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A CRYSTAL-STRUCTURE REFINEMENT OF SYNTHETIC BRANNERITE, UTi_2O_6, AND ITS BEARING ON RATE OF ALKALINE-CARBONATE LEACHING OF BRANNERITE IN ORE

J. T. SZYMAŃSKI
Mineral Sciences Laboratories, CANMET, Department of Energy, Mines & Resources, 555 Booth Street, Ottawa, Ontario K1A 0G1

J. D. SCOTT
Research and Development Division, Eldorado Nuclear Ltd., Suite 400, 255 Albert Street, Ottawa, Ontario K1P 6A9

ABSTRACT

The crystal structure of synthetic, stoichiometric brannerite, UTi_2O_6, has been refined to R=2.23% from 1845 reflections (1818 observed) collected with Mo$K\alpha$ radiation. Monoclinic, with space group $C2/m$, a 9.8123(15), b 3.7697(6), c 6.9253(9) Å, β 118.957(6)°, brannerite is isostructural with thorutite, $ThTi_2O_6$ (Ruh & Wadsley 1966). The co-ordination of U by O is distorted octahedral, the bond distances being 2 x 2.252(2), 4 x 2.296(1) Å. There is an additional pair of short nonbonded U-O contacts, 2 x 2.824(2) Å. The co-ordination around Ti is also distorted octahedral, with the Ti-O distance between 1.854(3) and 2.104(3) Å. The depth of penetration of an alkaline-carbonate leaching solution into natural brannerite from Eldorado, Saskatchewan, has been found to vary nonuniformly with both time and crystallographic direction of leaching attack. The rate of dissolution for a free crystal is 1.33 cubic micrometers per second or, using the density calculated from the cell data, 8.5 x 10^{-12} g/s.

Keywords: synthetic, stoichiometric brannerite, UTi_2O_6, structure refinement to 2.23%, powder data, alkaline carbonate leaching, leaching rate, crystal morphology, kinetics.

SOMMAIRE

La structure cristalline de la brannérite stoechiométrique synthétique, UTi_2O_6, a été affinée à R= 2.23% à partir de 1845 réflexions (1818 observées) obtenues en rayonnement Mo$K\alpha$. Monoclinique, groupe spatial $C2/m$, a 9.8123(15), b 3.7697(6), c 6.9253(9) Å, β 118.957(6)°, la brannérite est isostructurale de la thorutite, $ThTi_2O_6$ (Ruh & Wadsley 1966). Le polyèdre de coordination du U par le O est un octaèdre difforme, les longueurs de liaison étant de 2 x 2.252(2), 4 x 2.296(1) Å. Il y a deux contacts courts additionnels U–O sans liaison chimique à 2.824(2) Å. Le polyèdre de coordination du Ti est aussi un octaèdre difforme, avec distances Ti–O comprises entre 1.854(3) et 2.104(3) Å. La profondeur de pénétration d'une solution alcaline et carbonatée dans la brannérite d'Eldorado (Saskatchewan), varie de façon non uniforme en fonction du temps et de la direction cristallographique de l'attaque par lixiviation. Le taux de dissolution d'un cristal libre est de 1.33 μm³/s, soit 8.5 x 10^{-12} g/s, si l'on tient compte de la densité calculée Dx.

(Traduit par la Rédaction)

Mots-clés: synthétique, brannérite stoechiométrique, UTi_2O_6, détermination de la structure, affin à 2.23%, diagrammes de poudre, lixiviation carbonatée alcaline, taux de lixiviation, morphologie cristalline, cinétique.

INTRODUCTION

Brannerite, ideally UTi_2O_6, has recently become the principal ore mineral in several Canadian uranium mines. At both Eldorado, Saskatchewan, and Elliot Lake, Ontario, the brannerite is both very fine grained and entirely metamict, and thus it cannot be studied crystallographically in its natural form. Furthermore, the natural material has a variety of metals substituting for both uranium (Pb, Ca at Eldorado, Pb, Th, Ca, Y and Ce at Elliot Lake) and titanium (Si, Al, Fe). Brannerite commonly is deficient in uranium and has an excess of titanium (Kaiman 1973, Ferris & Ruud 1971). The simplified compositional formula for brannerite from the Elliot Lake district is (U, Th, *etc.*)$_{1-x}$Ti$_{2+x}$O$_6$, where x typically is 0.3, but may be as large as 0.75. The Eldorado brannerite, from the Fay Winze mine, may also be described by such a formula, with $x \simeq 0.3$; however, a more exact description of the stoichiometry is given by: $(U,Pb,Ca)_{0.6x}Ti_x(Si,Fe,Al,V)_{3.36-1.65x}O_6$, where $1.2<x<1.8$.

As part of a study of the alkaline-carbonate leaching of uranium from Eldorado brannerite-rich ore (Scott 1982), it became necessary to know the relationship between the structure of brannerite and its morphology, in order to interpret the apparently anomalous observation of two different leaching rates. The crystal structure of the synthetic thorium analogue of brannerie (thorutite, $ThTi_2O_6$) is available, but had been solved using rather inaccurate film data, and no morphological information was given (Ruh & Wadsley 1966); it was also incorrectly called brannerite in their publication. The data are sufficiently poor that it was felt necessary to refine the actual UTi_2O_6 structure. The synthesis of UTi_2O_6 is well documented (Kaiman 1959, Patchett & Nuffield 1960, Hughson 1974); the crystals used to determine the structure were grown by a cryolite-fusion technique, by Dr. G.M. Anderson of the Department of Geology, University of Toronto.

