Xanthiosite and aerugite

With Plate I

By R. J. Davis, M.A., D.Phil. and M. H. Hey, M.A., D.Sc.

Department of Mineralogy, British Museum (Natural History)

and

A. W. G. Kingsbury, F.G.S.

Department of Mineralogy, University Museum, Oxford

[Read 6 June 1963]

Summary. Two nickel arsenates from South Terras mine, St. Stephen-in-Brannell, Cornwall, have been shown to be identical with the minerals xanthiosite and aerugite, described by C. Bergemann in 1858, and with two synthetic products described by J. B. Taylor and R. D. Heyding (1958). Xanthiosite is pure golden-yellow, monoclinic, with a 10·174, b 9·548, c 5·766 Å, β 92° 58½′, space group $P2_1/a$; with $D_4^{15} = 5·42 \pm 0·10$, the unit cell contains $4[Ni_3(AsO_4)_2]$ (D_{calc} 5·388 $\pm$ 0·003). Aerugite is deep blue-green, monoclinic, with a 10·29, b 5·95, c 9·79 Å, β 110° 19′, space-group $C2$, Cm, or $C2/m$; the ideal unit cell formula is $2[Ni_9As_3O_{16}]$, with one-sixth of the arsenic trivalent; the natural mineral has a lower Ni:As ratio, around 2·6. Both xanthiosite and aerugite are minerals new to Britain.

THE South Terras mine (also known as the Resugga and Tolgarrick mine, and more vaguely as 'Grampound Road') lies in the valley of the river Fal adjoining Tolgarrick Mill, about one mile SW. of St. Stephen-in-Brannel, approximately 5 miles W. of St. Austell. Early references to a tin-lode and an 'iron-lode' contain scant detail, and omit mention of the associated minerals actinolite, axinite, and garnet, with magnetite in the 'iron-lode', which is a metamorphic deposit in greenstone rather than a true lode. Mining of the iron deposit revealed in 1873 an intersection with a uranium lode, which was later developed as one of the main Cornish uranium deposits until it was exhausted about 35 years ago.

The mineralization of this uranium lode, in common with that of other similar low-temperature Cornish cross-courses, is of the nickel–cobalt–arsenic–bismuth–silver–uranium type. Some parts of the lode were rich in arsenopyrite and löllingite with smaller amounts of nickel and cobalt arsenides and accessory chalcopyrite, chalcocite, pyrite, and a little galena. This is the first record of löllingite at South Terras, and

I have found it in other cross-courses bearing nickel, cobalt, and silver in south-west England.

There is no detailed record of the nickel and cobalt minerals occurring at South Terras, but rammelsbergite, gersdorffite, nickel-rich skutterudite, and an intergrowth of skutterudite with gersdorffite have been identified in samples that I have collected from the dumps in recent years. Many specimens show the characteristic pink and green 'blooms' of erythrite and annabergite, and scorodite and pharmacosiderite are among the other secondary arsenates occurring there.

The primary uranium mineral, pitchblende, only occurred in the upper parts of the lode, and died out in depth, giving way to the Ni-Co-As minerals; from its mode of occurrence, both within the lode and its occasional presence in the adjacent country-rock, it was evidently deposited at a relatively late stage. The veinstone of this lode was largely quartz, and in places this was very comby; this feature, together with the mineral assemblages and other characteristics of the lode, indicates clearly that there were several stages of mineralization. In considering the origin of the xanthiosite and aerugite, these different stages of mineralization are undoubtedly significant. Nearer the surface the vein was oxidized and consisted of gossany and cellular quartz with many secondary uranium minerals; this 'gossan' material was largely removed many years ago.

I found the xanthiosite and aerugite a few years ago in comby quartz vein-material, evidently derived from the deeper workings, adjoining the South Shaft. They were accompanied by various Ni–Co–As minerals, traces of decomposing pitchblende, and various alteration products, and their rather unusual green and yellowish colours at first suggested that they were probably secondary uranium compounds. When they came to be examined, arc-spectrograms showed that nickel and arsenic were the major constituents, with traces of Co and Cu. From this it was provisionally concluded that they were probably nickel arsenates, but further examination by X-ray powder diffraction methods failed to provide an identification.

Specimens were sent to the British Museum in 1959, but their X-ray powder photographs remained in the 'unidentified' files until they were found by Miss E. E. Fejer to match those of two synthetic nickel arsenates prepared by J. B. Taylor and R. D. Heyding (1958), which they formulated $3NiO.As_2O_5$ and $6NiO.As_2O_5$. It then appeared possible that the minerals might be identical with two described by C. Bergemann (1858) from Johanngeorgenstadt, Saxony, and named xanthiosite and

aerugite by G. J. Adam (1869); these species were regarded as doubtful by E. S. Dana (1892) and were omitted by C. Palache, H. Berman, and C. Frondel from the 7th edition of Dana's System (1951). Fortunately, old specimens were available in the British Museum collections; both species are present on two specimens from Johanngeorgenstadt, B.M. 32590, purchased in June 1861 from Dr. A. Krantz, who supplied Bergemann's original material, and B.M. 1907, 103, purchased from Dr. F. Krantz, and formerly in the collection of Prof. A. A. Damour. The whereabouts of Bergemann's original specimens, if indeed they are still extant, are unknown. Both British Museum specimens from Johanngeorgenstadt are small isolated crusts, without matrix, consisting of $1\frac{1}{2}$ to 2 mm layers of xanthiosite and aerugite, with little admixture of the two minerals. Bergemann, who had a much larger specimen at his disposal, states that the aerugite was cavernous, with native bismuth in some small cavities, and with small octahedra (some with faces of {110}) of bunsenite; there does not appear to have been much admixture of the xanthiosite and aerugite.

