

## BRANNERITE FROM CALIFORNIA

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### ABSTRACT

Brannerite is found in quartz veins about seven miles south of Coleville, Mono County, California. It is very similar in composition to brannerite from the type locality in Idaho and from elsewhere. Initially metamict brannerites from Idaho, California, and Morocco yield similar  $x$ -ray diffraction patterns after heating. It has proved impossible to index these patterns and so the crystallographic character of heated brannerite remains in doubt.

### OCCURRENCE

Several years ago Mr. John Halsey presented to the writer specimens of an unidentified radioactive mineral from Mono County, California. After some delay this was found to be the rare mineral brannerite, hitherto known in the United States only from placer deposits in Kelley Gulch, Custer County, Idaho, the type locality described by Hess and Wells (1920). The following statement concerning the California occurrence was supplied by Mr. Halsey.

"The brannerite was found in 1949 by Mr. D. B. Dean in the canyon of the West Walker River, seven miles south of Coleville, Mono County, California (Bridgeport Quadrangle, T7N, R23E, on the border of sections 4 and 9). Specimens for analysis were collected from several small prospect pits along an abandoned road on the east side of the river, 50 yards from U. S. highway 395.

"The brannerite occurs as a trace constituent of mesothermal quartz veins,  $\frac{1}{4}$  inch to 18 inches thick, which traverse late Mesozoic quartz-monzonite along closely spaced subparallel sheeting joints. The veins are considered to be related genetically to nearby pegmatite and aplite veins which are also controlled by sheeting joints and contain the same suite of accessory minerals.

"95% or more of the vein material consists of massive milky quartz. Smoky quartz and clear prismatic quartz are present in minor amount. The most abundant accessory silicate is muscovite. Biotite, orthoclase, epidote, hornblende, garnet, tourmaline and zeolites occur in trace amounts. Non-silicates are chiefly magnetite, pyrite, chalcopyrite and calcite. Molybdenite and bismuthinite occur in minute quantities.

"Of the accessory vein minerals brannerite is by far the least abundant. Fifteen tons or so of carefully sorted vein materials have yielded not more than 10 grams of the mineral. It is randomly distributed through the larger veins and is occasionally associated with slightly radioactive smoky quartz."

## CRYSTAL SYSTEM

In the original description of brannerite, Hess and Wells (1920) left the crystal system in doubt. They considered the mineral to be "an isometric paramorph after either a tetragonal or an orthorhombic form." George (1949) listed it as monoclinic without giving axial elements. This statement was based on inspection of large crystals from Fuenteovejuna, Cordoba, Spain (George, 1952).

The Mono County brannerite occurs in lustrous black crystals firmly embedded in quartz. These crystals are mostly slender prisms not over a few millimeters thick and a centimeter or more in length. This habit is similar to that of brannerite at Chateau Lambert, Vosges, recently described by Branche, Chervet and Guillemen (1951). Though it is very difficult to remove the crystals from the enclosing quartz without damage Mr. Halsey did succeed in isolating some in fairly good condition.

Seven crystals were measured on the reflecting goniometer. Only one showed terminal faces and these were not suitable for measurement. The prism zones included from 6 to 12 measurable faces on the several crystals. Though the measurements leave something to be desired they suffice to establish the character of the prism zone. The angles are close to those of tetragonal zones, e.g.  $\phi_{310}$   $18^{\circ}26'$ , but the development is clearly orthogonal. A single orthogonal zone dominating the habit is to be expected only in orthorhombic or monoclinic crystals. The results for the five better crystals are summarized in Table 1.

The axial ratio corresponding to simplest indices for all observed forms,  $a/b=0.528$ , is near the  $a/b$  ratio of ytrotantalite and samarskite. This ratio is associated with the indices {160} for the most persistent form. Simpler indices could be assigned to this form with corresponding change in ratio but only at the cost of introducing higher indices for some of the other observed forms.