EXPERIMENTAL

Examination of a well-formed crystal with an optical goniometer, and confirmation of the forms observed with precession photography, revealed the following morphology: crystal acicular in *b*, tabular in $\{20\bar{1}\}$ and bounded in {100}, {001} and very narrow $\{40\bar{1}\}$, terminated by {110} and $\{11\bar{1}\}$. A second smaller crystal, showing all these forms, was cut with a knife to give a flat tablet, elongate in *b* (0.16 mm), tabular in $\{20\bar{1}\}$ (0.088 mm wide) and 0.032 mm thick. It was mounted in a general orientation on a 4-circle diffractometer. Cell dimensions were obtained from a least-squares refinement of the fitted 2θ, χ and ω values (Busing 1970) of 158 reflections in the range $86>2\theta>50°$; they are given in Table 1.

Intensity data were collected using graphite-monochromated Mo$K\alpha$ radiation and a θ–2θ scan. The peak width was 1.7° plus the α_1–α_2 dispersion, and was scanned at a rate of 2°/minute in 2θ. Backgrounds were counted for 30 seconds on either side of the peak. Three standards were measured every 50 reflections to maintain a check on crystal alignment and instrument stability. The minor variations observed were used to correct the data using a linear scaling procedure. The hemisphere of data with *k* positive was collected to $2\theta = 120°$ in two segments, $\pm hkl$ and $\pm hk\bar{l}$. The data were corrected for absorption using a Gaussian integration procedure with a grid of 10x10x10 points (Gabe & O'Byrne 1970). The two segments were averaged to produce 1845 unique reflections, of which only 27 were considered "unobserved" on the criterion $L_{obs}>1.65\sigma(I)$. The absorption-correction factors varied between 2.77 and 12.69, and the overall agreement factor between the intensities of the two segments $(\Sigma(I\text{-}\bar{I})/\Sigma\bar{I})$, was 1.90%.

The starting co-ordinates for the refinement were taken from those of $ThTi_2O_6$ (Ruh & Wadsley 1966). The structure refined to $R = 12.8\%$ isotropically and $R = 2.23\%$ anisotropically using space group $C2/m$. In the latter refinement, an isotropic extinction parameter was included (Larson 1970). The scattering curves were prepared from the coefficients given by Cromer & Mann (1968) for the neutral atomic species U, Ti and O. These were corrected for dispersion using the real and anomalous coefficients given by Cromer & Liberman (1970). The final difference-synthesis was featureless throughout. A refinement was attempted using scattering curves for the charged species U^{4+} and Ti^{4+}, taken from the same source, and for O^{2-}, taken from Suzuki (1960). The residual remained unchanged, the positional parameters changed by a maximum of 0.1σ, and the thermal parameters, by a maximum of 0.5σ. There is nothing to choose between the two models from the point of view of crystallographic refinement, and the refined positional and thermal parameters given in Table 2 are for the "neutral atoms" model. Observed (10 x F_o) and calculated (10 x F_c) structure factors are given in

TABLE 1. CRYSTAL DATA

Synthetic brannerite, UTi_2O_6.
Formula weight: UTi_2O_6 = 429.83
Crystal system: monoclinic
Systematic absences: $hk\ell$, $h + k = 2n + 1$
Cell dimensions: a = 9.8123(15), b = 3.7697(6), c = 6.9253(9)Å
β = 118.957(6)°
Space group: $C2/m$ (#12)
Linear absorption coefficient: μ(Mo$K\alpha$) = 375.6 cm^{-1}
Density: $D_{calc.}$ = 6.37 Mg m^{-3}, $D_{obs.}$ not measured, but Patchett & Nuffield (1960) give 6.35 Mg m^{-3}.
Intensity Data: 2 segments of data ($\pm h.k.\ell$, $\pm h.k.\bar{\ell}$) collected to 2θ = 120°, averaged to give 1845 reflections, 1818 with $I > 1.65\sigma(I)$.

TABLE 2. POSITIONAL AND THERMAL PARAMETERS (x100) WITH STANDARD DEVIATIONS

Atom	site	point symmetry	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	2*a*	2/*m*	0.	0	0.	1.292(5)	0.387(4)	0.654(4)	0	0.685(4)	0
Ti	4*i*	*m*	0.82356(4)	0	0.39107(6)	0.429(10)	0.492(10)	0.548(10)	0	0.278(8)	0
O(1)	4*i*	*m*	0.97718(22)	0	0.30828(31)	0.48(5)	1.57(5)	0.56(5)	0	0.30(4)	0
O(2)	4*i*	*m*	0.65272(24)	0	0.10530(33)	0.75(5)	0.92(6)	0.71(5)	0	0.10(4)	0
O(3)	4*i*	*m*	0.28053(26)	0	0.40531(38)	1.16(6)	0.48(5)	1.44(7)	0	0.98(6)	0

The anisotropic temperature factors are expressed:- $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots 2U_{13}a^*c^*h\ell)]$

Table 3, available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

Because the natural material is generally deficient in U and has an excess of Ti (Kaiman 1973), the population parameter of U was varied in an attempt to find any significant nonstoichiometry in the crystal examined. The refined parameter actually *increased* by 1.7% (4σ), a result that cannot be considered meaningful and that is probably affected by the very strong correlation between this parameter and the extinction parameter and scale factor. The residual decreased negligibly, and it must be accepted that the synthetic brannerite used was stoichiometric, particularly in view of the microprobe analysis carried out. The bond lengths and angles resulting from this refinement are given in Table 4. The structure of synthetic brannerite, projected on the *a–c* plane, is illustrated in Figure 1, whereas the uranium and titanium co-ordination octahedra are illustrated in Figures 2 and 3, respectively.

TABLE 4. BOND LENGTHS AND ANGLES WITH STANDARD DEVIATIONS.

1) Coordination of U:

(a) bond lengths, (Å).