X-ray powder photographs show conclusively that xanthiosite and aerugite are valid species, identical with the minerals from South Terras mine and with J. B. Taylor and R. D. Heyding's synthetic products; new analyses and unit-cell data were obtained for both species [A. W. G. K.].

Xanthiosite

New analyses[1] of the South Terras mineral, of xanthiosite from the type locality, and of synthetic material, agree well with C. Bergemann's original analysis and with the theoretical composition for $Ni_3(AsO_4)_2$ (table I).

Very little pure material was available from the two mineral specimens, and for these a colorimetric procedure was followed. Xanthiosite does not dissolve readily in acids, though more readily than aerugite; a solution was obtained with 60 % perchloric acid on the water-bath, and this was diluted and aliquots taken for the colorimetric determination of nickel as the dimethylglyoxime complex in chloroform solution, of copper as the 2:2′-diquinolyl complex, of cobalt as the nitroso-R-salt complex, of iron as the sulphosalicylic acid complex, and of arsenic, after distillation as the trichloride, by the molybdenum blue method. More synthetic material was available, and for this the nickel was precipitated and weighed as the dimethylglyoxime complex; the filtrate was evaporated with nitric acid and arsenic precipitated and weighed as $NH_4MgAsO_4.6H_2O$. The amount of the pure synthetic mineral available was not adequate for a pyknometric specific gravity, but a satisfactory result was obtained with the Berman[2] torsion balance: the balance was

---

[1] X-ray powder photographs were taken of the powder prepared for each analysis; no impurities other than quartz were observed in any of the xanthiosite preparations.

[2] H. Berman, Amer. Min., 1939, vol. 24, p. 434 [MA. 7-399].

adjusted with the solid upper pan of the pan-and-basket fitting immersed in ethylene dibromide, the beaker lowered till the pan was just awash and the pan loaded, using a small spatula; after weighing the mineral immersed, the beaker was carefully lowered and removed, and the mineral washed into a weighed microbeaker with a little alcohol, dried, and weighed on the microbalance. Two determinations gave D_4^{15} 5·37, 5·47 ($\pm$0·10) on a 12 mg sample.

Taylor and Heyding describe their $3NiO.As_2O_5$ (synthetic xanthiosite) as dull green (p. 603): our synthetic material and all the natural

TABLE I. Chemical analyses and unit-cell contents of xanthiosite. Analyses by M. H. Hey. Maximum probable error of the unit-cell contents ± 2 %, derived mainly from the probable error of the specific gravity: calculated specific gravity 5·388.

	1.	2.	3.		1a.	2a.	3a.	4a.
As_2O_5	50·7	50·0	50·9	As	8·06	8·01	8·17	8·07
NiO	46·5	47·0	48·1	Ni	11·37	11·58	11·88	11·85
CoO	1·5	1·0	—	Co	0·37	0·25	—	0·05
CuO	0·6	0·7	—	Cu	0·11	0·16	—	0·13
FeO*	0·7	0·5	—	Fe	0·18	0·12	—	—
Sum	[100]	99·2	99·0	O	32·27	32·13	32·30	32·20
				$\Sigma R''$	12·03	12·11	11·88	12·03

1. Johanngeorgenstadt, B.M. 32590; on 2·66 mg, analysis recalculated to 100 % after deduction of 14·9 % quartz.

2. South Terras mine, B.M. 1963, 481; on 2·57 mg.

3. Synthetic xanthiosite, B.M. 1963, 507; on 7·5 mg.

1a to 3a. Unit-cell contents from analyses 1 to 3, using the unit-cell dimensions of table I and a density of 5·42$\pm$0·1.

4a. Unit-cell contents similarly calculated from C. Bergemann's analysis (1858) of Johanngeorgenstadt material.

* Total iron as FeO.

specimens are a pure golden yellow, which suggests that Taylor and Heyding's material contained appreciable aerugite, though they do not record any aerugite lines on the powder photographs; nor do they quote analytical data for their $3NiO.As_2O_5$ preparation.

