	22.02	36.04	99.40	1.77
77.27	63.64	0.27	0.25	22.12	36.11	99.66	1.77
76.90	63.42	0.61	0.57	22.04	36.01	99.54	1.78
Digenite-like phase							
77.59	62.92	0.80	0.74	22.61	36.34	101.00	1.74
76.71	62.96	0.65	0.61	22.39	36.43	99.75	1.74
76.70	63.11	0.43	0.40	22.38	36.49	99.52	1.74
Djurleite-like phase							
78.17	65.12	0.40	0.38	20.90	34.51	99.48	1.90
78.30	64.22	1.39	1.30	21.22	34.48	100.91	1.90
Blaubleibender covellite							
68.92	51.96	0.93	0.80	31.63	47.25	101.48	1.12
68.15	51.21	0.98	0.84	32.21	47.96	101.34	1.09

structural and chemical identity of all the phases which these data represent. However, as discussed, there is a certain disparity in the reported compositions of these copper sulphides. The compositions of samples generated by electrochemical methods have been reported to be $Cu_{1.80-1.86}S$ by Koch and McIntyre (1976), $Cu_{1.77}S$ by Brage et al. (1979) and $Cu_{1.75}S$ by Cavalotti and Salvago (1969). EPMA of the mineral sample from the El Teniente deposit by Clark (1972) gave a composition of $Cu_{1.83}S$ with trace amounts of iron ($< 0.10\%$).

Our results suggest a composition of $Cu_{1.75}Fe_{0.02}S$ ($M_{1.77}S$) for roxbyite mineral samples from Olympic Dam. This metal-to-sulphur ratio is in good agreement with Brage et al. (1979) and Cavalotti and Salvago (1969) for the synthetic electrochemically-formed phases, but is slightly lower than that determined by Clark (1972) for his natural mineral. However, significantly, iron is reported in both the El Teniente and Olympic Dam minerals.

The analyses of the roxbyite-like product from the reaction of the 'chalcocite' concentrate with sulphuric acid also indicated the presence of iron. EPMA of sulphide phases in typical reaction products are given in Table 4. These analyses indicate a series of phases with compositions at approximately $M_{1.90}S$, $M_{1.74-1.80}S$ and $M_{1.1}S$. X-ray diffraction analysis indicates the presence of both digenite-like and roxbyite-like phases. A single crystal taken from a typical reaction product, when aligned, has provided Weissenberg data which show that (epitaxial) intergrowth of the digenite-like and the roxbyite-like phases can occur. For this reason it is proposed that the analyses of $M_{1.74}S$ (Table 4) possibly represent the digenite-like material in the product, not just the lower compositional end of the roxbyite-like phase. The djurleite-like phase produced is a copper-deficient one of composition $\sim M_{1.90}S$. The blaubleibender covellite ($Cu_{1.1}S$) also has a lower copper content than that found in the concentrate.

This argument is supported by analyses of the predominant copper sulphide mineral associated with the bornite in rock specimen 2508. Gandolfi XRD patterns (Table 5) indicate that this mineral is digenite. SEM Link energy-dispersive analyses have given a composition corresponding to M_xS with $1.72 \leqslant x \leqslant 1.75$. This range of metal-to-sulphur ratio is lower than the accepted value for ideal digenite ($Cu_{1.80}S$). However, it agrees favourably with the metal-to-sulphur ratio of the synthetic digenite ($\sim Cu_{1.70}Fe_{0.03}S$) formed near the low copper and iron-containing limit of the composition field determined by Morimoto and Gyobu (1971) in their study of the composition and stability of digenite. The composition of the pre-

dominant Cu–(Fe)–S mineral in specimen 2508 is actually closer to the theoretical value for anilite ($Cu_{1.75}S$). However, the presence of a 3.00 Å peak in the XRD pattern and the absences of several relatively strong ones at 3.36–3.32, 2.69 and 2.59 Å do not support its identification as anilite. The better overall agreement is with the digenite XRD patterns (Table 5).

In the oxidation of chalcocite to covellite by chemical (rather than electrochemical) methods, digenite has been observed as an intermediate, while djurleite has only been proposed to be an intermediate (Thomas et al., 1967; King et al., 1975). A roxbyite-like phase of composition around $M_{1.77}S$ has not been reported as a reaction intermediate, except for King et al. (1975) who suggested that a polymorph of digenite (in other words, a phase similar to that described by Cavalotti and Salvago, 1969) was formed as an intermediate in the oxidation of synthetic chalcocite under certain (unspecified) conditions. However, the presence of such a phase is not substantiated by the XRD data they have tabulated in their paper.