TABLE 1. SUMMARY OF GONIOMETRIC MEASUREMENT OF 5 CRYSTALS OF BRANNERITE FROM MONO COUNTY, CALIFORNIA

$hk0$	$\phi$	Range of $\phi$	Number of observations	Calculated for $a:b=0.528$
010	$0^{\circ}00'$		5	
160	18 12	$16^{\circ} 4' - 19^{\circ}39'$	15	$17^{\circ}31'$
130	31 42	30 22 - 32 35	5	32 16
120	45 35	43 29 - 47 25	5	43 26
590				46 28
110	61 34	60 28 - 63 36	8	62 10
210	75 5	74 5 - 75 39	4	75 12
310	79 37	79 2 - 80 12	2	80 1
610	84 58	84 38 - 85 30	4	84 58

## COMPOSITION

The identification of brannerite from Mono County, California, was accomplished by density determination and comparison of diffraction patterns with those obtained from type material. It was later confirmed by spectrographic examination and chemical analysis.

The density of brannerite from Mono County was found by the Berman balance on four closely checking fragments to be 5.43. This just matches the highest value in the range of specific gravity, 4.5 to 5.43, reported with the description of brannerite from the original locality by Hess and Wells (1920).

TABLE 2. BRANNERITE FROM "DEAN'S MINE" ON THE WALKER RIVER  
IN MONO COUNTY, CALIFORNIA  
Sample No. AP-1, Lab. No. 66779

Constituent	%	Constituents for R <sub>2</sub> O <sub>3</sub>	%
SiO <sub>2</sub>	0.5	Rare Earth Oxides	6.5 <sup>a</sup>
CaO	2.8	ThO <sub>2</sub>	5.0
Total R <sub>2</sub> O <sub>3</sub>	92.2	UO <sub>2</sub>	8.2
(Including Rare Earths)		UO <sub>3</sub>	32.0
Total H <sub>2</sub> O	2.6	TiO <sub>2</sub>	32.9
Mn, Mg	.x	FeO	2.4
	98.2+		87.0

<sup>a</sup> Mostly yttrium and erbium.

1. The determined constituents of the R<sub>2</sub>O<sub>3</sub> precipitate (when calculated to the proper oxides) amount to 86.7%. The difference of 92.3% (i.e. total R<sub>2</sub>O<sub>3</sub>) and 86.7% (determined constituents of R<sub>2</sub>O<sub>3</sub>) is 5.6%. This missing 5.6% is due to Pb, Cb, Ni, Bi, Zr, and Ta. Spectrographic qualitative analysis of a small sample by J. Stich shows that these chemically undetermined elements are present in trace amounts, a "trace" being approximately 0.1-1%.

2. It is impossible on a chemical basis to state definitely what the valence state of iron is in the mineral. Quadrivalent uranium is in excess over iron so that in preparing a solution of the sample any ferric iron would be reduced by the quadrivalent uranium, forming equivalent amounts of ferrous iron and hexavalent uranium.

Following a preliminary spectrographic examination by Dr. T. G. Kennard of Kennard and Drake, Los Angeles, an analysis of the newly identified brannerite was made by analysts of the U. S. Geological Survey through the kind offices of Dr. John C. Rabbitt, chief of the Trace Elements Section. The analysis was carried out on 97 mgs. of carefully purified fragments plus a somewhat greater weight of material slightly contaminated with quartz. The report of the analysis is given in Table 2.

As may be seen from Table 3 the composition of California brannerite is close to that of brannerite from other localities. It seems probable that the silica content reported for the mineral from Chateau Lambert is

TABLE 3. ANALYSES OF BRANNERITE

	1	2	3	4
CaO	2.9	2.74	2.7	2.8
BaO	0.3	0.01		
SrO	0.1	0.01		
Mn, Mg	—	—		.x
PbO	0.2	2.34	3.2	
FeO	2.9	3.11	5.4	2.4
Ce <sub>2</sub> O <sub>3</sub>	none	1.10	0.3	6.5
(Y, Er) <sub>2</sub> O <sub>3</sub>	3.9*		1.8†	
UO <sub>2</sub>	10.3	—	—	8.2
UO <sub>3</sub>	33.5	—	—	32.0
U <sub>3</sub> O <sub>8</sub>	—	51.76	43.2	—
ThO <sub>2</sub>	4.1	1.20	0.3	5.0
SnO <sub>2</sub>	—	—	1.3	—
ZrO <sub>2</sub>	0.2	N.D.	—	—
TiO <sub>2</sub>	39.0	32.45	35.2	32.9
SiO <sub>2</sub>	0.6	0.16	3.3	0.5
CO <sub>2</sub>	0.2	—	—	—
H <sub>2</sub> O	2.0	2.35	3.7	2.6
Total	100.2	97.21	100.6	—
S.G.	5.42	5.17	4.82	5.43

1. Kelly Gulch, Custer County, Idaho (Hess and Wells, 1920). "No Mg, Sn, W, Ta, Mo, V, Cu or F could be detected." "... quartz... undoubtedly accounts for the SiO<sub>2</sub>..."