The *X-ray powder data* (6-cm camera, Cu-$K\alpha$ radiation) for both specimens from Johanngeorgenstadt (B.M. 32590 and B.M. 1907, 103), for the South Terras mineral (B.M. 1963, 481), and for synthetic material (B.M. 1963, 507) are identical, line for line, to the highest Bragg angles. An 11·46-cm camera powder photograph of B.M. 32590 (table II and fig. 1a, pl. I) is in excellent agreement with the data given by J. B. Taylor and R. D. Heyding (1958), though they did not record many of the weakest lines and several lines they recorded as single are now found to be doublets. A number of these very weak lines, including one recorded by Taylor and Heyding, could not be indexed on the proposed unit cell, nor as forbidden reflections of the cell, nor as any plausible impurity;

TABLE II. X-ray powder data for xanthiosite, B.M. 32590, from Johanngeorgenstadt, Saxony. 11·46 cm diameter camera, Cu-$K\alpha$ radiation. a 10·174±0·005 Å, b 9·548±0·002 Å, c 5·766±0·001 Å, β 92° 58½'±1', space group $P2_1/a$. B, broad; D, double, not resolved in poor photographs.

d	I	hkl	$\sin^2\theta_O$	$\sin^2\theta_C$	d	I	hkl	$\sin^2\theta_O$	$\sin^2\theta_C$
—	—	110	—	0·0123	2·410	mw	{$12\bar{2}$ 231}	0·1021	{0·1014 0·1018}
5·75	m	001	0·0180	0·0179					
5·06	vvw	200	0·0231	0·0230			{040		{0·1043
—	—	011	—	0·0244	2·373	wB	212	0·1054	0·1055
4·79	vvw	020	0·0258	0·0261			122		0·1056
—	—	$11\bar{1}$	—	0·0291			$40\bar{1}$}		0·1058}
4·48	vw	210	0·0296	0·0296			{140		{0·1101
4·32	sB	{111 120}	0·0317	{0·0313 0·0318}	2·305	vwBB	330	0·1116	0·1105
4·02	vvw	—	—	—			$41\bar{1}$		0·1124
3·90	ms	$20\bar{1}$	0·0390	0·0388			401}		0·1143}
3·70	mw	201	0·0434	0·0431	2·243	vw	{$22\bar{2}$ 420}	0·1179	{0·1166 0·1182}
3·67	ms	021	0·0442	0·0440	2·215	mw	411	0·1209	0·1208
—	—	$21\bar{1}$	—	0·0454	2·204	vw	041	0·1221	0·1222
3·57	vvw	—	—	—	2·185	vvw	{$31\bar{2}$ 222}	0·1243	{0·1237 0·1250}
3·46	vsB(2)	{$12\bar{1}$ 220 211}	0·0496	{0·0487 0·0491 0·0496}	—	—	331	—	0·1253
3·42	vvw	121	0·0508	0·0508	2·153	vwB	{$14\bar{1}$ 240}	0·1280	{0·1269 0·1274}
3·32	vvw	—	—	—			{141		{0·1291
3·19	ms	310	0·0584	0·0584	2·130	mB	032	0·1307	0·1304
3·13	vvw	—	—	—			331		0·1316
3·03	ms	{130 $22\bar{1}$}	0·0648	{0·0644 0·0649}			$42\bar{1}$}		0·1319}
2·956	vvw	—	—	—	2·100	vw	$13\bar{2}$	0·1345	0·1340
2·923	mw	221	0·0695	0·0692	—	—	312	—	0·1364
2·862	vvw	002	0·0724	0·0717	2·069	vwB	132	0·1386	0·1382
—	—	$31\bar{1}$	—	0·0731					
2·784	vvw	031	0·0765	0·0766					
2·757 2·739	vsD(3)	{320 012}	0·0781	{0·0779 0·0782}					
		311	0·0791	0·0795					
2·690 2·666	vsD	{$13\bar{1}$ 230 112}	0·0820	{0·0813 0·0817 0·0818}					
		131	0·0835	0·0834					
2·621	s	112	0·0864	0·0861					
—	—	$20\bar{2}$	—	0·0905					
2·576	vvw	—	—	—					
—	—	400	—	0·0922					
2·529	vvsB(1)	$32\bar{1}$	0·0927	0·0927					
2·466	vw	{$21\bar{2}$ $23\bar{1}$}	0·0976	{0·0970 0·0975}					
—	—	022	—	0·0978					
—	—	410	—	0·0987					
—	—	{$20\bar{2}$ 321}	—	0·0990					

d	I	d	I
2·033	vw	1·619	mw
1·995	vvw?	1·605	vvw
1·986	m	1·589	vwB
1·944	mwB	1·582	vvwB
1·913	w	1·570	vw
1·873	vvwB	1·544	s
1·850	mw	1·527	s
1·831	vvw	1·521	vvw
1·813	wB	1·504	mw
1·784	wB	1·492	s
1·732	vwB	1·487	vvw
1·708	vwB	1·461	vw
1·678	mw	1·436	s
1·664	w	1·426	ms
1·645	w	&c.	
1·631	w		

they are present on photographs of both synthetic and natural xanthiosite, and since they cannot be accounted for by parasitic iron radiation from the tube[1] or by other known nickel arsenic oxides, they remain at present unexplained.

