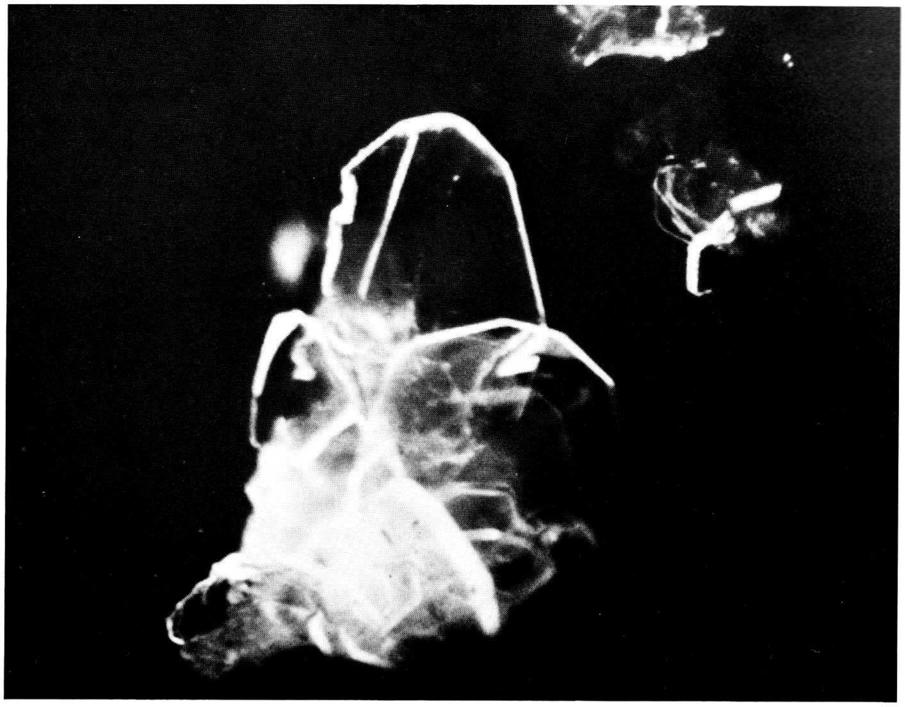

Fig. 1. **Cluster of brannockite crystals photographed while fluorescing under short-wave ultraviolet light.** ***Photograph by Julius Weber.***

Brannockite, A New Tin Mineral

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INTRODUCTION

In 1968 one of the authors (JSW) was informed of the existence of a fluorescent mineral from the Foote Mineral Company's spodumene mine at Kings Mountain, Cleveland County, North Carolina. The informant was Mr. Carter Hudgins of Marion, North Carolina, who collected and donated to the National Museum of Natural History an extremely fine specimen.

An x-ray powder diffraction pattern was immediately taken. The pattern bears a strong resemblance to that of osumilite in terms of line positions, but intensities show substantial differences. The habit — very thin, transparent hexagonal plates — extended the analogy. The early evidence appeared to suggest that the mineral is a structural analog of osumilite, and ensuing studies proved this to be the case.

Brannockite is the lithium-tin analog of osumilite, with the formula $KLi_3Sn_2Si_{12}O_{30}$. It is free of the elements aluminum, iron and magnesium and the only significant departure from a "clean" composition is less than a percent of Na_2O. Four analogs of osumilite are now known but brannockite is the only tin and lithium bearing member of the group and also the only one found in a pegmatite. Osumilite occurs in volcanic rocks; roedderite, merrihueite and yagiite all are limited in occurrence to meteorites. Milarite, a hydrous potassium, calcium and beryllium aluminosilicate is considered a structural analog, however its anomalous optics (biaxial?) casts doubt upon its true structural nature.

brannockite
$(K,Na)Li_3Sn_2[Si_{12}O_{30}]$
merrihueite
$(K,Na)_2Fe_2(Fe,Mg)_3[Si_{12}O_{30}]$
osumilite
$(K,Na,Ca)(Fe,Mg)_2(Al,Fe^{II},Fe^{III})_3[Al_2Si_{10}O_{30}] \bullet H_2O$
roedderite
$(Na,K)_2Mg_2(Mg,Fe)_3[Si_{12}O_{30}]$
yagiite
$(Na,K)_{1.5}Mg_2(Al,Mg,Fe)_3[Al_2Si_{10}O_{30}]$

The mineral is named for Dr. Kent C. Brannock, Chemist, Tennessee Eastman Company, Kingsport, Tennessee, who first called the authors' attention to the rare minerals

