STUDIES OF RADIOACTIVE COMPOUNDS
X—THE SYNTHESIS AND CRYSTALLOGRAPHY OF BRANNERITE

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ABSTRACT

Precession and Weissenberg films of a single crystal of synthesized brannerite show that the compound is monoclinic, $C2/m$, with $a = 9.87$, $b = 3.76$, $c = 6.95$ Å, $\beta = 119° 30'$. The cell contains $2[UTi_2O_6]$. Sp. gr. (meas.) = 6.35, (calc.) = 6.36. The cell constants and space group are compatible with the forms observed by Pabst on natural crystals in terms of the theoretical form development predicted by the Donnay generalization of the Bravais law. It suggests that brannerite regains its original structure on ignition.

The x-ray powder diffraction patterns of ignited brannerite from Blind River, Ontario almost invariably show the presence of rutile or anatase and other minerals intimately associated with the brannerite. The appearance of the grains is affected by these impurities. The variable chemical constitution and physical properties of the grains have influenced some geologists to doubt the existence of the mineral in this region. They suggest that the act of heating, which is necessary to produce the x-ray pattern, causes the mineral to be synthesized from one or more mineral phases in the grains (Brotzen, 1958). Kaiman (1959) has recently reported the successful synthesis of brannerite from the oxides of uranium and titanium, but not under the usual ignition conditions. Concurrently, similar research was carried on at this University. Mixtures of pitchblende and rutile or anatase in the ratio of 1 to 2 recrystallized to U_3O_8 and rutile when heated in an open crucible over a flame or in a muffle furnace. The same results were obtained when the mixture was seeded with natural brannerite from Blind River. An excess of carbon, added to prevent the formation of U_3O_8, resulted in an ignition product of UO_2 and rutile. Finally, NaCl was added to the carbon mixture. The flux reacted with the mixture producing a compound, possibly a sodium uranium oxide, whose major diffraction data showed some similarity to those of brannerite. The experiments confirm that brannerite is not synthesized under ordinary ignition conditions and that the mineral is a constituent of the ore.

With the advice and assistance of Professor A. Lund and Mr. H. Hancock of the Department of Metallurgy, efforts were now made to

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TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR BRANNERITE[1]

Blind River[2]		Synthetic[3]			
I	d meas.	I	d meas.	d calc.	hkl
3	6.03	36	6.04	6.04	001
8	4.77	96	4.74	4.77	$\bar{2}01$
2	4.31	19	4.29	4.29	200
10	3.43	>100	3.44	3.44	110
4	3.33	>100	3.35	3.37	$\bar{2}02$
4	3.27	13	3.28	3.29	$\bar{1}11$
3	3.02	36	3.02	3.02	002
5	2.92	36	2.90	2.89	201
5	2.76	33	2.77	2.77	111
4	2.51	31	2.53	2.53	$\bar{1}12$
4	2.46	33	2.47	2.47	$\bar{3}11$
				2.44	$\bar{4}01$
		17	2.41		
				2.39	$\bar{4}02$
		8	2.303	2.31	$\bar{2}03$
6	2.281	27	2.292	2.30	$\bar{3}12$
		12	2.276	2.27	310
vf	2.156	9	2.144	2.14	400
vf	2.078	7	2.080		
		36	2.043		
3	2.023				
		23	2.015		
		5	1.911		
4	1.903	19	1.903		
2	1.866	24	1.881		
vf	1.778	4	1.798		
		8	1.749		
f	1.737	5	1.732		
		3	1.723		
3	1.695	20	1.709		
vf	1.667	5	1.675		
		7	1.642		
		19	1.630		
4	1.621				
		18	1.609		
		6	1.597		
		9	1.578		
4	1.568	7	1.569		
		6	1.561		
		6	1.558		
		1b	1.493		
vf	1.482	3	1.486		
vf	1.458	4	1.450		
vf	1.441	2	1.431		
vf	1.410	2	1.415		
		3	1.384		
2	1.367	4	1.376		
		3	1.308		
		2	1.266		
		5	1.263		
		2	1.242		
		2	1.239		
		5	1.234		
		3	1.218		
		3	1.200		

[1] For nickel filtered copper radiation.

[2] Film method; camera diameter 57.3 mm.

[3] Diffractometer method; intensities based on determination of relative peak heights. Fifty-four additional weak reflections were observed.

synthesize brannerite under other conditions. Very pure tetravalent uranium oxide ($UO_{2.06}$) supplied by Mr. Hancock, was mixed with reagent grade TiO_2 in the atomic proportions 1 to 2, finely ground, pressed into a pellet and sintered at a low vacuum (10^{-3} mm. Hg) in a graphite container at 900°C for eighteen hours. No reaction took place. The material was re-ground and heated at 1200°C for the same length of time. This yielded a sintered product which gave a composite x-ray pattern of UO_2 and brannerite. Mr. Hancock then suggested melting the sintered pellet in an arc furnace with an adjustable electrode and a water-cooled base in an argon atmosphere. The arc was broken over the pellet and the large current easily melted it. The cooled product showed a group of long thin radiating crystals. The portion of the pellet which had rested on the water-cooled base still contained a slight amount of UO_2 but the remainder was composed entirely of brannerite. It is estimated that the pellet reached a temperature of 2000°C.