$O(1)^2$, $O(1)^9$	2.252(2) ;	$O(2)^6$, $O(2)^{11}$	2.296(1)
$O(2)^5$, $O(2)^{12}$	2.296(1) ;	[$O(3)$; $O(3)^{10}$	2.824(2)]

The above pairs of atoms are centrosymmetrically related through the origin, (U position).

(b) bond angles, (°).

	$O(2)^5$	$O(2)^6$	$O(3)$
$O(1)^2$	92.76(7)	92.76(7)	63.52(8)
$O(2)^5$	—	110.35(6)	60.80(4)
$O(2)^6$	—	—	60.80(4)

2) Coordination of Ti:

(a) bond lengths, (Å)

$O(1)$	1.854(3) ;	$O(3)^3$	1.944(1)
$O(1)^7$	2.053(2) ;	$O(3)^4$	1.944(1)
$O(2)$	1.875(2) ;	$O(3)^8$	2.104(3)

(b) bond angles, (°).

	$O(1)^7$	$O(2)$	$O(3)^3$	$O(3)^4$	$O(3)^8$
$O(1)$	78.23(9)	96.83(10)	104.16(9)	104.16(9)	159.79(7)
$O(1)^7$	—	175.06(12)	94.14(6)	94.14(6)	81.56(9)
$O(2)$	—	—	87.04(6)	87.04(6)	103.38(10)
$O(3)^3$	—	—	—	151.55(12)	77.19(9)
$O(3)^4$	—	—	—	—	77.19(9)

3) Coordination of oxygens, (°).

(a) Angles around O(1):

$Ti - O(1) - U^1$	139.65(8)
$Ti - O(1) - Ti^7$	101.77(10)
$U^1 - O(1) - Ti^7$	118.58(11)

(b) Angles around O(2):

$Ti - O(2) - U^3$	116.60(6)
$Ti - O(2) - U^4$	116.60(6)
$U^3 - O(2) - U^4$	110.35(9)

(c) Angles around O(3):

$U - O(3) - Ti^5$	94.63(6)	$Ti^5 - O(3) - Ti^6$	151.55(17)
$U - O(3) - Ti^6$	94.63(6)	$Ti^5 - O(3) - Ti^8$	102.82(9)
$U - O(3) - Ti^8$	96.33(9)	$Ti^6 - O(3) - Ti^8$	102.82(9)

Above superscripts indicate the following equivalent positions:

1:	1+x, y, z	5:	-½+x, ½+y, z	9:	1-x, -y, -z
2:	-1+x, y, z	6:	-½+x, -½+y, z	10:	-x, -y, -z
3:	½+x, ½+y, z	7:	2-x, -y, 1-z	11:	½-x, ½-y, -z
4:	½+x, -½+y, z	8:	1-x, -y, 1-z	12:	½-x, -½-y, -z

POWDER PATTERN OF BRANNERITE

Most brannerite specimens give no powder-diffraction pattern, or at best only a few diffuse lines because of the generally metamict nature of the natural material (Pabst 1954, Patchett & Nuffield 1960). Ignited natural brannerite and synthetic brannerite give a good diffraction pattern, which has been indexed by Patchett & Nuffield (1960) on the basis of their monoclinic cell. This is close to the one given here, apart from a surprising difference of ½° in β. In view of the much greater precision in the present data on the unit cell, we have calculated a fully indexed powder-pattern as far as d = 1.30 Å (Table 5). This was obtained from the computer program POWGEN (Hall & Szymański 1975), which calculates the equivalent powder-diffraction intensities on the basis of observed single-crystal-diffractometer intensities. It can be seen that there are minor differences in indexing of lines, and some differences in intensities. For comparison, the earlier pattern of Pabst (1954) is included, as the latter shows better agreement with ours at high d-values.

ELECTRON-MICROPROBE ANALYSES

Several crystals of synthetic UTi_2O_6 were mounted in polished sections and analyzed under the following conditions (Mr D.R. Owens, analyst): accelerating voltage 20 kV; specimen current $\simeq$ 0.03 μA; counting period 10 seconds; standards and X-ray lines: synthetic UO_2 for U$M\alpha$, synthetic TiO_2 for Ti$K\alpha$. The microprobe analysis showed the synthetic brannerite to be homogeneous and stoichiometric to within the limits of accuracy of the system, and resulted in the formula $U_{1.01}Ti_{1.99}O_6$, based on 6 atoms of oxygen.

Representative crystals of the Fay Winze brannerite used in the leaching studies, together with their enclosing chlorite gangue, were also analyzed (Table 6). The analyses were done at 20 kV with a specimen current of 0.03 μA (Mr. P. Carrière, analyst). The following emission lines and standards were used, in addition to those named above: Fe$K\alpha$, hematite; Ca$K\alpha$ and Si$K\alpha$, synthetic rare-earth standard REE3; Pb$L\alpha$, PbO; V$K\alpha$, synthetic V_2O_5; Mg$K\alpha$ dolomite; Al$K\alpha$, chromite standard CHROMGS3; Cl$K\alpha$, NaCl.