Taylor and Heyding indexed their powder data on an orthorhombic cell with a 5·693, b 8·30, c 11·04 Å, but since the lines at d 3·67, 3·48,

[1] R. J. Davis, Journ. Sci. Instr., 1963, vol. 40, p. 79.

2·75, 2·68, and 2·21 Å are now found to be resolvable doublets this cell could not be fitted to the powder data.

Single crystal X-ray data. A small fragment from B.M. 32590, Johanngeorgenstadt, yielded equi-inclination Weissenberg photographs (Cu-$K\alpha$ radiation), $0kl$ to $5kl$ inclusive, showing hkl reflections present in all orders, $0k0$ present for k even, and $h0l$ only for h even; there were numerous random reflections at low angles from satellite crystals, and some possible indication of $h0l$ reflections for h odd. However, the latter were not confirmed on very long-exposure $h0l$ precession photographs (Mo-K and Cu-K radiations), and we accept the glide-plane extinction as probably genuine, whence the space-group is $P2_1/a$. Cell dimensions by the methods of Farquhar and Lipson,[1] using [100], [101], and [10$\bar{1}$] as oscillation axes, are a 10·174±0·005, b 9·548±0·002, c 5·766±0·001 Å, β 92° 58$\frac{1}{2}$′±1′.

A careful search among the random reflections on all moving-film and oscillation photographs for signs of super-cell reflections was negative. There is thus no explanation of the extra powder lines mentioned above.

The unit-cell contents were computed for all four available analyses, using the above cell-dimensions and the density (5·42) determined on our synthetic material, B.M. 1963, 507 with the results included in table I. The cell clearly contains $4[Ni_3(AsO_4)_2]$, for which the calculated density would be 5·388±0·003.

Aerugite

New analyses were made of the South Terras mineral, of type locality aerugite, and of synthetic material, and agree well with C. Bergemann's original analysis and reasonably well with Taylor and Heyding's analysis[2] of artificial material (table III); as with xanthiosite the analytical powders were checked by X-ray photographs.

Like many other anhydrous nickel salts[3] aerugite is very difficult to dissolve in acid; digestion with 60 % perchloric acid on the water bath for two days left it undissolved, but solution was effected in boiling perchloric acid in about 15 min. This gave reliable figures for the metals, but the arsenic figures appeared less satisfactory, and the analysis of the artificial material was therefore repeated using a sodium hydroxide fusion to effect solution; a little sodium peroxide was added to ensure complete oxidation of the arsenic. The analyses were made by the same methods as for xanthiosite (p. 74). Since the presence of trivalent arsenic was suspected, it was felt essential to attempt a determination of the state of oxidation; this proved unexpectedly difficult, and the results are not entirely satisfactory.

[1] M. C. M. Farquhar and H. Lipson, 1946. Proc. Phys. Soc. London, vol. 58, p. 200.
[2] The theoretical figures cited by Taylor and Heyding (1958, p. 604, table VI) for $6NiO.As_2O_5$ are in error: the correct values are Ni 51·94, As 22·10 %; for $Ni_9As_3O_{16}$ they are Ni 52·35, As 22·27 %. [3] T. Isaacs, Min. Mag., 1963, vol. 33, p. 663.

Because very little natural material was available, all the tests and determinations were made on two synthetic samples, B.M. 1963, 508 and 509 (table III, nos. 4 and 5). Qualitative tests on both showed that trivalent arsenic is present in appreciable amount: to partial solutions, obtained by short heating with 60 % perchloric acid, strong sulphuric acid, or strong hydrochloric acid, or by fusion with caustic soda

TABLE III. Chemical analyses, atomic ratios to a basis of 32 oxygen atoms, and calculated specific gravities of aerugite. Analyses 1 to 4 by M. H. Hey.

	1.	2.	3.	4.	5.	6.	7.
As_2O_5	36·3	37·6	34·51	33·53	34·55	32·46	28·47
As_2O_3	n.d.	n.d.	0·5	0·93	n.d.	n.d.	4·91
NiO	60·9	61·3	65·38	66·43	65·45	67·54	66·62
CoO	1·2	0·7	—	—	—	—	—
CuO	0·3	0·7	—	—	—	—	—
FeO*	1·3	0·6	—	—	—	—	—
Sum	[100]	100·9	100·39	100·89	[100]	[100]	100·00
Sp. gr. calc.	5·76	5·73	5·80	5·83	5·80	5·86	5·95
As^v	6·15	6·29	5·88	5·72	5·91	5·61	5
$As^{...}$			0·10	0·18			1
Ni	15·91	15·77	17·15	17·13	17·22	17·97	18
Co	0·31	0·18	—	—	—	—	—
Cu	0·08	0·17	—	—	—	—	—
Fe	0·34	0·17	—	—	—	—	—
Ni/As†	2·71	2·59	2·87	2·95	2·91	3·20	3

1. Johanngeorgenstadt, B.M. 1907, 173; on 4·33 mg, analysis recalculated to 100 % after deduction of 13·9 % quartz.

2. South Terras mine, B.M. 1963, 481; on 4·82 mg.

3. Synthetic aerugite, B.M. 1963, 508; on 16·1 mg; As_2O_3 on 8 mg.

4. Synthetic aerugite, B.M. 1963, 509; contains some bunsenite; on 0·19 g; As_2O_3 on 33 mg.

5 and 6. Synthetic aerugite; analyses (a) and (b) of Taylor and Heyding, 1958, table VI, recalculated to 100 %, assuming that the analytical deficiencies of 6·28 and 4·45 % respectively are silica glass.