\* Reported as "Yt<sub>2</sub>O<sub>3</sub>, etc. Average molecular weight 350." Helium was identified spectrographically (Wells, 1920).

2. Fuenteovejuna, Cordoba, Spain (George, 1949).

3. Chateau Lambert, Vosges, France (Branche, Chervet and Guillemen, 1951).

† Reported as "Y<sub>2</sub>O<sub>3</sub>."

4. Walker River, Mono County, California (Table 2).

attributable to quartz contamination. Brannerite being metamict as recorded by Palache, Berman and Frondel (1944), the water content is presumably acquired incidental to metamictization.

The formula of brannerite has long been in doubt. Since it has not been possible to obtain cell dimensions (*vide infra*) the new data do not relieve this situation. There are, however, numerous related minerals whose formulas may be written in the form  $XV_2O_6$ , where X includes ions of radius near 1.0 Å mostly in eight-fold coordination and Y embraces ions of radius near 0.75 Å mostly in six-fold coordination, following Machatschki (1941). Among such minerals may be included euxenite, samarskite, tapiolite and others. Table 4 shows that the analysis of brannerite from Idaho may be fitted to such a formula. The close match depends, of course, on suitable distribution of Fe between X and Y posi-

TABLE 4. FITTING OF ANALYSIS OF BRANNERITE FROM KELLEY GULCH, CUSTER COUNTY, IDAHO, TO IDEAL FORMULA,  $XY_2O_6$ 

	Wt. %	Mol quotient $\times 10^3$	Number of oxygen	Number of cations	
CaO	2.9	52	52	Ca	52
BaO	0.3	2	2	Ba	2
SrO	0.1	1	1	Sr	1
PbO	0.2	1	1	Pb	1
(Y, Er) <sub>2</sub> O <sub>3</sub>	3.9	11*	33	(Y, Er)	22
UO <sub>2</sub>	10.3	38	76	U	38
UO <sub>3</sub>	33.5	117	351	U	117
ThO <sub>2</sub>	4.1	16	32	Th	16
ZrO <sub>2</sub>	0.2	2	4	Zr	2
				Fe	11
FeO	2.9	40	40		
				Fe	29
TiO <sub>2</sub>	39.0	494	982	Ti	494
			<hr/> Total 1544		
				1544    6.00 O	

\* Taking molecular weight of combined oxides to be 350, as given by Hess and Wells, 1920.

tions. It may be noted that in 1929 Machatschki assigned Fe to the X positions while in 1941 he assigned it to the Y positions.

#### X-RAY EXAMINATION

Through the courtesy of Dr. George Switzer, brannerite from the original locality in Kelley Gulch, Custer County, Idaho, was made available from the United States National Museum. This consisted of a small portion of the crushed material used for analysis by Hess and Wells, USNM 105793, and some loose crystals, USNM 96873, which included several varieties of euxenite, some closely resembling brannerite, and other heavy minerals. Mr. M. C. Stinson kindly furnished an additional sample of concentrate containing brannerite from his claims in Kelley Gulch and finally a further supply was obtained by purchase from Minerals Unlimited, Berkeley.

Through the kindness of Mr. John B. Jago of San Francisco it was possible to obtain some brannerite from the Bou-Azzer mine, Morocco. This brannerite is in anhedral black grains, up to a few millimeters in dimensions, intergrown with gray quartz and accompanied by a trace of sulfides and clay minerals.