DISCUSSION

The systematic absences found for this structure (hkl, $h+k=2n+1$), are consistent with space groups $C2/m$, $C2$ or Cm. The morphology

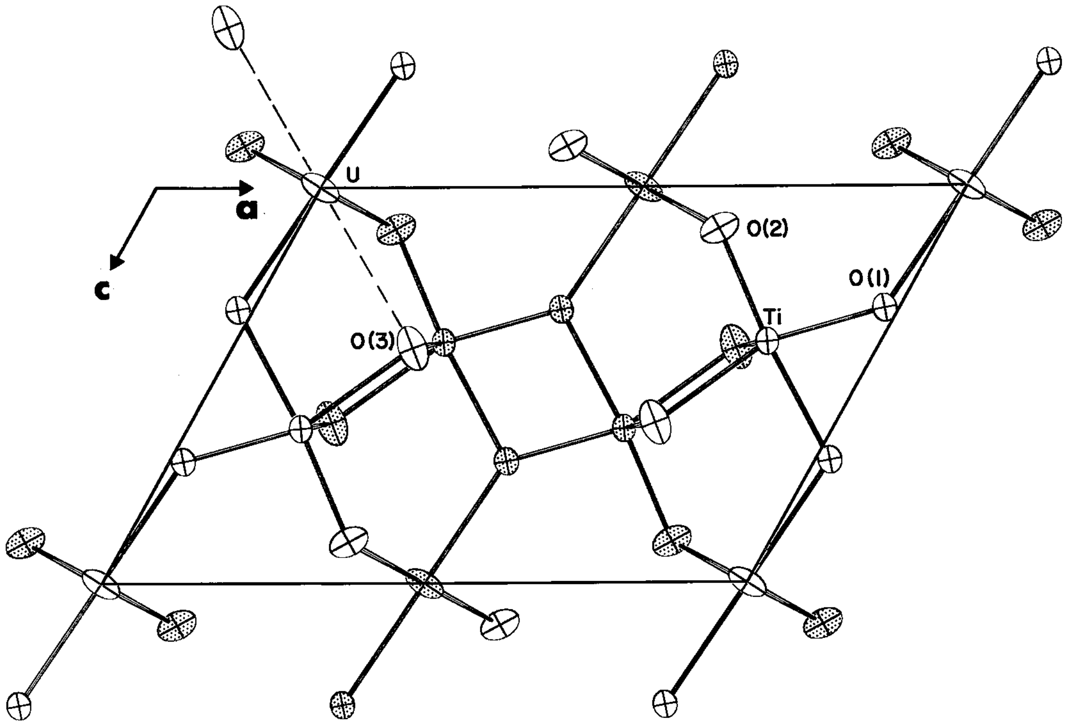

FIG. 1. The structure of brannerite projected on the a–c plane. The stippled atoms are in the plane $y = \pm\frac{1}{2}$, the rest are at $y = 0, 1$. The designated atoms are the ones whose co-ordinates appear in Table 2. The non-bonded short contact U-O(3) is indicated by a dashed line.

indicates crystal class $2/m$. Refinement of the structure of brannerite was carried out following the example of Ruh & Wadsley (1966) for thorutite, in space group $C2/m$. When refinement was complete, examination of the thermal parameters, especially a comparison of U_{22} with U_{11} and U_{33}, indicated no untoward thermal vibrations, which could have been an indication of atoms not quite lying in the mirror plane, and hence reducing the structure to a lower-symmetry space group. The final residual of 2.23% and a generally featureless final difference-synthesis were taken as confirmation of the correctness of the choice of space group. No attempt was made to lower the symmetry and continue refinement.

Only a qualitative comparison of the present refinement with the refinement of the isostructural thorutite (Ruh & Wadsley 1966) can be made. The latter was carried out using rather poor Weissenberg-film data (*h0l* to *h5l*, with no cross-correlating data for scaling purposes). The heavy-metal–oxygen bond lengths are very comparable if one bears in mind that the difference in metal radii between $^{VI}Th^{4+}$ and $^{VI}U^{4+}$ is about 0.05 Å (Shannon 1976): 2x2.36(5), 4x2.35(4) Å for Th–O, 2x2.252(2), 4x2.296 (1) Å for U–O. For Ti–O, there should be no difference between the structures and indeed, to within about one standard deviation, the bond lengths are the same: for thorutite and brannerite, Ti–O(1) = 1.83(4), 1.854(3); Ti–O(1)^7 = 2.06(4), 2.053(2); Ti–O(2) = 1.83(5), 1.875 (2); Ti–O(3)^3 = 1.94(7), 1.944(1); Ti–O(3)^8 = 2.20(7), 2.104(3) Å, respectively.

The structural relation of thorutite, $ThTi_2O_6$, to anatase, TiO_2, in terms of metal–oxygen polyhedra has been discussed by Ruh & Wadsley (1966), and the same relationship holds for brannerite and anatase. Anatase is often found as an alteration coating on brannerite (Pabst 1954, Pabst & Stinson 1960). It is not surprising, therefore, to find that anatase is one of the products of alkaline-carbonate leaching of brannerite. It is worth noting that the metamorphic recrystallization of a naturally formed alteration layer of anatase (*e.g.*, see Figure 52-18 of Ruzicka & Littlejohn 1982) will severely inhibit the alkaline leaching of the underlying brannerite.

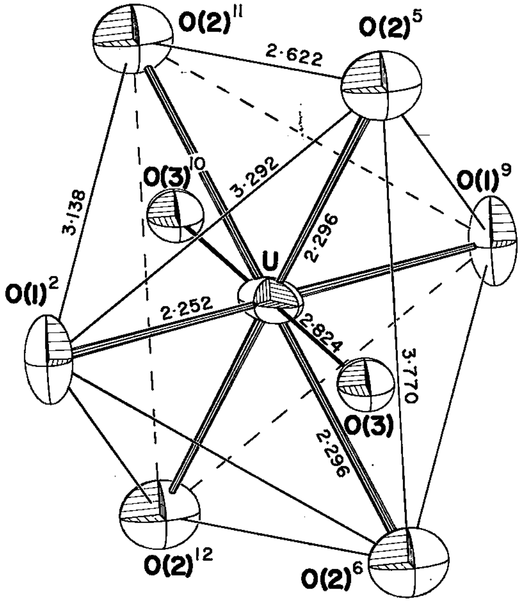

FIG. 2. The co-ordination octahedron around uranium, showing bond lengths and non-bonded distances. The non-bonded U–O(3) short contact is indicated by the heavy solid line. U is at a centre of symmetry and the crystallographic mirror is through O(1), U, O(3).