7. Theoretical composition for $Ni_{18}As_6O_{32}$; total As as As_2O_5, 34·17 %.

The original analysis of C. Bergemann, 1858, gives when recalculated: (As+P) 6·24, (Ni+Co+Cu) 16·41, Ni/As 2·63, sp. gr. (calc.) 5·74.

* Total iron as FeO.

† (Ni+Co+Cu+Fe)/(As^v+$As^{...}$).

for a few seconds and extraction with water, strong hydrochloric acid and a few drops of M ICl were added; in each case, extraction with a little carbon tetrachloride gave a distinct iodine colour. As was expected, the longer heating necessary to obtain complete solution in perchloric or sulphuric acid resulted in complete oxidation, and so did caustic soda fusion for as short a time as one minute.

8 mg of the pure synthetic aerugite, B.M. 1963, 508, and 100 mg of B.M. 1963, 509, which contains a little bunsenite, were dissolved by heating in sealed tubes with 1 ml and 5 ml of strong hydrochloric acid respectively for 3 days at 130° C; the solutions

were diluted to 20 ml with strong hydrochloric acid, 2 ml M ICl added, and the liberated iodine extracted with carbon tetrachloride, using one 5-ml, two 2-ml, and four 1-ml portions; the extracts were bulked to 15 ml and colorimetered at λ 520 mμ against iodine standards made using $M/20$ KI treated with HCl and ICl and similarly extracted. Both determinations gave approximately 0·5 % As_2O_3, which is much less than had been expected.

As oxidation by the air remaining in the sealed tubes seemed a possibility, a larger sample (250 mg) of B.M. 1963, 509 was heated with 5 ml strong hydrochloric acid in a tube sealed after displacing the air with nitrogen; after 4 days at 130° C, green crystals were present in the tube, above a yellow powdery deposit; the temperature was raised, finally to 180° C for a week, when solution appeared to be complete; but when the tube was opened, a small, dull yellow insoluble residue was found and the solution failed to reduce iodine monochloride.

Finally, 33 mg of B.M. 1963, 509 were sealed in a tube with 5 ml of strong hydrochloric acid and 0·5 ml M ICl; after 12 hrs at 150° C, solution appeared to be complete, and colorimetry of the liberated iodine indicated 0·93 % As_2O_3. We conclude that our synthetic aerugite contains at least 1 % As_2O_3, and possibly more; natural material has not been tested.

The *X-ray powder data* (6-cm camera, Cu-$K\alpha$ radiation) for both specimens from Johanngeorgenstadt (B.M. 32590 and B.M. 1907, 103), for the South Terras mineral (B.M. 1963, 481), and for synthetic material (B.M. 1963, 508 and B.M. 1963, 509) are identical, line for line, to the highest Bragg angles, except that much of the aerugite on B.M. 32590 is mixed with traces of xanthiosite and that the second synthetic specimen gave a few additional lines due to admixed bunsenite (NiO). An 11·46-cm camera powder photograph of carefully selected, xanthiosite-free material from B.M. 32590 (table IV and fig. 1b, pl. I) is in excellent agreement with the data given by J. B. Taylor and R. D. Heyding (1958), though they did not record a number of the weakest lines, and the line at d 2·40 Å that they recorded as single is now seen to be a doublet (d 2·428 and 2·409 Å); the line at 2·08 Å that they indexed as 230 is absent from our photographs except for that of the impure second synthetic specimen (fig. 1c, pl. I) and is the strongest line of bunsenite.

Taylor and Heyding indexed their powder data on the basis of an orthorhombic cell with a 5·594, b 9·27, c 12·04 Å, but there are appreciable discrepancies between their observed and calculated d-values, and the doubling of the line at 2·40 Å could not be accounted for. An attempt to index our powder data by Ito's method was not successful,[1] and an effort was therefore made to isolate a single crystal of aerugite.

Single-crystal X-ray data. The only suitable fragment isolated for single-crystal work was a polycrystal. A rotation photograph is shown

[1] This failure is to be attributed to the fact that almost every line proves to be the resultant of two or more reflections, as will be seen from table IV.