The  $\alpha$ -ray study was mostly carried out on fragments of single crystals

in the manner previously described (Pabst, 1952, p. 145-146). Brannerite from the three localities is essentially metamict but all of the California brannerite and most of that from Idaho yield a few weak "powder" lines not attributable to associated minerals. Examples of these lines are recorded in Table 5. It is apparent that these correspond closely to lines

TABLE 5. DIFFRACTION PATTERNS OF UNHEATED FRAGMENTS OF BRANNERITE AND OF BRANNERITE HEATED AT "MODERATE" TEMPERATURES COMPARED WITH STRONG LINES IN MICROLITE AND URANINITE PATTERNS

Brannerite, Custer County, Idaho		Brannerite, Mono County, California		Uraninite, Quebec, $a_0=5.468\text{\AA}$ (Arnott, 1950)	Microlite, Virginia, "Ignited" $a_0=10.424\text{\AA}$ (Arnott, 1950)
Unheated fragment	Same fragment after 2 hours at 600° C.	Unheated fragment	Same fragment after 15 hours at 520° C.	Strong lines only	Strong lines only
<i>I</i> <i>d</i>	<i>I</i> <i>d</i>	<i>I</i> <i>d</i>	<i>I</i> <i>d</i>	<i>I</i> <i>d</i> <i>hkl</i>	<i>I</i> <i>d</i> <i>hkl</i>
1+ 3.11 $\text{\AA}$	2+ 3.08 $\text{\AA}$	4 3.10 $\text{\AA}$	4- 3.11 $\text{\AA}$	10 3.157 $\text{\AA}$ (111)	6 5.98 $\text{\AA}$ (111)
1 1.92	1 2.68	1 2.69	1- 2.70	5 2.734 (002)	4 3.11 (113)
1 1.626	2 1.91	3 1.91	3- 1.91	8 1.935 (022)	10 2.98 (222)
	2 1.630	3- 1.626	2+ 1.627	8 1.648 (113)	3 2.58 (004)
		1- 1.238		3 1.252 (133)	8 1.836 (044)
		1- 1.213		3 1.221 (024)	8 1.563 (226)
		1- 1.104		3 1.116 (224)	3 1.194 (266)
		1- 1.037		3 1.052 (333, 115)	3 1.165 (048)
					3 1.064 (448)
					3 1.003 (666, 22.10)

ascribable to a cubic face-centered material with  $a_0$  5.39 or 10.78  $\text{\AA}$  and that the lines are similar in relative intensities to those of the strongest lines in a uraninite or microlite pattern. Prolonged heating at temperatures not in excess of 600° C. produced only a slight weakening of this pattern. No shifts in position or relative intensity and no new lines could be detected. Similar lines suggesting a rudimentary pyrochlore structure but with lattice constant smaller than the usual 10.3-10.4  $\text{\AA}$  have been obtained from unheated euxenites from several localities.

Physical changes upon the heating of brannerite are not conspicuous. A small weight loss occurs even at 600° C. before the formation of new phases begins. The appearance of clean core fragments is not notably altered by heating. They remain black and sharp edged. Only in a few cases was some dulling of the luster observed in pieces that had been heated to the highest temperatures employed.

Upon heating to 800° C. or more brannerite fragments from all three

localities develop a characteristic and constant diffraction pattern.<sup>1</sup> This pattern consists of perfectly smooth "powder" arcs with no suggestion of orientation. In California brannerite a slight coarsening of grain could be detected after 3 hours or more of heating at 1,300° C. No such effect was observed in the Idaho or Morocco brannerite. Table 6 shows the close correspondence of diffraction patterns for material from the three localities.

Attempts were made at indexing this pattern by the methods of Lipson (1949) and of Ito (1950) and by trials of partial lattices based on the goniometric measurements and of hypothetical lattices based on the linear elements of delorenzite, a rare orthorhombic mineral of related composition. No solution was found. In view of the possible similarity of formula type and partial correspondence of axial ratios to yttrantalite and samarskite, a comparison was made with the diffraction patterns of these minerals but no marked resemblance was seen. Though the lattice of brannerite remains unknown it seems reasonable to suppose that the diffraction pattern found is that of a single phase since a large number of lines show no variation in spacing or intensity in a number of specimens from different sources treated at various temperatures between 800 and 1,300° C.

Some patterns obtained from heated brannerite showed a few lines in addition to those found to be constant and reported in Table 6. Extra or enhanced lines near 3.1, 2.7, 1.9 and 1.63 Å were registered by two or more heated specimens from each of the localities. These are close to the strongest uraninite lines, (111), (002), (022) and (113) and to the lines found in patterns of unheated brannerite. Presumably they may be ascribed to remnants of the structure existing before heating. Though a trace of rutile was detected in a few patterns of heated brannerite no difference in pattern was found between material close to the crusted surface and from the inner parts of crystals.

