Nigerite, a new tin mineral.

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THE discovery of nigerite, a new tin-bearing mineral, by R. Jacobson and J. S. Webb[1] claims more than the passing interest of an addition to the few known species containing appreciable tin. Nigerite is the first mineral to be discovered in which both tin and aluminium are essential constituents. Its chief interest to mineralogists lies in its close relationship to minerals like spinel and corundum based on a close-packed or nearly close-packed assemblage of oxygen ions.

Samples of nigerite submitted to us for investigation consist of brittle, lustrous, brown, weakly magnetic, hexagonal plates up to 5×2 mm. in size but mostly much smaller. These samples also contained grains of cassiterite, columbite, gahnite, sillimanite, quartz, andalusite, and chrysoberyl, which were easily separated by hand-picking. Many nigerite crystals were encountered intergrown with or enclosing cassiterite, columbite, quartz, and sillimanite and these also were set aside as unsuitable for chemical study. A preliminary spectrographic examination, kindly undertaken for us by Mr. B. S. Cooper of the Research Laboratories of the General Electric Company, Wembley, revealed the presence of Sn, Zn, Fe, Al, and Si; and minor amounts of Mn, Li, Mg, and Ti.[2] A separate portion of the mineral was also examined in the

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[1] R. Jacobson and J. S. Webb, Min. Mag., 1947, vol. 28, pp. 118–128.

[2] Examination of a separate sample by D. L. Williams in the Museum confirmed these results except for Li and Ti. He also found Pb, Ca, and P. This discrepancy is probably due to non-uniformity of sample.

same laboratories by Mr. L. A. Thomas for piezoelectricity but no positive effect was discovered.

A larger sample also carefully cleaned and hand-picked and containing no visible accessory minerals was then handed to Dr. Hey for complete analysis.

Chemical analysis of nigerite (M. H. Hey).

The material available for analysis (2 grams) contained a small amount of quartz and sillimanite, present as minute inclusions and films on most of the grains, but no other impurities could be observed under the microscope.

Nigerite is insoluble in acids, and is very imperfectly attacked by fusion with sodium carbonate or caustic soda, but readily gives a clear fusion with borax and with sodium pyrosulphate. For the main part of the analysis the mineral was fused with sodium pyrosulphate, and after solution and elimination of SiO_2 the tin was distilled as bromide from the sulphuric acid solution at 200° C.; in the distillate tin was precipitated by NH_3 and weighed as SnO_2. The residue was treated with H_2S and the precipitate examined in the usual manner; it proved to be wholly PbS, which was converted to $PbSO_4$ for weighing. The oxidized filtrate from the sulphides was precipitated by ammonia at pH 7, and the precipitate dissolved and reprecipitated twice, ignited and weighed (Al_2O_3, Fe_2O_3, TiO_2, and some ZnO), then fused with sodium pyrosulphate, and iron and titania precipitated with cupferron; after igniting and weighing, the Ti was determined colorimetrically. Ammonium citrate was added to the filtrate from the cupferron precipitate, then ammonia and ammonium sulphide, and the small precipitate of ZnS collected, ignited to ZnO, and weighed, alumina being obtained by difference. In the filtrate from the ammonia precipitate, Zn and Mn were precipitated as sulphides and weighed as oxides, the manganese being determined colorimetrically; calcium was found to be absent, and Mg was determined as 8-hydroxyquinolate and tested for Zn. A second portion was used for determination of loss at 200° C. and on ignition, and for a check tin determination (precipitation of Sn and Pb as sulphides and separation by Am_2S).

The ferrous iron determination by the modified Rowledge method (Min. Mag., 1941, vol. 26, p. 116) encountered unexpected difficulties, the tube swelling up and bursting during fusion; this suggested that the mineral contains a considerable amount of water which is not lost on ignition at about 900° C., and a water determination made in the Gooch

tubulated crucible with anhydrous borax as flux confirmed this. By the kindness of Mr. A. T. Green, Director of the British Refractories Research Association, Dr. G. R. Rigby carried out a Rowledge fusion on nigerite in the Mellor Laboratories, Stoke-on-Trent, using for the purpose an evacuated sealed silica-glass tube, and heating it in an atmosphere of nitrogen, since silica-glass is slightly permeable to gases at 950° C. This result may be somewhat low, since there may have been some oxidation of FeO by the water present, but the effect is not likely to be great.[1] There was no noticeable attack on the silica tube except at the surface of the melt; there, a marked attack was observed, presumably through the co-operation of the flux $(B_2O_3 + NaF)$ and water released from the mineral.