X-RAY SINGLE CRYSTAL STUDY

A single tiny crystal was selected from the radiating group and approximately aligned on the optical goniometer to rotate about the needle-axis, and then precisely aligned with orientation photographs on a precession camera. Subsequent zero and upper level films revealed that this axis is the *b*-axis of a monoclinic cell and the crystal was transferred to a Weissenberg instrument for a more precise determination of the β angle. The final cell constants are as follows:

$$a = 9.87,\ b = 3.76,\ c = 6.95\ \text{Å}\ (\text{all} \pm 0.02\ \text{Å}),\ \beta = 119°\ 30'\ (\pm 15')$$

$$\text{Space group } C2/m$$

Table 1 presents the *x*-ray powder data for both synthetic and natural ignited brannerite, indexed on the basis of these cell constants. The excellent agreement between the two sets of measured spacings confirms the identity of the synthesized compound with ignited brannerite. The agreement between measured and calculated spacings indicates that the accuracy claimed for the cell constants is justified.

Recently Öztunali (1959) reported a triclinic cell with

$$a = 5.27,\ b = 3.54,\ c = 6.31\ \text{Å}$$
$$\alpha = 77°\ 30',\ \beta = 108°\ 40',\ \gamma = 100°\ 10'\ (\text{all} \pm 1°)$$

which he obtained with rotation and Weissenberg films from a synthetic brannerite crystal measuring 0.07 mm. in size. His measured powder spacings are in good agreement with the powder data given in Table 1, indicating that the synthetic product was in fact brannerite. Öztunali evidently overlooked the monoclinic symmetry by inadvertently rotating his crystal about a non-axial direction—possibly the [110] row of the monoclinic cell. The calculated value for the period along this row is 5.28 Å, in good agreement with the length of Öztunali's *a* axis. The remaining five triclinic elements have less obvious relationships in the monoclinic cell. Table 2 shows the results of our efforts to index the first six powder diffraction arcs in terms of the triclinic elements. The discrepancy between the measured spacings and the six largest spacings calculated for the triclinic cell is clearly too great to be eliminated by refining the triclinic elements. It suggests that the interpretation of the single crystal photographs is in error.

TABLE 2. BRANNERITE

Measured spacings		Six largest spacings calculated for triclinic cell	
This paper	Öztunali		
6.04	6.06	5.89	001
4.74	4.756	4.96	100
4.29	4.281	4.50	$\bar{1}01$
3.44	3.452	3.43	010
3.35	3.351	3.34	101
3.28	3.288	3.22	011

THE COMPOSITION OF BRANNERITE

Three determinations of the specific gravity of a fragment weighing 6.7 mg. ranged between 6.31 and 6.40 and averaged 6.35.

The ideal composition of brannerite must be very close to the composition of the mixture that was used to form the pellet. Kaiman concluded from polished section studies of his synthetic products that the ideal composition of brannerite is more nearly represented by UTi_2O_6 than by $U_2Ti_5O_{14}$. Table 3 compares the calculated specific gravities for these formulas and the formula, $U_3Ti_5O_{16}$, given in Dana's System of Mineralogy (1944). The measured specific gravity is in excellent agreement with the cell contents $2[UTi_2O_6]$, and it may be assumed with Kaiman that this formula represents the composition of brannerite.

It is interesting to note that other AB_2O_6 compounds include the tapiolite-mossite, columbite-tantalite, euxenite-polycrase and eschynite-priorite series and the mineral samarskite. These compounds differ from brannerite in that they crystallize in the tetragonal and orthorhombic systems.

THE MORPHOLOGY OF BRANNERITE

The symmetry of natural brannerite has been described as tetragonal or orthorhombic (Hess & Wells, 1920) and monoclinic (George, 1949) from inspection of crystals which are typically rough. Prismatic crystals recently discovered in Mono County, California are apparently more favourable for goniometric study than most. Pabst (1954) recognized

TABLE 3. BRANNERITE: FORMULA

Formula	*Z*	Calc. Sp. gr.
$U_3Ti_5O_{16}$	1	8.95
$U_2Ti_5O_{14}$	1	6.95
UTi_2O_6	2	6.36

TABLE 4. BRANNERITE: MEASURED AND CALCULATED ANGLES

1		2		3	
*hk*0	ϕ	*hk*0	ϕ	*hk*0	ϕ
010	0°00′	100	84°58′	100	90°00′
160	18 12	510	66 46	510	65 27
130	31 42	310	53 16	310	52 43
120 590	45 35	210 950	39 23	210	41 12
110	61 34	110	23 24	110	23 39
210	75 05	130	9 53	130	8 18
310	79 37	150	5 21	150	5 01
610	84 58	010	0 00	010	0 00