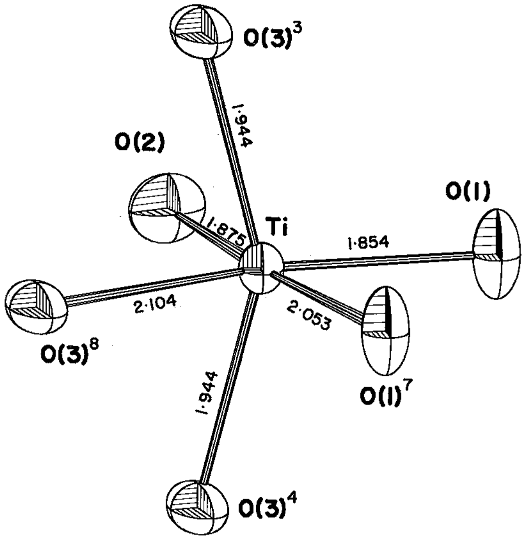

FIG. 3. The distorted octahedral co-ordination of oxygen atoms around titanium. The ellipsoids are drawn at 95% probability (Johnson 1965). The legend for equivalent positions is given in Table 4.

THE LEACHING OF BRANNERITE

The foregoing research was originally undertaken in order to explain the observation of two distinct leaching rates for brannerite crystals. It was obvious that the two rates were associated with two different morphological directions; however, there was no correlation known with the crystal structure and no obvious method of turning the actual measurements of depths of penetration of leachant with time into an overall leaching rate on an ideal free crystal.

Optical goniometry and precession measurements of the synthetic crystals established their cross-sectional morphology as: elongate in *b*, bounded by {100}, {001} anl $\{20\bar{1}\}$. Equivalent morphology, with the addition of {010}, was apparent for the larger brannerite crystals in chlorite veins in the 01 ore zone, 32 level, Fay Winze mine; the well-defined monoclinic angle ($\beta = 119°$) observed on such crystals is, in fact, the dominant, characteristic used for their recognition (Ruzicka & Littlejohn 1982). The crystallographic orientation in polished section could therefore be defined for 18 crystals having [010] normal to the plane of the section (Ti layer normal, Fig. 1), and 12 crystals having [001*] normal (U plane parallel to the section, Fig. 1). The lengths of the associated morphological axes were measured on scanning-electron-microscope (SEM) photographs (Fig. 4), and the relative morphological relationships ($a' = 1.80c'$, $a' = 0.835b'$) were derived by linear least-squares. It is probable that the $a'c'$ line does not pass through the origin as the $a'b'$ line does, because of a real change in morphology between the smaller crystals (<10 μm in c') and the larger ones; nevertheless, all data points were included to give an overall "average" morphological ratio. Since these are relative values, and b' is known to be the longest morphological axis, an arbitrary "large free crystal" was defined as having $a' = 83.5$ μm, $b' = 100$ μm, $c' = 46.4$ μm, $\beta = 119°$.

The polished sections were then leached for varying periods of time in an alkaline carbonate solution equivalent to that used in the Eldorado mill, (20 g/L $NaHCO_3$, 35 g/L Na_2CO_3, 40 g/L Na_2SO_4, 90°C). The depths of penetration of the leachant on crystal sections of known orientation were measured from 4000x SEM photographs taken at 0° and 30° tilt (Table 7, Fig. 5). The volume of brannerite dissolved from an ideal free crystal at time *t* was taken to be the difference between the original volume of the arbitrary morphological cell given above, and the volume of a cell of dimensions: $a'' =$

TABLE 5. COMPARISON OF POWDER DATA FOR BRANNERITE

#	hkℓ	$d_{calc.}$[1]	d_{obs}[2]	I_{calc}[3]	I_{obs}[4]	I_{obs}[5]
1	$\underline{0}01$	6.060	6.04	51	36	30
2	$\bar{2}01$	4.753	4.74	77	96	50
3	200	4.293	4.29	29	19	20
4	$\underline{1}10$	3.452	3.44	100	>100	100
5	$\bar{2}02$	3.357	3.35	61	>100	60
6	$\bar{1}11$	3.287	3.28	19	13	
7	002	3.030	3.02	34	36	30
8	201	2.902	2.90	44	36	50
9	$\underline{1}11$	2.776	2.77	51	33	40
10	$\bar{1}12$	2.535	2.53	44	31	40
11	$\bar{3}11$	2.470	2.47	48	33	70
12	$\bar{4}01$	2.427	2.41	18	17	20
13	$\bar{2}03$	2.308	2.303	10	8	
14	$\bar{3}12$	2.296	2.292	27	27	
15	310	2.279	2.276	23	12	70
16	400	2.146	2.144	12	9	20
17	$\underline{1}12$	2.085	2.080	13	7	10
18	$\bar{4}03$	2.046	2.043	23	36	40
19	$\underline{0}03$	2.020	2.015	17	23	20
20	$\bar{3}13$	1.924	--	14	-	
21	$\bar{1}13$	1.913	1.911	16	5	
22	311	1.905	1.903	31	19	
23	020	1.885	1.881	22	24	
24	021	1.800	1.798	7	4	
25	$\underline{4}01$	1.771	--	3	-	
26	$\bar{2}21$	1.752	1.749	14	8	
27	$\bar{5}12$	1.735	1.732	8	5	
28	$\underline{2}20$	1.726	1.723	6	3	
29	$\bar{2}04$	1.712	1.709	15	20	
30	$\bar{5}11$	1.706		12		
31	$\bar{4}04$	1.678	1.675	5	5	
32	$\bar{2}22$	1.644	1.642	20	7	
33	$\bar{6}02$	1.635	--	8	-	
34	$\bar{5}13$	1.632	1.630	26	19	
35	113	1.612	1.609	23	18	
36	$\underline{0}22$	1.600	1.597	13	6	
37	$\bar{6}03$	1.584	--	4	-	
38	$\underline{2}21$	1.581	1.578	18	9	
39	$\bar{3}14$	1.572	1.569	15	7	
40	510	1.563	1.561	14	6	
41	203	1.560	1.558	7	6	
42	$\underline{3}12$	1.556		7		
43	$\bar{1}14$	1.499	1.493	8	1B	
44	$\bar{4}21$	1.489	1.486	9	3	
45	$\bar{2}23$	1.460	--	5		
46	$\bar{5}14$	1.454	--	3		
47	402	1.451	1.450	7	4	
48	600	1.431	1.431	7	2	
49	$\underline{4}20$	1.416	1.415	6	2	
50	$\bar{4}23$	1.386	1.384	13	3	
51	$\bar{4}05$	1.379	1.376	3	4	
52	$\underline{0}23$	1.378		11		
53	$\bar{7}12$	1.309	1.308	10	3	
54	$\bar{7}13$	1.303		3		