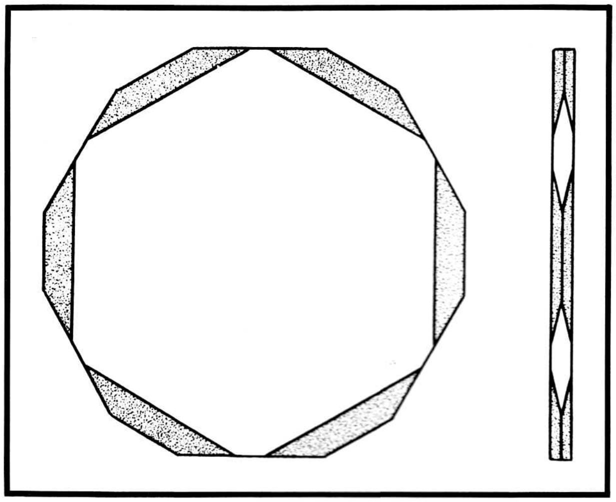

Fig. 2. **Two views of idealized brannockite crystals.**

of this locality and was instrumental in helping them obtain specimens. He has been a constant source of inspiration throughout the course of our studies of the Foote mine's minerals, an effort leading to the description of the new species switzerite, eakerite and tetrawickmanite prior to the present one, and the identification of more than eighty established species.

OCCURRENCE AND PROPERTIES

Brannockite occurs in minute amounts in late hydrothermal portions of the lithium-tin enriched pegmatite mined primarily for spodumene near Kings Mountain. It is found in vugs and on flat fracture surfaces in leached pegmatite associated with bavenite, pyrite, tetrawickmanite, stannian titanite (4-6% Sn), albite and quartz. Due to the small size of the crystals (<1 mm), their perfect transparency and absence of color, brannockite is very difficult to see unless viewed under short-wave (only) ultraviolet light which causes the mineral to fluoresce a bright blue-white. Many crystals have extremely tiny pyrite crystals scattered over their surfaces but the relative ages of brannockite and bavenite could not be determined.

Brannockite is uniaxial negative with birefringence about .002-.001, $\epsilon = 1.566$ and $\omega = 1.567$. There is no optical evidence of twinning or cleavage. The mineral is brittle but hardness was not determined owing to the minuteness of the crystals.

The crystals of brannockite are so tiny, transparent, and rarely free of attached minerals (bavenite and pyrite especially) that the technique of flotation in methylene iodide (thinned with acetone) was used because all that was needed was one clean crystal. The densities of other minerals in larger crystals were carefully measured. These were then placed in the same solution with a brannockite crystal for comparison. Phenacite from Brazil (2.960) remained suspended well above brannockite while brazilianite from Brazil (2.985) was suspended slightly below the new mineral. On this basis a density of 2.980 was assigned to brannockite. The calculated density (Z = 2) is 3.08 gm/cm³.

MORPHOLOGY

The crystals are not complex, only four forms were noted in goniometric studies: {100}, {110}, {114} and {001}. The pinacoid {001} is by far the dominant form as all crystals are very thin plates; the ratio of thickness to breadth being about 1:20. The beveling form {114} is readily discernible on all crystals (Fig. 2). The axial ratio by goniometry is $c/a = 1.430$, which agrees well with the 1.421 ratio calculated from the refined x-ray data.

CHEMISTRY

First attempts at determining the composition of brannockite were with the electron microprobe. The only elements detected and determined in this preliminary analysis were tin and silicon. The very low summation and comparison with the chemistry of the mineral's analogs suggested the presence of significant amounts of one or more light metals. Many of the associated late hydrothermal minerals at the Foote mine are enriched in either beryllium or lithium.

Semiquantitative analyses using a combination of techniques (including flame and d.c. arc emission spectroscopy, spark source mass spectrometry, and electron microscopy) performed at Oak Ridge National Laboratory on a few crystals showed that brannockite contains the alkalis lithium and potassium in substantial amounts, and is free of beryllium. A return to the microprobe and a more thorough analysis gave 4.5% K_2O. A 3.08 mg sample was then analysed by flame photometry which finally provided a more quantitative value for the lithium content and supported the microprobe results for potassium.

The complete analysis (Table I) is in excellent agreement with the ideal, within the limits of the techniques employed and in consideration of the meager amounts of brannockite sacrificed.

Table I. Analysis of brannockite.

	$KLi_3Sn_2Si_{12}O_{30}$	BRANNOCKITE	
K_2O	4.2%	3.72+	4.5*
Li_2O	4.0	3.75+	
Na_2O		0.74+	
SnO_2	27.1	28.2*	
SiO_2	64.7	65.8*	
	100.0	102.2	103.0

* by electron microprobe
\+ by flame photometry
Precision of analytical techniques is about ±3% of amount present.

CRYSTALLOGRAPHY

Precession x-ray photographs show brannockite to be hexagonal, space group *P6/mcc*. The precession and powder photographs of osumilite and brannockite are almost identical, indicating a strong structural similarity between the two minerals.