The density was determined by the floatation method in Clerici solution; nigerite just floats in saturated Clerici solution, and the density, corrected to vacuum and for 0·48 % quartz, was found to be D_4^{16} 4·51. The hardness is between 8 and 9; the basal plane of a larger crystal can be scratched by corundum, while topaz is abraded.

TABLE I. Chemical analysis of nigerite (I), atomic quotients* (P/M), ionic radii (R), empirical unit-cell contents (II), and atomic ratios to a basis of 24(O,OH) (III). The oxides are given in order of decreasing ionic radius of the metals. Conversion factor* $F = (\frac{1}{2}\sqrt{3a^2cD})/(1\cdot651 \times 99\cdot35) = 10\cdot66$.

	I.		P/M	R.	II.	III.	
PbO	0·94	Pb	0·004	0·84	0·05	0·04	⎫ with 0·33 Mg and
MnO	0·09	Mn	0·001	0·80	0·01	0·01	⎬ 0·09 Fe··· = 1·24
FeO	2·65	Fe··	0·037	0·75	0·39	0·39	⎭
ZnO	4·51	Zn	0·055	0·74	0·59	0·59	{0·38 / 0·21}
SnO₂	25·33	Sn	0·168	0·71	1·79	1·77	2·00
TiO₂	0·17	Ti	0·002	0·68	0·02	0·02	to R··· group
MgO	1·28	Mg	0·032	0·65	0·34	0·33	
Fe₂O₃	11·90	Fe···	0·149	0·60	1·59	1·57	{0·09 to R·· group / 1·48} 12·00
Al₂O₃	50·91	Al	0·998	0·50	10·66	10·52	
H₂O†	1·57	OH	0·174	—	1·86	1·84	
SiO₂	0·48	O	—	—	22·47	22·16	
	99·83‡						
		Σ(O,OH)			24·33	24·00	
		Σ(metals)			15·44	15·24	

* Min. Mag., 1939, vol. 25, p. 403.
† H₂O lost at 200° C., 0·11 %; at 900° C., 0·38 %.
‡ CaO < 0·01 %; P₂O₅, Li₂O, not determined.

[1] This conclusion is supported by the recalculation of the analysis to atomic ratios on a basis of 24(O,OH); if the Fe··· is assigned with the Al, the excess over the most probable value of 12·00 is only 0·09, corresponding to 0·72 % Fe₂O₃.

From the analysis and the observed density and unit-cell dimensions, the empirical unit-cell contents and the atomic ratios to a basis of $(O,OH) = 24$ were calculated. The results (table I) clearly indicate an ideal repeat[1] of $(Zn,Mg,Fe^{\cdot\cdot})(Sn,Zn)_2(Al,Fe^{\cdot\cdot\cdot})_{12}O_{22}(OH)_2$. Calculations based on generously assigned maximum probable errors of the chemical analysis and physical determinations show that the (O,OH) figure must be within the limits $22\cdot8-25\cdot2$ and is almost certainly very near $24\cdot0$, while the sum of the metal atoms must be between $14\cdot8$ and $16\cdot2$ and is almost certainly appreciably greater than 15; the structure has, of course, ample interstitial vacancies for this excess of metal atoms over the ideal repeat.

Crystallography of nigerite (F. A. B. and H. P. S.).

All the crystals and crystal fragments of nigerite so far examined possess a brilliantly reflecting basal plane. Trigonal pyramid faces are also developed on some crystals and as the mineral gives a good uniaxial positive figure[2] when examined with the polarizing microscope it was rightly concluded to belong to a trigonal class of the hexagonal system. The reflected images from the pyramid faces are, however, disappointing. Larger crystals yield weak and confused images from all but the basal plane, whilst more perfect small crystals are so thin that the pyramid faces yielding bright reflections to the unassisted eye prove on goniometric examination to be giving diffuse diffracted images. It was, therefore, possible only to index the pyramid forms after X-ray measurement of the axial ratio and no sufficiently accurate independent goniometric value was obtained.