[1] d(calc) values obtained from POWGEN (Hall & Szymański 1975).

[2] d(obs) values from Patchett & Nuffield (1960).

[3] I(calc) obtained from converting single-crystal diffractometer intensities, (POWGEN).

[4] I(obs) values from Patchett & Nuffield (1960).

[5] I(obs) values from Pabst (1954). Only reflections indexed in JCPDS 8-2 included.

TABLE 6. RESULTS OF MICROPROBE ANALYSES

Brannerite	323591 wt.%	323692 wt.%	synthetic
U	35.16	35.10	56.4
Pb	2.02	2.12	-
Ca	3.99	4.52	-
Ti	22.00	21.47	22.3
Si	2.67	2.33	-
Fe	1.95	2.13	-
Al	0.19	0.30	-
V	0.70	0.75	-
Total:	68.68	68.72	78.7
Chlorite*	**323591 wt.%**		
Si	14.10		
Mg	14.18		
Fe	14.41		
Al	7.80		
V	0.15		
Ca	0.42		
Cl	0.51		
Total:	51.57		

*$(Mg_{3.58}Fe_{1.58}Al_{0.85})_{\Sigma 6.01}(Si_{3.08}Al_{0.92})_{\Sigma 4.00}O_{10}(OH)_8$ a magnesium clinochlore (V probably substitutes for Fe and Cl is present as $CaCl_2$ brine inclusions).

$a' - 2d(Ti)$, $b'' = b' - 2d(Ti)$, $c'' = c' - 2d(U)$, where $V = a''b''c''\sin(180-\beta)°$, and $d(Ti)$ and $d(U)$ are the depths of penetration given in Table 7. The results of these calculations are plotted in Figure 6; from the slope of this line the rate of dissolution of an ideal free crystal of brannerite suspended in leaching solution was calculated to be 1.33 cubic micrometers per second (between 2 and 48 hours into the leach). It is unfortunate that no method could be devised to obtain the density of the natural crystals used; however, taking the calculated value of the density (Table 1), a dissolution rate of 8.5×10^{-12} g/s is obtained.

The practical significance of all of the above work is that the "refractory" nature of brannerite-rich ores in an alkaline leaching solution definitely is *not* due to the insolubility of brannerite. A *free* brannerite crystal of maximum dimension 89 μm will be completely dissolved in 48 hours; in the mill, the leach runs for 96 hours, and more than 98% of the brannerite crystals observed are less than 50 μm in length. The true answer to the "refractory" ore problem has proven to be the total insolubility, combined with the extreme plasticity, of the enclosing chlorite gangue; this aspect of the research will be reported separately (Scott 1982).

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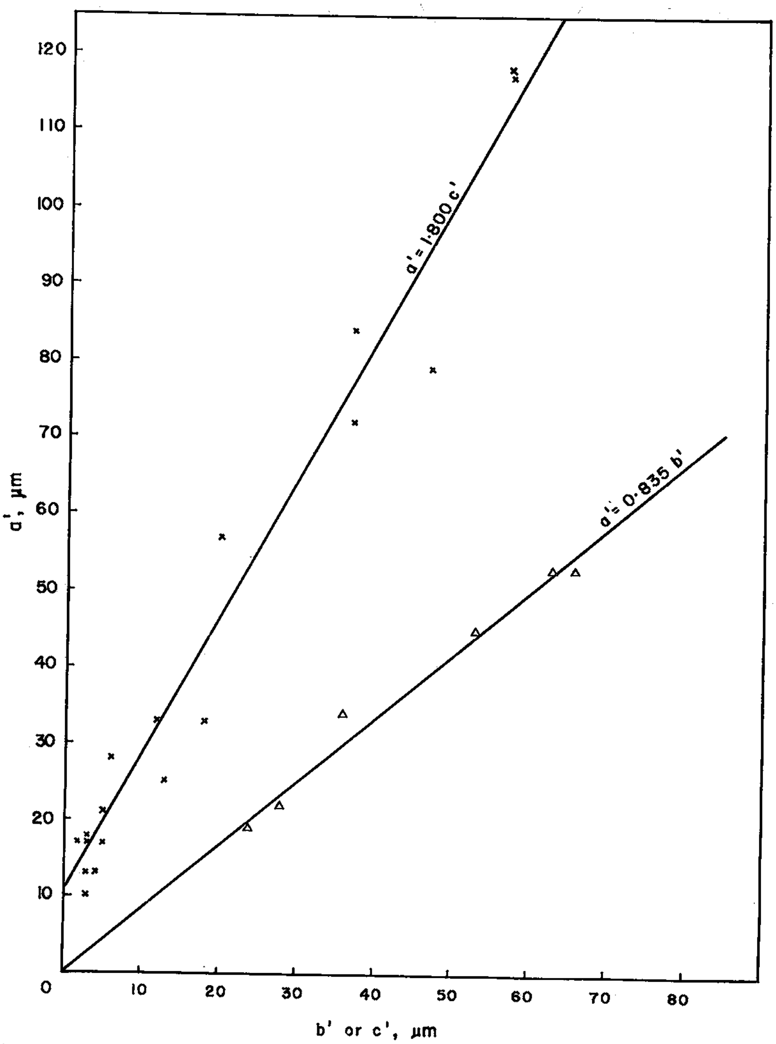

FIG. 4. Morphological axial relationships derived from measurement or lengths, in polished sections, of crystal faces of known index. Each small triangle represents two extremely close measurements, made on different crystals.