1. The measured angles and indices of Pabst (1954).
2. Pabst's angles and indices transformed to the structural setting.
3. Angles calculated from the structural constants.

that the form development of these crystals is dominated by the presence of one strong orthogonal zone of faces parallel to the prism axis. This is characteristic of orthorhombic or monoclinic symmetry. Pabst's measured angles (Table 4, column 1) ranged over several degrees of arc, but despite this he was able to assign reasonable indices to the faces. When Pabst's *a* and *b* axes are interchanged, the transformed angles agree well with angles calculated for planes in the (*hk*0) zone of the structural cell (Table 4, columns 2 & 3). The agreement appears to be too consistent to be fortuitous. It strongly suggests that the morphological zone in the natural crystals is identical with the structural zone in the synthesized crystal even though the habits of the crystals are very different. However it is not unreasonable to believe that the *x*-ray crystal, synthesized in an instant at 2000° C, developed a habit that is unusual in terms of the habit of natural crystals.

It is interesting to note that with the exception of {100}, {010} and {210}, the {*hk*0} forms observed on the crystals have indices in which $h + k = 2n$ in the structural setting. This is the condition for *x*-ray reflection by {*hk*0} planes of a base-centred cell. According to the Donnay (1942) generalization of the law of Bravais the relative importance of forms of a crystal species are proportional to the spacings of the corresponding structural planes in the simplest notation that conforms to the space group condition. Column 1 of Table 5 lists the first fifty-three (*hk*0) planes in order of decreasing spacing. The starred planes correspond to the permissible reflections from the base-centered cell. The reflecting planes which conform to the simplest space group notation are repeated in column 2. Finally, the last column gives the indices of these planes reduced to morphological notation. This is the theoretical order of importance of {*hk*0} crystal forms according to the Donnay rule. It is significant that the first seven indices account for all but one of the eight forms observed by Pabst. The harmony which obviously exists between

TABLE 5. BRANNERITE: THEORETICAL FORM DEVELOPMENT OF BRANNERITE

1		2	3
*hk*0	*d*	*hk*0	*hk*0
100	8.59		
200*	4.29	200	100**
010	3.76		
110*	3.44	110	110**
300	2.86		
210	2.83		
310*	2.27	310	310**
400*	2.15		
410	1.88		
020*	1.88	020	010**
120	1.84		
500	1.72		
220*	1.72		
320	1.57		
510*	1.56	510	510**
600*	1.43		
420*	1.41	420	210**
610	1.34		
520	1.26		
030	1.25		
130*	1.23	130	130**
700	1.23		
230	1.20		
710*	1.17	710	710
330*	1.15		
620*	1.14		
430	1.08		
800*	1.07		
810	1.03		
720	1.03		
530*	1.01	530	530
900	0.95		
630	0.94		
040*	0.94		
140	0.93		
820*	0.93	820	410
910*	0.93	910	910
240*	0.92	240	120
340	0.88		
730*	0.87	730	730
440*	0.86		
10.0.0*	0.86		
920	0.85		
10.1.0	0.84		
540	0.82		
830	0.81		
640*	0.78	640	320
11.0.0	0.78		
10.2.0*	0.78		
11.1.0*	0.77	11.1.0	11.1.0
930*	0.76	930	930
050	0.75		
150*	0.75	150	150**

1. (*hk*0) lattice planes of brannerite; spacings determined by graphical method of Peacock (1938). The starred planes correspond to permissible *x*-ray reflections.
2. Reflecting planes which conform to simplest space group notation.
3. The same planes with indices reduced to morphological notation. The double-starred indices correspond to Pabst's observed crystal forms.

the morphology of Mono County brannerite and the space group symmetry of synthesized brannerite supports the relationship derived above between Pabst's interfacial angles and the *x*-ray constants.

The present research has indicated that natural brannerite regains its original structure on ignition. This is known to occur when the cubic metamict minerals betafite and microlite-pyrochlore are ignited but authoritative data on the structural cells of metamict minerals with lower symmetry are lacking. Arnott (1950) obtained indirect evidence on the recrystallization of euxenite. He was able to index the powder pattern of an ignited sample of this mineral in terms of morphological measurements and derive rational cell constants. Recent work by Ferguson (1957) has suggested that natural fergusonite, ignited above 800°C, recrystallizes with its original structure, but conclusive proof rests on finding natural crystals which are better suited for goniometric study than those previously discovered. It appears that crystals of metamict minerals are typically rough, and this characteristic together with the well known fact that crystal fragments become polycrystalline on ignition has limited research on these minerals.

It was frequently noticed during this research that the period of heating necessary to recrystallize natural brannerite varies. The period is related to the physical appearance of the grains. For example, black to brownish-black lustrous grains produce the characteristic powder pattern after a few minutes of heating. Reddish grains with a duller lustre require several hours of heating before the characteristic pattern is obtained, and passes through several intermediate stages in the interval. The data indicate that the degree of disorder in the structure varies. Since the fresher-looking grains regain the ultimate structure more rapidly it seems that geological weathering increases the degree of disorder.

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