Cell parameters were determined by computer refinement of x-ray powder data (Table II), using the program

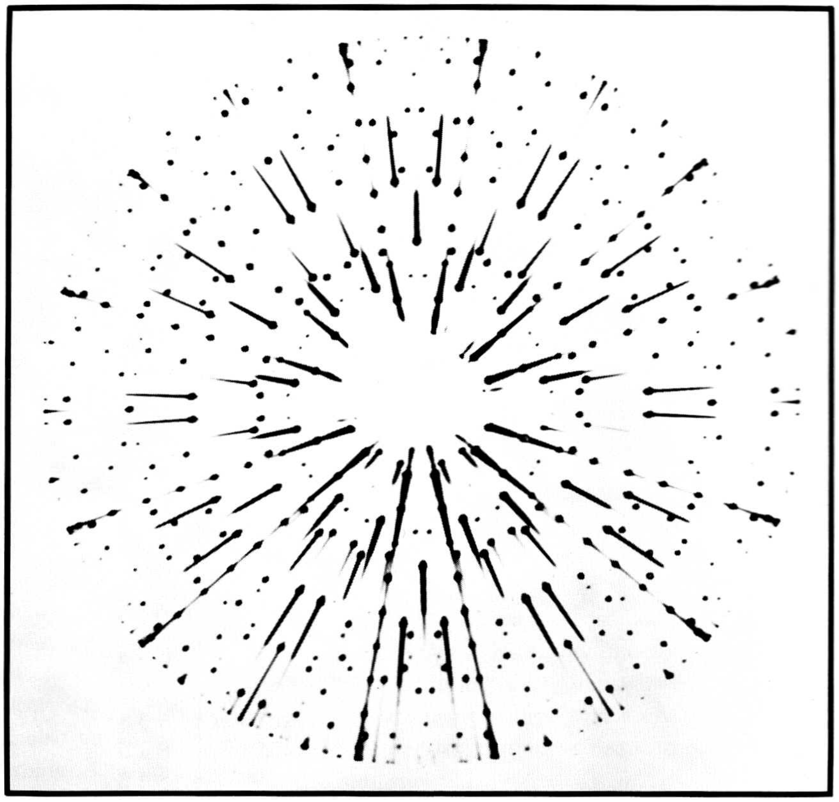

Fig. 3. **O-level precession photograph (001) showing twinned crystals.**

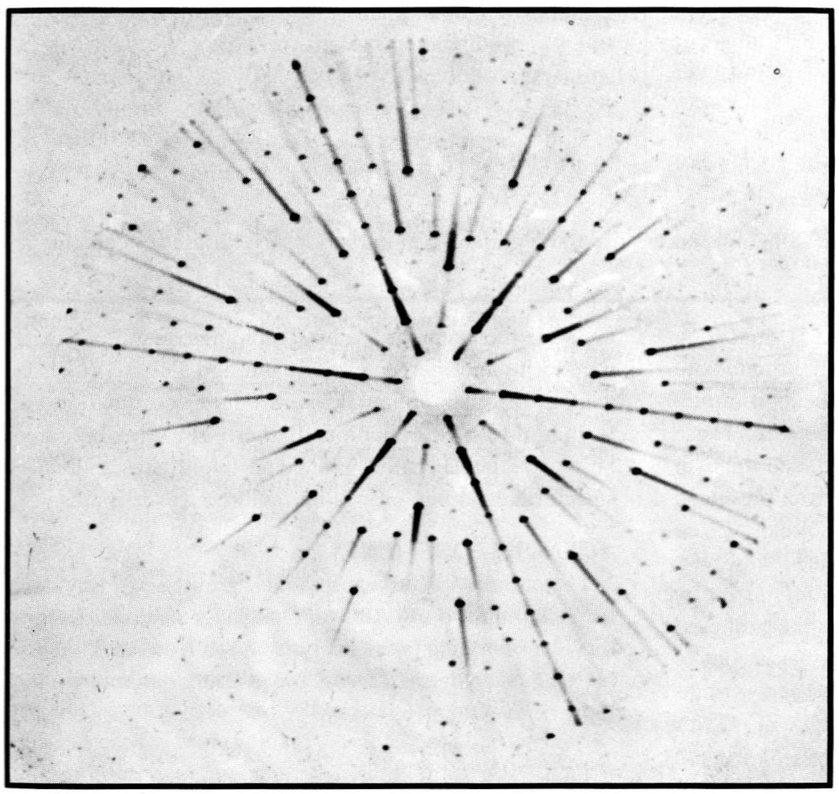

Fig. 4. **O-level precession photograph (001) of an untwinned crystal.**

of Appleman and Evans. Indices for a starting set of *d*-values were assigned by analogy with those of osumilite. Successive refinements and addition of new lines produced a completely indexed pattern. The refined cell parameters are $a = 10.0167(2)$Å and $c = 14.2452$Å. The cell volume is 1237.814Å^3, and Z = 2.