The chemical oxidation of djurleite to blaubleibender covellite in Olympic Dam flotation concentrates does yield a roxbyite-like phase as an intermediate. The presence of roxbyite in the deposit itself and the formation of the roxbyite-like reaction intermediate are probably due to the stabilization of the structure by iron, which is widely dispersed through the deposit in the hematite, chalcopyrite and bornite. An indication of the importance of iron in the lattice of roxbyite was foreshadowed to some extent in the work of Biegler and Constable (1976). On a few occasions an intermediate similar to roxbyite was identified by XRD during the electrochemical reduction of chalcopyrite to chalcocite (Biegler, pers. comm.). However, by comparison, it was not observed when chemically pure chalcocite was oxidized to covellite by ferric ions (Thomas et al., 1967). The observation of the roxbyite-like phase in some of the electrochemical studies of the Cu–S system (Cavalotti and Salvago, 1969; Koch and McIntyre, 1976) is probably because of the better control over the rate of oxidation that can be achieved by these techniques, permitting metastable phases to be observed. A similar observation was made by Potter (1977) concerning low-digenite, which is not stable in the Cu–S system below 70 °C and is stabilized naturally only by the presence of iron. Potter (1977) was nonetheless able to determine the composition limits of electrochemically prepared metastable low-digenite in his investigation of the Cu–S system.

The reaction sequence of djurleite → roxbyite → digenite (as synthetic equivalents) determined by Ragozzini et al. (1986) for oxidation of the Olympic

TABLE 5. XRD powder data for digenite phase from Roxby Downs specimen 2508 compared with JCPDS patterns for digenite and anilite.

Digenite Synthetic Cu$_{1.8}$S JCPDS 23-962		Digenite (low) Calculated pattern JCPDS 26-476		Roxby Downs specimen 2508 Gandolfi pattern		Digenite* Leonard Mine Montana JCPDS 9-64		Anilite Synthetic Cu$_{1.75}$S (no grinding) JCPDS 22-250	
d	I	d	I	d	I	d	I	d	I
		5.333	6						
		4.000	5						
3.35	4	3.385	4					3.36	20
								3.32	18
3.21	35	3.200	30	3.19	m	3.21	40	3.20	55
3.01	14	3.042	24	3.00	wm	3.05	10		
		2.954	31						
2.779	45	2.771	22	2.764	m	2.79	40	2.77	65
								2.75	6
		2.679	16					2.69	14
								2.59	30
2.553	4	2.499	12	2.513	w	2.53	5	2.54	30
		2.412	12			2.40	5	2.39	10
		2.248	23						
2.141	10	2.171	7	2.174	w	2.17	10	2.16	40
								2.13	15
		2.027	6					2.05	5
1.967	100	1.9594	100	1.949	vs	1.973	100	1.956	100
						1.877	5	1.873	10
1.814	2							1.847	4
1.752	6	1.7778	5			1.781	5		
		1.7597	2						
1.678	20	1.6710	14	1.675	m	1.686	30	1.677	35
		1.6472	2						
		1.6329	3						
		1.6217	3						
1.607	4	1.5999	3						
		1.5815	2						
		1.5790	2						
		1.5419	2						
		1.5208	2						
		1.4770	4						
1.392	10	1.4086	2			1.395	10		
		1.3856	5						
		1.3720	3	1.369	w				
		1.3166	6	1.312	w	1.320	5		
		1.2544	2						
		1.2393	2						
		1.1795	2						
		1.1313	9	1.127	m	1.139	20		
				1.065	w	1.074	10		
				0.9803	w	0.986	10		
				0.9363	w	0.943	10		

*Original but now deleted pattern for digenite.

Dam concentrates in sulphuric acid, supports our finding that roxbyite is a phase in the Cu–(Fe)–S system which has a metal-to-sulphur ratio higher than that of digenite at room temperatures.