TABLE IV. X-ray powder data for aerugite, B.M. 32590, from Johanngeorgenstadt, Saxony. 11·46-cm diameter camera, Cu-$K\alpha$ radiation. a 10·29±0·02, b 5·95±0·01, c 9·79±0·02 Å, β 110° 19'±5', space group $C2$, Cm, or $C2/m$. B. broad. All permitted values of $\sin^2\theta$ are shown up to 0·1550.

d	I	hkl	$\sin^2\theta_o$	$\sin^2\theta_c$	d	I
9·19	ms	001	0·0070	0·0071	1·872	vvw
5·05	s	{110, 20$\bar{1}$}	0·0233	{0·0231, 0·0232}	1·834	w
					1·815	vw
4·82	vw	{200, 11$\bar{1}$}	0·0255	{0·0255, 0·0255}	1·793	w
					1·711	vvw
—	—	002	—	0·0282	1·692	mw
4·12	mw	{111, 20$\bar{2}$}	0·0350	{0·0349, 0·0350}	1·634	vw
					1·605	mw
3·76	vs(2)	{201, 11$\bar{2}$}	0·0420	{0·0419, 0·0420}	1·589	m
					1·562	mw
—	—	112	—	0·0607	1·547	vvw
—	—	20$\bar{3}$	—	0·0610	1·534	w
3·06	m	003	0·0633	0·0635	1·485	s
2·971	w	{020, 31$\bar{1}$}	0·0672	{0·0670, 0·0672}	1·430	ms
					1·381	w
2·862	s	{11$\bar{3}$, 202}	0·0724	{0·0726, 0·0724}	1·372	w
					1·336	mw
2·824	w	{021, 310, 31$\bar{2}$}	0·0744	{0·0741, 0·0742, 0·0744}	1·315	wB
					1·283	wB
					1·265	mw
—	—	311	—	0·0852	1·253	mw
2·564	ms	{22$\bar{1}$, 40$\bar{1}$}	0·0903	{0·0902, 0·0905}	1·248	w
					1·239	vvw
2·529	m	{220, 40$\bar{2}$}	0·0928	{0·0925, 0·0929}	1·228	vvw
					1·214	w
2·492	s	{022, 311, 31$\bar{3}$}	0·0955	{0·0952, 0·0952, 0·0956}	1·204	mwB
					1·181	vwB
					1·155	w
2·428	ms	{11$\bar{3}$, 20$\bar{4}$}	0·1006	{0·1006, 0·1010}	1·148	vwB
					1·124	vvw
2·409	ms	{400, 22$\bar{2}$}	0·1023	{0·1021, 0·1020}	1·116	vwB
					1·098	vvw
2·329	s(3)	{11$\bar{4}$, 221, 40$\bar{3}$}	0·1094	{0·1073, 0·1089, 0·1095}	1·091	w
					1·085	vwB
					1·069	vwB
2·295	vw	004	0·1126	0·1128	1·066	vwB
2·252	vw	{203, 11$\bar{4}$}	0·1170	{0·1170, 0·1173}	1·053	vvw
—	—	401	—	0·1278	1·042	vw
—	—	22$\bar{3}$	—	0·1280	1·031	mw
—	—	312	—	0·1304		
—	—	023	—	0·1305		
—	—	31$\bar{4}$	—	0·1309		
2·060	vvs(1)	{222, 40$\bar{4}$}	0·1398	{0·1386, 0·1402}		
1·959	vw	11$\bar{4}$	0·1547	0·1546		

in fig. 2a, pl. I; it superposes perfectly on a powder photograph taken in the same camera. An oscillation photograph (fig. 2b) showed a distinctive set of elongated spots forming layer-lines with equatorial symmetry. On a zero-layer Weissenberg photograph (fig. 2c) it was possible

to pick out distinctive streaks forming loops and axial rows defining the net of fig. 2d, which would account for all observed reflections of this shape. $h1l$ and $h2l$ equi-inclination Weissenberg photographs confirmed the net and confirmed that aerugite is monoclinic, showing hkl reflections with $h+k$ even. The cell and symmetry were confirmed by 11 precession photographs (Cu-K radiation) taken around [001], [100], [101], and [10$\bar{1}$], and on these the net could be more readily distinguished (fig. 2e). A careful search among random reflections yielded no evidence of a super-cell, but there were a few very weak reflections that might be indexed with $h+k$ odd, and for one of them there was possibly a corresponding extremely weak powder line, not listed in table IV (21$\bar{1}$, $\sin^2\theta_{calc.}$ 0·0400, $\sin^2\theta_{obs.}$ 0·0390). The space-group is very near one of $C2/m$, $C2$, or Cm, and the cell dimensions, from the powder data by graphical methods, are a 10·29$\pm$0·024, b 5·95$\pm$0·01, c 9·79$\pm$0·02 Å, β 110° 19'$\pm$5'.

It may be noted that $a:b$ is $\sqrt{3}$ almost exactly, and β is very near the tetrahedral angle 109° 28', thus giving rise to the numerous unresolved doublets on the powder photograph. A unit cell with $a = c = 10\cdot32$, $b = 5\cdot96$ Å, $\beta = 109°$ 28', would contain four close-packed layers of eight oxygen atoms each at 2·98 Å separation; the layers are stacked parallel to (001) in sequence either $ABABA \ldots$ or $ABACA \ldots$; such a lattice would contain R atoms in octahedral holes with R–O 2·11 Å and X atoms in tetrahedral holes with X–O 1·83 Å. NiO$_6$ octahedra in bunsenite have Ni–O 2·08 Å while the accepted value for As–O in AsO$_4$ tetrahedra is 1·62 Å. The hypothetical cell can be deformed to the true one, within the experimental error, by increasing β by 1° and shrinking c by 5 %; the latter is presumably connected with the shrinkage of the XO_4 tetrahedra. The unit cell strongly suggests 32 oxygen atoms.