Precession photographs of several brannockite crystals appeared as shown in Fig. 3. Twinning was suspected because of an obvious doubling of rows of strong spots on the photographs. A search for untwinned material eventually produced a crystal that gave the photograph in Fig. 4. Many of the crystals examined gave *c*-axis, zero-

Table II. Brannockite — Powder X-ray Data.

h k l	I/Io[1]	dcalc(Å)	dmeas(Å)	h k l	I/Io[1]	dcalc(Å)	dmeas(Å)
1 0 0	6	8.675	8.693	5 1 1	2	1.549	1.548
0 0 2	8	7.122	7.141	5 0 5	2	1.482	1.482
1 0 2	7	5.505	5.504	2 2 8	4	1.451	1.453
1 1 0	2	5.008	5.000	5 1 4	1	1.427	1.428
2 0 0	8	4.337	4.343	6 0 2	3	1.417	1.416
1 1 2	10	4.096	4.109	5 2 0	3	1.389	1.389
2 0 2	1	3.705	3.722	4 2 6	1	1.349	1.344
0 0 4	2	3.561	3.559	4 3 4	3	1.324	1.325
1 1 3	1	3.446	3.467	2 1 10	1	1.307	1.310
2 1 0	4	3.279	3.295	6 1 2	2	1.300	1.297
2 1 1	5	3.195	3.198	4 0 9	2	1.278	1.278
1 2 2	3	2.978	2.977	6 0 6	3	1.235	1.236
1 1 4	9	2.902	2.905	6 1 5	4	1.200	1.200
2 0 4	1	2.752	2.754	3 0 11	3	1.182	1.182
3 0 2	6	2.679	2.681	3 2 10	2	1.158	1.158
2 2 0	6	2.504	2.502	0 0 13	3	1.096	1.096
2 1 4	2	2.412	2.413	5 2 9	6	1.044	1.044
2 2 2	5	2.362	2.362	6 3 6	2	.9928	.9928
3 0 4	5	2.245	2.245	9 0 3	1	.9446	.9447
3 1 3	6	2.146	2.147	7 3 4	1	.941	.941
2 0 6	1	2.082	2.088	6 3 8	1	.931	.932
2 2 4	2	2.048	2.048	8 2 6	1	.8795	.8795
3 1 4	6	1.994	1.992	8 3 5	2	.8415	.8414
4 1 0	2	1.893	1.892	4 3 14	2	.8283	.8283
4 1 1	2	1.876	1.874	6 6 3	2	.8221	.8221
3 0 6	6	1.835	1.833	10 1 2	1	.8180	.8180
0 0 8	3	1.781	1.784	10 1 4	1	.8022	.8022
4 0 5	5	1.726	1.725	9 3 2	2	.7969	.7969
4 1 4	4	1.671	1.671	11 0 3 } 10 1 6	2	.7779	.7779
4 2 2	2	1.598	1.599				
4 1 5	1	1.577	1.577				

[1] Visual estimates from powder photograph. Silicon used as internal standard, Cu radiation (Ni filtered) camera 114.6 mm diameter.

level precession photographs the same as Fig. 3, indicating a non-random relationship between pairs of brannockite crystals. Two lines of spots in the twin precession photographs are common to both individuals of the twin. These lines pass through the reflections 210 and 510, and the twin would, at first glance, appear to be equally well produced by using either of these directions as a twin axis. Close scrutiny of the untwinned and twinned nets, however, indicated that some weak maxima are not duplicated by twinning about [510] , and therefore [210] is the proposed twin axis for brannockite. The measured displacement of the twinned nets in brannockite precession photographs is 21°23', quite close to the calculated value of 21°47' for twice the angle between (210) and (110).

COORDINATION AND STRUCTURAL FORMULA

The general formula for osumilite-type minerals is $Me^{XII}Me_2^{VI}Me_3^{IV}(Si,Al)_{12}^{IV}O_{30}$ where Na, K and Ca are generally present in 12-fold coordination, Mg and Fe in both 6- and 4-fold coordination, and Al, Mn and Ti in 4-fold coordination. The ideal formula of brannockite is $KSn_2Li_3Si_{12}O_{30}$, which fits well the general structural formula for the osumilite group (including osumilite, yagiite, roedderite and merrihueite)(Bunch and Fuchs, 1968). By analogy, Sn in brannockite is in 6-fold coordination and Li is in 4-fold coordination. If there is a distribution of Sn and Li between the 4-fold and 6-fold sites a detailed structural examination will be required to verify this.

ACKNOWLEDGEMENTS

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