(1959): In 1960, Ramdohr visited Stanford, and I saw him at that time. He gave me a copy of Öztunali's dissertation and asked for comment. I wrote to him later, explaining Öztunali's triclinic cell was surely wrong. He had not considered that an orthogonal zone is a clear indication of monoclinic or orthorhombic symmetry. Ramdohr never answered, nor was any correction ever published. ... Karkhanavala (1959) published a lot more ... (misleading information) ... on brannerite, leading to its listing in Crystal Data, 2nd Edition, (1963) as A .8068, *i.e.*, triclinic. I also had some inconclusive correspondence with Karkhanavala. Both the erroneous triclinic cell, plus a misleading

TABLE 7. DEPTH OF PENETRATION OF LEACH SOLUTION INTO BRANNERITE CRYSTALS

Polished Section	Leaching Time (hours)	Penetration (*d* µm)* U plane	Ti plane
323692E	2	1.0	~0.1
323692K	4	1.2	0.5
323692C	6	1.4	1.1
323692B	8	1.5	1.9
323591E	8	1.5	1.7
323592J	12	1.9	3.1
323692G	12	1.8	2.6
323591A	16	2.1	3.9
323591B	24	4.2	5.0
		4.3	5.2
323591F	24	5.7**	5.3
323591C	48	10.5	9.5
323692F	72	N/A***	N/A***

* distance of wall retreat with time; the estimated error is ± 0.2 µm for 2- through 16-hour values, and ± 0.5 µm for 24 and 48 hours. ** Anomalous value, malformed crystal, may be Ti plane in *b'a'* orientation. *** Complete dissolution of 100-µm crystals.

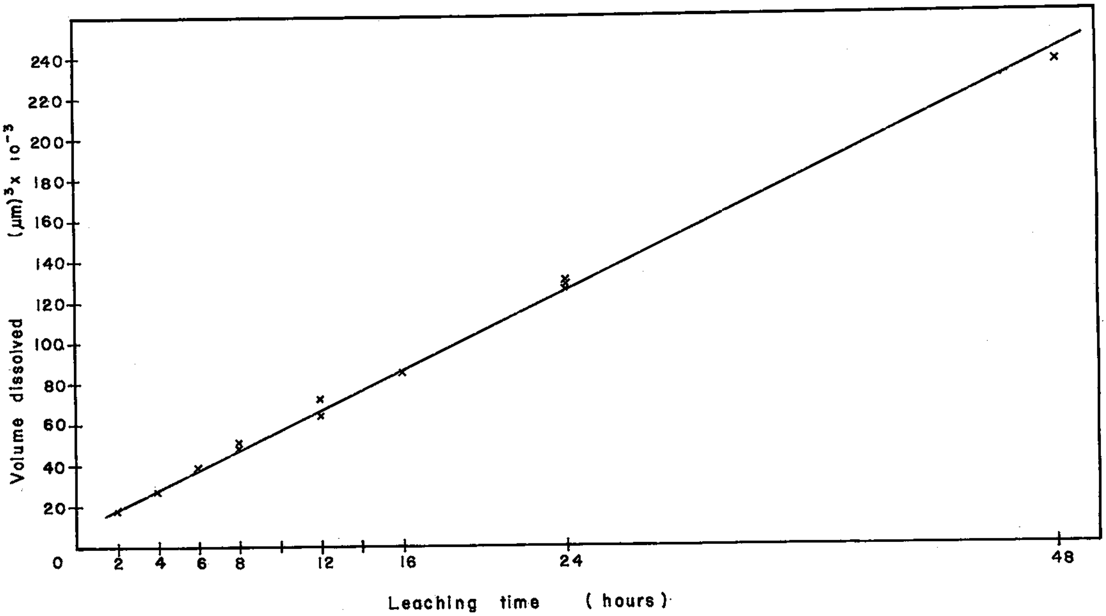

FIG. 5. Depth of penetration of leaching solution with time for the two structurally different planes.