Unit-cell contents. Three specific gravity determinations, made on 12 to 20 mg of B.M. 1963, 508 by the same procedure as for xanthiosite, gave D_4^{18} 5·96, 6·02, 5·85; a pyknometric determination on 2 g of B.M. 1963, 509 (which contains a little bunsenite) gave 5·7$\pm$0·15. Taylor and Heyding (1958) record considerable attack on the container during their syntheses, and if we correct their observed specific gravity of 5·66 on the assumption that their analytical deficiency of about 6 % is silica glass, we arrive at a figure of 5·75.

Using the overall mean of these five determinations, 5·85$\pm$0·07, together with the observed unit-cell dimensions, analyses 4 and 5 lead to 32·3 and 32·1 atoms of oxygen per unit cell respectively, with a probable error of $\pm$0·4 arising from the density and cell-size data; the

estimate of As_2O_3 may be low, and an increase in this would lead to a decrease in the oxygen, probably not exceeding 0·4 atom.

The recalculation of the analyses to a basis of 32 oxygen (table III) is subject to some uncertainty, since the natural material may contain trivalent arsenic, and Taylor and Heyding's material probably did. It will be seen that neither the metal nor the arsenic contents approach integral values on a basis of 32 oxygen, but this is not surprising; the formation of aerugite from annabergite via xanthiosite takes place by a series of topochemical reactions, in which the close-packed unit of 32 oxygen atoms clearly plays a dominant role, and it is not unusual in such a reaction series for some of the structures to be stable over a wide range of composition. The evidence points to an ideal formula $Ni_{18}As_6O_{32}$ for aerugite, with one-sixth of the arsenic trivalent. The synthetic material approaches this composition, but has a Ni: As ratio around 2·9 and is lower in trivalent arsenic; natural aerugite has a still lower Ni: As ratio, around 2·6, with As well above 6 and Ni below 18 atoms per 32 oxygen. The natural material, which is closely associated with xanthiosite, is probably near the nickel-poor end of the stable range, and the synthetic material, some of which contained a little bunsenite, is probably near the nickel-rich end; the ideal composition $Ni_{18}As_6O_{32}$ may well be outside the stable range.

Syntheses

Anhydrous nickel arsenates have been reported by several workers. J. F. L. Hausmann (1850) described green crusts and microscopic green monoclinic[1] crystals from the walls of a furnace; these were probably crystals of aerugite.[2]

A. Girard (1852), O. Ducru (1900), and H. Guérin and J. Masson (1955) obtained yellow anhydrous arsenates that were probably xanthiosite, while J. B. Taylor and R. D. Heyding (1958) obtained xanthiosite by vacuum pyrolysis of $Ni_2As_2O_7$ at 750° C; it decomposed to aerugite in an air-stream at 1000° C, or to bunsenite *in vacuo* at 850° C.

We have repeated some of these syntheses. Good results were obtained by heating a synthetic annabergite: the first product, which was ochre-

---

[1] 'Es erscheint nähmlich am häufigsten ein sechsseitiges Prisma, mit zwei breiteren Seitenflächen, welches an den Enden entweder schräg abgestumpft, oder zugeschärft ist.'