We believe that roxbyite has a structure similar to those of low-chalcocite and djurleite based upon hexagonal close-packed layers of sulphur atoms with copper atoms occupying mainly triangular interstices. However, as in the case of djurleite and low-chalcocite (Evans, 1979), tetrahedral copper sites (and others approaching linear coordinations) are ordered through the structure. Copper–sulphur bonding distances in a triangular environment typically average 2.3 Å, while those in a tetrahedral one average 2.35 Å. Iron can be accommodated in both regular tetrahedral sites with M–S bonds of 2.26 Å (e.g. chalcopyrite), and in distorted tetrahedral sites with three bonds of 2.28 Å (which are nearly equal to the value in triangular coordination) and one of 2.37 Å (e.g. bornite). Thus iron atoms could be accommodated in the bonding network proposed and probably a subtle, but complicated, ordering scheme of copper and iron is necessary to stabilize the lattice in roxbyite, and this in turn is unique to the mineral. A similar, but to some extent disordered, arrangement is proposed to prevail in the roxbyite-like synthetic phase which has been observed to form during the reaction of flotation concentrates with sulphuric acid.

It can be noted that by assuming such hexagonally close-packed sulphur layers in roxbyite, the d-spacing of 1.933 Å for the 086 plane is equivalent to the spacing which Goble (1981) used to define the radius of the sulphur atoms in such a close-packed arrangement (the 046 plane for djurleite). This sulphur atom radius for a Cu:S ratio of 1.77:1 is characteristic of the leaching pathway for hexagonally-close-packed sulphur atoms which was defined when chalcocite was leached in concentrated ferric sulphate solutions (> 0.1 M) through djurleite, spionkopite and

yarrowite to covellite (Fig. 7*b* of Whiteside and Goble, 1986).

References

Biegler, T., and Constable, D. C. (1976) Upgrading and activation of chalcopyrite concentrates by slurry electrolysis. *Trans. Inst. Mining Metall. Sect. C,* **85,** C23–9.

Brage, M. C., Lamache, M., and Bauer, D. (1979) Contributions a l'etude des sulfures de cuivre non stoechiometriques. *Electrochim. Acta,* **24,** 25–30.

Cavalotti, P. and Salvago, G. (1969) Electrodic behaviour of copper sulphides in aqueous solutions. *Electrochim. Metall.* **4,** 181–210.

Clark, A. H. (1972) A natural occurrence of hexagonal $Cu_{1.83}S$ in Rancagua, Chile. *Nature (London) Phys. Sci.* **238,** 123–4.

Cook, W. R., Shiozawa, L., and Augustine, F. (1970) Relationship of copper sulphide and cadmium sulphide phases. *J. Appl. Phys.* **41,** 3058–63.

Evans, H. T. (1979) The crystal structures of low chalcocite and djurleite. *Z. Kristallogr.* **150,** 299–320.

Goble, R. J. (1981) The leaching of copper from anilite and the production of a metastable copper sulfide structure. *Can. Mineral.* **19,** 583–91.

King, J. A., Burkin, A. R., and Ferreira, R. C. H. (1975) Leaching of chalcocite by acidic ferric chloride solutions. In *Leaching and Reduction in Hydrometallurgy* (A. R. Burkin, ed.). Inst. Mining Metall. London, 36–45.

Koch, D. F. A., and McIntyre, R. J. (1976) The application of reflectance spectroscopy to a study of the anodic oxidation of cuprous sulphide. *J. Electroanal. Chem.* **71,** 285–96.

Morimoto, N., and Gyobu, A. (1971) The composition and stability of digenite. *Am. Mineral.* **56,** 1889–909.

Potter, R. W. (1977) An electrochemical investigation of the system copper–sulfur. *Econ. Geol.* **72,** 1524–42.

Ragozzini, R. J., and Sparrow, G. J. (1987) Selective dissolution of uranium from Olympic Dam copper concentrates. *Hydrometallurgy,* **18,** 367–82.

——Ross-Smith, M. A., Sparrow, G. J., and Walker, G. S. (1986) Selective dissolution of uranium from a copper flotation concentrate. Ibid. **16,** 377–93.

Roberts, D. E. (1983) *Mineral chemistry of sulphides, Olympic Dam deposit.* Unpubl. report.

——and Hudson, G. R. T. (1983) The Olympic Dam copper–uranium–gold deposit, Roxby Downs, South Australia. *Econ. Geol.* **78,** 799–822.

Segnit, E. F. (1981) *Cu–Ag ore from the Dianne Mine, Mareeba District, Queensland.* Unpubl. report.

Thomas, G., Ingraham, T. R., and McDonald, R. J. C. (1967) Kinetics of dissolution of synthetic digenite and chalcocite in aqueous acidic ferric sulphate solutions. *Can. Metall. Q.* **6,** 281–92.

Whiteside, L. S., and Goble, R. J. (1986) Structural and compositional changes in copper sulfides during leaching and dissolution. *Can. Mineral.* **24,** 247–58.