Hess and Wells (1920) stated that brannerite is "brownish yellow on the outside but the visible weathering has extended to a depth not exceeding the thickness of paper." Such a crust is lacking on the California and Morocco brannerite but is found covering most of the surface of specimens from Idaho. In many places it is more than "the thickness of paper," commonly being several tenths of a millimeter thick. Fragments of crust from several crystals were examined by *x*-rays. They invariably showed a weak pattern of anatase with broad lines indicating a fine state of division of the crystalline particles constituting the crust. Upon heat-

<sup>1</sup> The earlier report of "two kinds of cryptocrystalline material" (Pabst, 1952, pages 152-153) obtained in brannerite from the type locality was in error.

TABLE 6. X-RAY "POWDER" DIFFRACTION PATTERNS FROM FRAGMENTS OF BRANNERITE HEATED TO ABOUT 1,000° C.

Mono County, California		Custer County, Idaho (USNM 105793)		Bou-Azzer mine, Morocco	
<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
3	6.07 Å	4	6.03 Å	3	5.88 Å
5	4.70	6	4.73	5	4.70
2	4.31	3	4.32	2	4.29
10	3.42	10	3.41	10	3.41
6	3.32	6	3.32	6	3.29
3	3.02	3+	3.02	3	2.98
5	2.91	5	2.92	5	2.90
4	2.76	4	2.75	4	2.74
4	2.511	4	2.508	4	2.491
7	2.455	6	2.462	7	2.449
2	2.426	1	2.432	2-	2.429
7	2.276	6	2.276	6	2.270
2	2.151	2	2.161	2	2.158
1	2.080	1+	2.078	1	2.067
4	2.029	4	2.032	4	2.021
2	2.017	2	2.014	1-	2.000
8	1.903	8	1.903	7	1.903
6	1.861	6	1.864	5	1.857
1	1.776	1-	1.778	1-	1.779
3	1.729	3	1.735	3	1.731
4	1.700	3	1.702	2	1.704
				2	1.684
6	1.623	6	1.625	7	1.618
4	1.609	2	1.609	2	1.598
2	1.585	1-	1.588	?	
5	1.569	5	1.570	6	1.565
3	1.557	2	1.557	2	1.545
1	1.489			3d	1.477
2	1.481	2d	1.484		
2-	1.461	2	1.458	2-	1.457
2+	1.440	3	1.444	2	1.441
1-	1.411	1+	1.413	2-	1.410
4+d	1.371	5d	1.370	4d	1.369
3-	1.308	2	1.311	3	1.308
1+d	1.289	2d	1.287	2	1.286
2-	1.268	1	1.267	1+	1.263
3	1.255	3	1.253	3	1.247
1-	1.242	?	?		
3	1.230	3-	1.229	4	1.227

Plus about 20 more lines, mostly broad and diffuse.



ing, these crustal fragments yield a sharp and complete rutile pattern with a few extra lines whose origin has not been established.

Similar anatase crusts were observed on euxenite found with the Idaho brannerite. These are likewise converted to rutile by heating. This superficial resemblance of associated minerals apparently led to the inclusion of a little euxenite in the analyzed material for some grains in USNM 105793 turned pale brown on heating and yielded a euxenite powder pattern. This seemed strange since Hess and Wells (1920) had stated that no tantalum or niobium "could be detected." Dr. Switzer kindly arranged for a new spectrographic examination of USNM 105793 through Dr. John C. Rabbitt in the Trace Elements Section of the United States Geological Survey. This showed niobium to be present in "minor amount." Another spectrographic examination carried out by Mr. George M. Gordon of the Division of Mineral Technology, University of California, on a crystal from USNM 96873 yielding a euxenite pattern showed niobium and tantalum in a ratio of approximately ten to one. Thus the presence of a trace of euxenitic material in the analyzed type sample of brannerite is indicated but the amount of contamination is not such as to seriously impair the analysis.

Though much of the California brannerite is not crusted a small amount of orange colored material adjacent to it was found to be coarse quartz interspersed with titanium oxide which yielded a rutile pattern upon heating. Other products of alteration remain unidentified.

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