Laue photographs of several hexagonal plates and platy fragments of nigerite are identical and show threefold patterns with planes of symmetry (i.e. three vertical planes parallel to the $c[0001]$ axis). Single crystal rotation photographs of a small hexagonal plate of nigerite set optically with $a[10\bar{1}0]$ and $c[0001]$ axes vertical in turn yield a 5·72 c 13·86 Å. (equivalent to a 5·71, c 13·83 kX). The latter bracketed values have been used by one of us (M. H. H.) with the appropriate factor 1·651 in calculating the unit-cell contents (table I). No systematic halvings of the diffractions observed on oscillation photographs about the $a[10\bar{1}0]$ axis can be found and the possible space-groups,

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[1] Zn has been assigned to complete the Sn positions, since it has the nearest ionic radius to Sn of the other metals present.

[2] So far only approximate values of the refractive indices of nigerite have been obtained by the Becke line method, ω 1·80, ϵ 1·81.

taking also Laue symmetry into consideration, are D_{3d}^3—$C\bar{3}m$, D_{3d}^1—$C\bar{3}1m$, D_3^1—$C312$, D_3^2—$C32$, C_{3v}^1—$C3m$, and C_{3v}^2—$C31m$. The axial ratio calculated from the unit-cell dimensions is $a:c = 1:2\cdot423$. Both large and small crystals show faces of the trigonal pyramid ($10\bar{1}1$) the calculated angle for $(0001):(10\bar{1}1)$ being $70°\ 20'$ and observed goniometric values for one of the best-developed but thin crystals of nigerite ranging from $69°\ 41'$ to $72°\ 3\frac{1}{2}'$. Two other pyramid forms observed on the same crystal are ($10\bar{1}3$) and a doubtful ($3\cdot0\cdot\bar{3}\cdot16$). The crystals of nigerite so far encountered show few forms and these, with the sole exception of the basal plane, are poorly developed. This renders the determination of crystal class by goniometric measurement uncertain. There is some probability, from the distribution of the faces observed as well as from the lack of any marked piezoelectricity, that the crystals so far studied do not possess uniterminal axes either in or perpendicular to the basal plane. It may prove, therefore, that the choice of space-group can be restricted by further investigation of crystal form to $C\bar{3}m$ or $C\bar{3}1m$, the only two of the six space-groups given above which are non-polar.

Although no crystal-structure determination of nigerite has so far been attempted, the dimensions and contents of the unit cell, which are the results of the X-ray and chemical study, suggest that the crystal structure will prove to be based upon a nearly close-packed hexagonal arrangement of oxygen and hydroxyl ions. The unit cell of a hexagonal close-pack of oxygen ions each $2\cdot7$ Å. in diameter has dimensions a $2\cdot7$, c $4\cdot4$ Å., the c dimension being twice the height of a tetrahedron of oxygen ions, standing on its base. This unit contains two oxygen ions. If twelve of these units are stacked so that a new cell is constructed containing twenty-four oxygen ions with $a' = 2a$, $5\cdot4$ Å. and $c' = 3c$, $13\cdot2$ Å., we have an approximation in dimensions to the unit cell of nigerite. The location of the metal ions Sn, Al, Fe, Zn, Mg, &c., in the tetrahedral and octahedral interstices of such an arrangement must be found by X-ray methods and it may prove possible also to discover how the two hydroxyl and twenty-two oxygen ions are distributed over the twenty-four sites of the nearly close-packed hexagonal array of positive ions.