[2] J. W. Mellor (1933) states: 'J. F. L. Hausmann obtained monoclinic crystals approximating nickel oxyarsenate, $NiO.Ni_3(AsO_4)_2$ . . .'; but Hausmann gives neither formula nor analysis in the reference cited, and we have been unable to trace any authority for the formula.
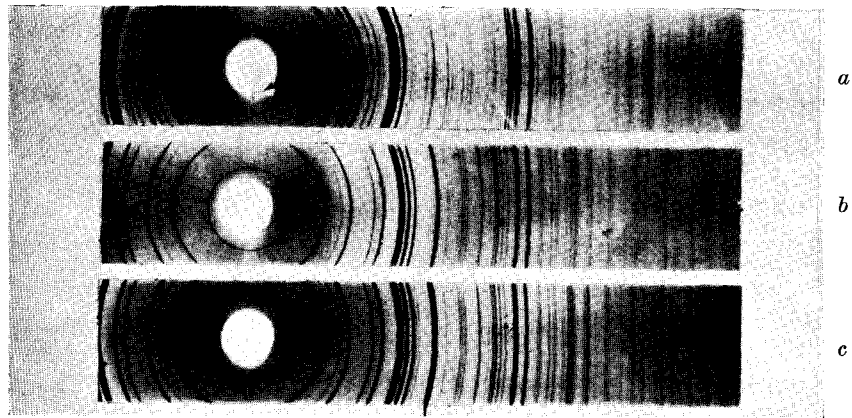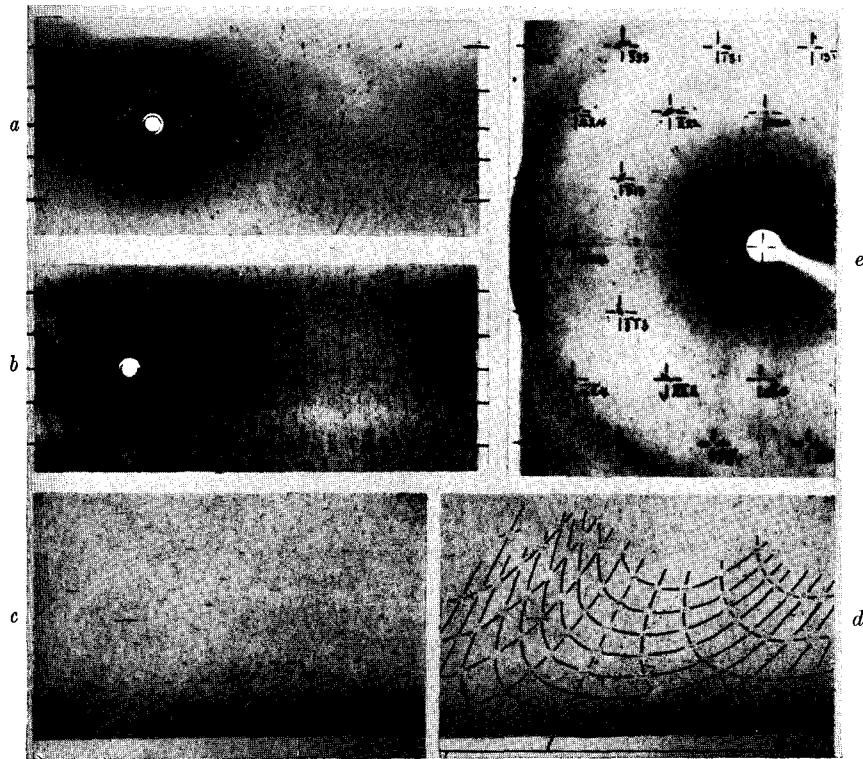
FIG. 1

FIG. 2

DAVIS, HEY, AND KINGSBURY: XANTHIOSITE AND AERUGITE

yellow and anhydrous, gave a good X-ray powder pattern distinct from
that of xanthiosite, and is presumably a polymorph of the latter; at
600 to 750° C it was transformed to an oriented pseudomorph consisting
of xanthiosite, which in turn transformed to an oriented pseudomorph
composed of aerugite at about 850 to 1000° C. A more detailed study
of these transformations is in hand.

References

ADAM (G. J.), 1869. Tabl. Min., p. 43.
BERGEMANN (C.), 1858. Journ. prakt. Chem., vol. 75, p. 239.
CHESTER (A. H.), 1896. Dict. Names Minerals.
DANA (E. S.), 1892. Syst. Min., 6th edn, p. 870.
DUCRU (O.), 1900. Compt. Rend. Acad. Sci. Paris, vol. 131, p. 702; also Ann.
     Chim. Phys., 1901, ser. 7, vol. 22, p. 214.
GIRARD (A.), 1852. Compt. Rend. Acad. Sci. Paris, vol. 34, p. 910.
GUÉRIN (H.) and MASSON (J.), 1955. *Ibid.*, vol. 241, p. 415.
HAUSMANN (J. F. L.), 1850. Abh. Kgl. Ges. Wiss. Göttingen, vol. 4, p. 270.
MELLOR (J. W.), 1933. Compreh. Treat. Inorg. Theor. Chem., London, vol. 9,
     p. 231.
PALACHE (C.), BERMAN (H.), and FRONDEL (C.), 1951. Dana's Syst. Min., 7th edn,
     vol. 2.
TAYLOR (J. B.) and HEYDING (R. D.), 1958. Canad. Journ. Chem., vol. 36, p. 597.

EXPLANATION OF PLATE I

FIG. 1. X-ray powder photographs of material from B.M. 32590, Johanngeorgen-
stadt, Saxony, taken in 11·46 cm Philips camera with filtered Cu-$K\alpha$ radiation.
(*a*) bright yellow xanthiosite, (*b*) bright green aerugite, hand-picked from traces of
     xanthiosite. (*c*) Synthetic aerugite (B.M. 1963, 509) containing bunsenite.

FIG. 2. Single crystal X-ray photographs of aerugite fragment used for this work:
(*a*) rotation with chosen crystal set to *b*-axis, layer lines indicated by lines at edges;
(*b*) oscillation photograph around the same axis as (*a*), layer lines indicated as for
(*a*); (*c*) zero layer Weissenberg photograph around the same axis; (*d*) as (*c*) but with
the reciprocal net superposed; (*e*) precession photograph around [101] axis located
from (*d*), reciprocal net indicated by dashes. All photographs taken with Cu-$K\alpha$
                              radiation.

[*Manuscript received 7 June 1963.*]