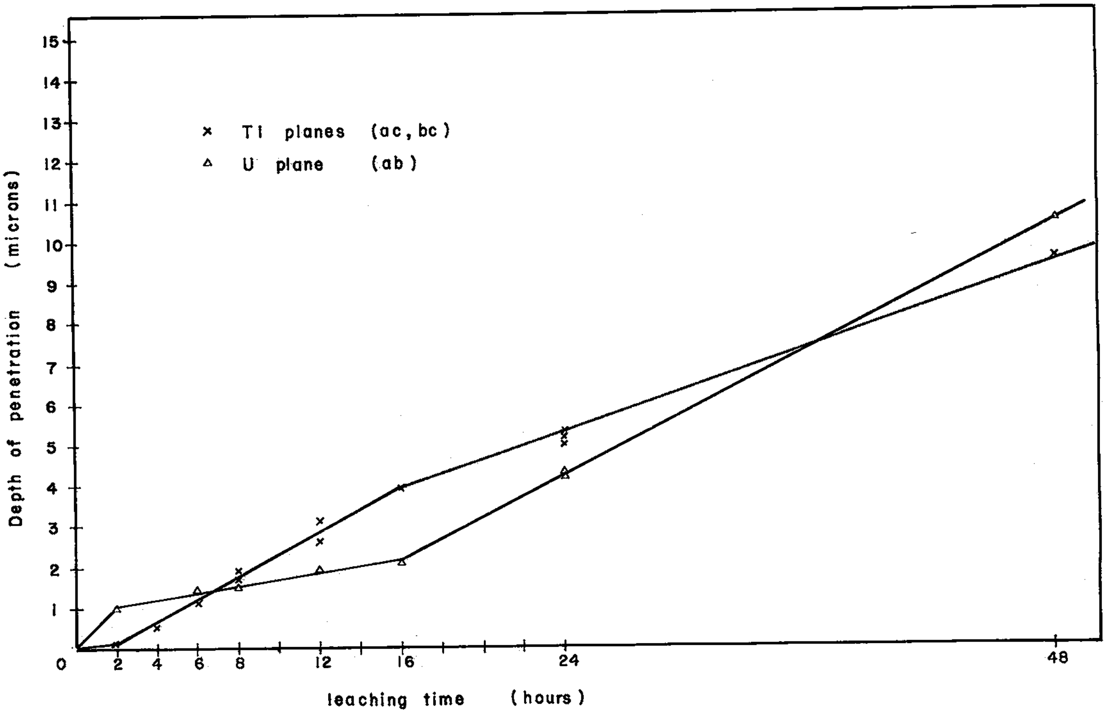

FIG. 6. Volume dissolved with time from a $b' = 100$ µm free crystal of brannerite.

statement in brackets and the misnaming of $ThTi_2O_6$ are continued in Crystal Data, 3rd Edition [Vol. II: Inorganic compounds], (1973). Maybe it would be well to warn users of Crystal Data about this persistence of errors, long after they have been made known."

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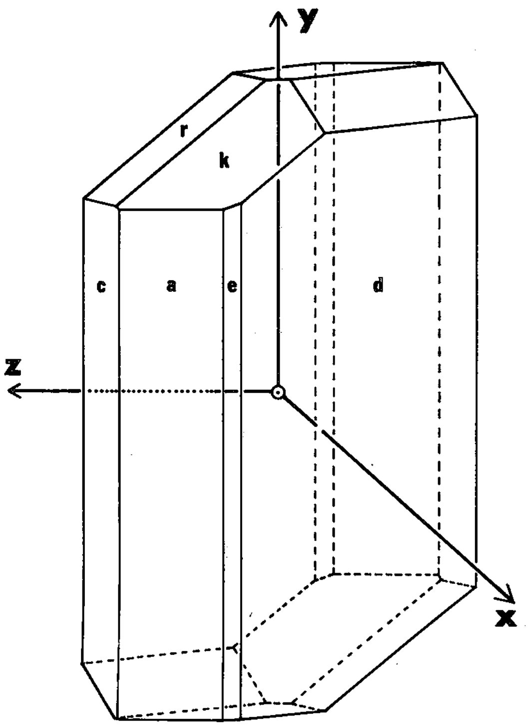
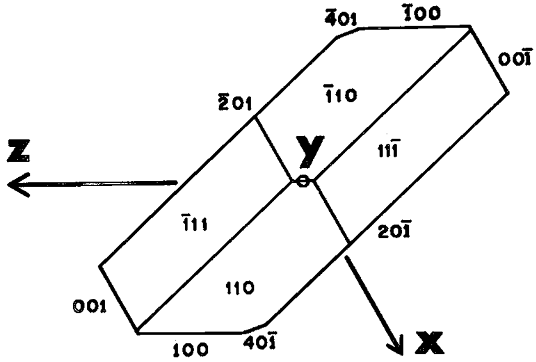
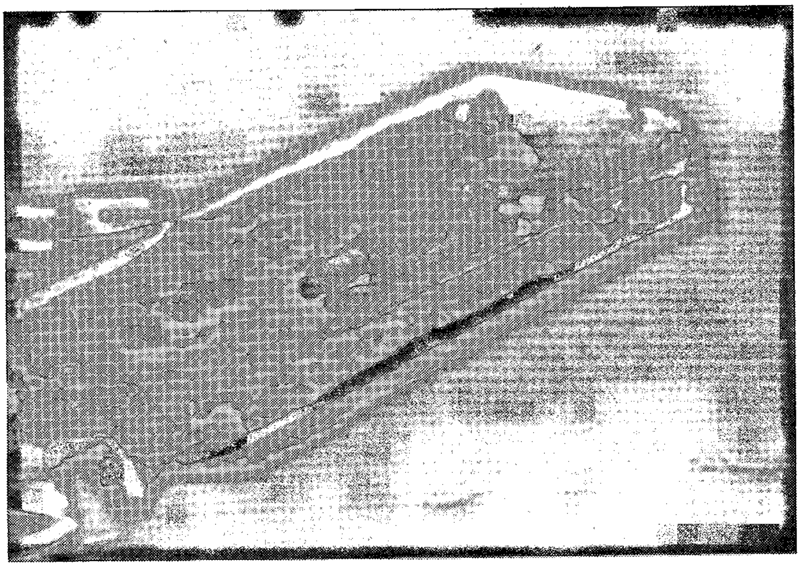
SUPPLEMENTARY FIGURES





End-on view of synthethic brannerite lath.

Synthetic brannerite crystal, viewed at 30° to the y–z plane and normal to z. The forms observed are *a* 100, *c* 001, *d* $20\bar{1}$, *e* $40\bar{1}$, *k* 110 and *r* $\bar{1}11$.



Crystal of natural brannerite in polished section after 24 hours of leaching. Note the similarity of the habit to that of the synthetic material in end-on view.