The high refractive index and low birefringence, the hardness, and high specific gravity of nigerite are all properties common to other minerals based upon hexagonal close-packed oxygen assemblages like corundum or chrysoberyl. The value of the refractive index calculated for a close-packed assemblage of oxygen atoms, each $2\cdot7$ Å. in diameter, is $1\cdot71$

neglecting the contribution of the metal ions.[1] It is reasonable to expect the refractive index of nigerite to be higher than 1·71, for, although it is not quite close-packed, the presence of ions with high refractivity like iron and tin will more than counterbalance the decrease of refractivity due to this expansion.
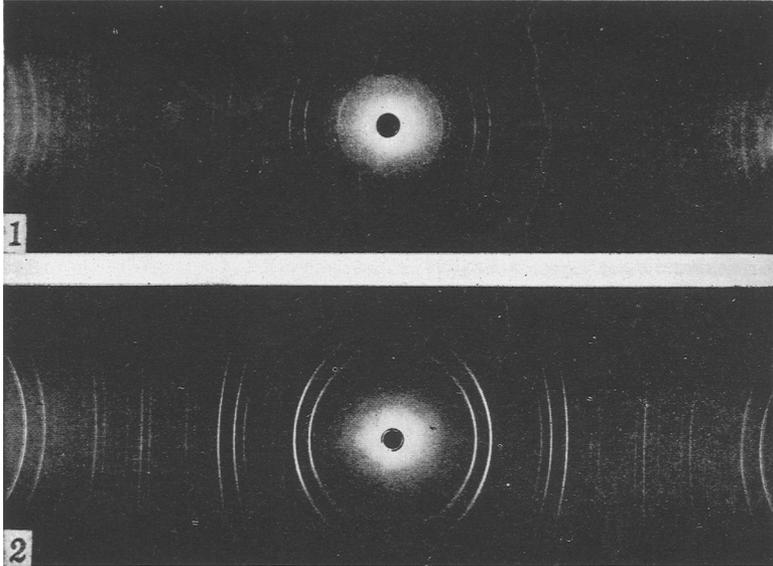
FIG. 1. X-ray powder photographs of nigerite (1) and gahnite (2) from Kabba, Nigeria, taken with filtered copper radiation in a cylindrical camera diameter 6 cm.

The most direct evidence of the hexagonal close-packing of the oxygen and hydroxyl ions in nigerite is afforded, however, by the oriented overgrowth of nigerite on the octahedral planes of gahnite. This spinel has already been described as one of the accessory minerals by Jacobson and Webb, who refer to an octahedron of gahnite coated with nigerite. Each face (111) of this specimen is covered with a single crystal of nigerite. The crystal-structure of the spinels is based upon a cubic close-packing of oxygen ions and it is obvious that a single layer of this cubic arrangement perpendicular to (111) is identical with a single layer of the hexagonal close-packed arrangement perpendicular to (0001). Hence the oxygen ions in the basal plane of nigerite can fit exactly to

[1] W. L. Bragg and J. West, Proc. Roy. Soc. London, Ser. A, 1927, vol. 114, p. 456. [M.A. 3–342.]

those in an octahedral face of gahnite. A relationship between crystal-structures and, therefore, the X-ray photographs of nigerite and gahnite is, of course, to be expected and is well shown by the strong lines on the powder photographs of the two minerals reproduced in

TABLE II.   X-ray powder data for nigerite.

2r cm.	Intensity.	Spacing Observed. kX.	Spacing Calculated. kX.	Index.	2r cm.	Intensity.	Spacing Observed. kX.	Spacing Calculated. kX.	Index.
1·91	ms	4·64	4·656	10$\bar{1}$1	6·96	vw	1·348	1·353	11$\bar{2}$9
2·22	m	4·00	4·023	10$\bar{1}$2	7·05	vw	1·333	1·332	1·0·$\bar{1}$·10
2·66	vw	3·35	3·372	10$\bar{1}$3	7·42	m	1·276	1·275	31$\bar{4}$4
3·15	vs	2·83	2·855	11$\bar{2}$0	7·72	w	1·233	1·236	40$\bar{4}$0
			2·834	10$\bar{1}$4				1·231	40$\bar{4}$1
3·71	vs	2·42	2·434	20$\bar{2}$1				1·228	31$\bar{4}$5
			2·427	11$\bar{2}$3	7·85	w	1·216	1·218	1·0·$\bar{1}$·11
4·15	mw	2·17	2·179	20$\bar{2}$3				1·217	40$\bar{4}$2
4·52	m	2·00	2·011	20$\bar{2}$4				1·213	22$\bar{4}$6
4·58	w	1·977	1·987	11$\bar{2}$5	8·04	vw	1·192	1·194	40$\bar{4}$3
4·93	m d	1·843	1·843	20$\bar{2}$5				1·193	30$\bar{3}$8
			1·835	10$\bar{1}$7	8·25	vw	1·167	1·164	40$\bar{4}$4
5·05	w	1·804	1·804	21$\bar{3}$2	8·40	vw	1·150	1·153	0·0·0·12
			1·794	11$\bar{2}$6				1·150	1·1·$\bar{2}$·11
5·28	vw	1·731	1·732	21$\bar{3}$3*	8·56	w	1·132	1·131	32$\bar{5}$1
			1·729	0008	8·64	w	1·124	1·124	30$\bar{3}$9
5·58	s	1·644	1·644	21$\bar{3}$4				1·123	1·0·$\bar{1}$·12
5·61	vvw	1·636	1·637	30$\bar{3}$1*	9·10	ms	1·079	1·077	32$\bar{5}$4
			1·632	10$\bar{1}$8	9·40	ms	1·052	1·050	32$\bar{5}$5
5·97	s	1·541	1·543	20$\bar{2}$7	9·49	w	1·044	1·046	22$\bar{4}$9
6·32	vw d	1·469	1·477	11$\bar{2}$8				1·045	41$\bar{5}$3
			1·468	10$\bar{1}$9				1·044	2·0·$\bar{2}$·12
6·51	ms	1·430	1·428	22$\bar{4}$0				1·043	2·1·$\bar{3}$·11
6·60	ms	1·413	1·417	20$\bar{2}$8	9·95	mw	1·008	1·006	40$\bar{4}$8
			1·416	30$\bar{3}$5*	10·06	vw	1·000	1·000	41$\bar{5}$5
6·87	w	1·363	1·358	21$\bar{3}$7				1·000	3·0·$\bar{3}$·11

* Spots corresponding to these indices are either very weak or not observed on a rotation photograph of a single crystal of nigerite about the [0001] axis.

The above data were obtained from an X-ray photograph of powdered nigerite taken with filtered copper radiation λ1·539 kX in a cylindrical camera, 5·73 cm. diameter. Relative intensities are given as: vs very strong, s strong, ms medium strong, m medium, mw medium weak, w weak, vw very weak, vvw very very weak; d, doublet measured as a single line.

fig. 1. Indexed powder data of nigerite are given in table II and the spacings calculated from the unit-cell dimensions are also tabulated. Several lines are unresolved doublets or triplets, and it is possible on the basis of an indexed rotation photograph of a single crystal of nigerite about the c-axis [0001] to exclude those planes which yield very weak spots or spots which are too weak to observe. These are asterisked in the table. The X-ray data obtained for Nigerian gahnite a 8·09 kX are

in close agreement with those published for gahnite from the Erik Mattsgrufvan, Falun, Sweden, by Sven Holgersson,[1] and with data for artificial $ZnAl_2O_4$ by L. Passerini[2] and by G. L. Clark, A. Ally, and A. E. Badger.[3]

The refractive indices and specific gravities of gahnite range from 1·782 and 4·38 to 1·818 and 4·57,[4] the corresponding values for the artificial compound being 1·805 and 4·55.[5] L. J. Spencer's range of specific gravity for the mineral is 4·478–4·602.[6] Nigerian gahnite has a refractive index very close to 1·80 and sinks in saturated Clerici solution so that its specific gravity is $>4·5$. It is probable, therefore, that the Nigerian mineral is close in composition to the ideal formula $ZnAl_2O_4$.

[1] S. Holgersson, Lunds Univ. Årsskr., Ny Földj, Avd. 2, 1927, vol. 23, no. 9, p. 31.

[2] L. Passerini, Gazz. Chim. Ital., 1930, vol. 60, p. 394.

[3] G. L. Clark, A. Ally, and A. E. Badger, Amer. Journ. Sci., 1931, ser. 5, vol. 22, p. 541. [M.A. 5–178.]

[4] Dana's System of mineralogy. 7th edit., New York, 1944, p. 691. [M.A. 9–85].

[5] E. S. Larsen and H. Berman, Microscopic determination of the nonopaque minerals. 2nd edit., 1934, p. 58.

[6] L. J. Spencer, Min. Mag., 1927, vol. 21, p. 362.