

# THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 37

MAY-JUNE, 1952

Nos. 5 and 6

## STUDIES OF RADIOACTIVE COMPOUNDS:

### IV—PITCHBLENDE FROM LAKE ATHABASKA, CANADA<sup>1</sup>

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#### ABSTRACT

Six specimens of pitchblende have been analyzed for their  $U^4$  and  $U^6$  content and  $x$ -ray powder photographs obtained before and after heat treatments. The cell edges of pitchblende range continuously from 5.470 to 5.395 Å. The decrease is due to oxygen entering interstitial positions in the  $UO_2$  structure with a consequent change of  $U^4$  to the smaller  $U^6$  ion. The lowest cell edge represents a composition of near  $UO_{2.6}$ ; the solid solution range of laboratory-prepared cubic oxides ceases at about  $UO_{2.2-2.3}$ . Oxidation is not uniform throughout a pitchblende specimen and this together with a reduction in grain size results in loss of definition in the powder pattern. The term metamict is not applicable in this connection.

The cell dimensions of  $U_3O_8$  increase as oxygen enters the structure.

It is not unusual to observe that the cell edge of a mineral species varies with the locality. This may be attributed to one or more of several causes, such as differences in chemical composition, atomic arrangements or the like. However, except in the case of zoned crystals and like phenomena, one does not expect this variation in different portions of the same specimen. In this respect is pitchblende an oddity, for not infrequently no single cell size can be regarded as characteristic for a particular locality.

It has been reported in the literature and frequently observed in this laboratory, that pitchblende may give a weak and diffuse  $x$ -ray powder pattern or actually on occasion, no pattern at all. In our opinion no satisfactory explanation has been offered to account for this.

The present investigation was concerned with the two problems outlined above. At the outset it was decided to exclude from the present study, specimens of uraninite. The terms pitchblende and uraninite are here employed in the most widely accepted usage. Both terms refer to

<sup>1</sup> Extracted from a thesis for the M.A.Sc. degree, University of Toronto.

the mineral with the ideal composition  $\text{UO}_2$  and the fluorite-like structure. Pitchblende applies to material which is formed from hydrothermal solutions. It is usually fine-grained and seldom crystallized and contains only minor amounts of the rare earth elements and thorium. Uraninite is characteristically a syngenetic mineral in granitic igneous rocks. It is frequently crystallized and contains appreciable amounts of the rare earth elements and thorium. The cell edge of uraninite is characteristically longer than that of pitchblende, approaching that of thorianite. This is in part due to thorium entering the structure and substituting for uranium. The role of the rare earth elements in the  $\text{UO}_2$  structure is not fully understood. Thus to reduce the problem of the variation in cell dimensions to simple proportions it was decided to confine the study to pitchblende which is relatively free of extraneous elements.

We are indebted to Dr. H. V. Ellsworth and Dr. S. C. Robinson, senior members of the Radioactivity Laboratory of the Geological Survey of Canada, Ottawa. Dr. Ellsworth kindly assisted us in working out the details of the procedure for the chemical analysis of the uranium specimens. Most of the specimens used in this study were collected by Dr. Robinson.

The value  $\text{CuK}\alpha_1 = 1.5405 \text{ \AA}$  has been used in the calculation of spacings and cell dimensions in this paper. Cell constants extracted from other papers have been converted to  $\text{\AA}$  units if originally given in  $\text{kX}$  or mistakenly as  $\text{\AA}$  units.

#### EXPERIMENTAL INVESTIGATION

Six specimens from the Lake Athabaska district, Canada were chosen for study, an effort being made to obtain a range from fresh through to highly altered material. Their descriptions follow:

No. 1.—Nicholson Mine. Pitchblende in masses up to  $\frac{1}{2}$  inch across. Colour black to steel gray, H. 5, density 8.20, brittle, fracture conchoidal. The pitchblende appeared fresh although bright canary yellow alteration products occurred in minor fractures.

No. 2.—Nicholson Mine. Pitchblende as a cement in ferruginous quartzite breccia. Colour dull black, H.  $4\frac{1}{2}$ , density 7.12, less brittle than No. 1, did not fracture easily. The pitchblende appeared to be altered along fractures and in contact with the breccia where it was somewhat softer.

No. 3.—Martin Lake. Pitchblende as veinlets 2 or 3 mm. wide in coarsely crystalline, reddish calcite gangue. Colour black, H.  $4\frac{1}{2}$ , density 5.55, fracture conchoidal.

No. 4.—Martin Lake, No. 2 flow. Pitchblende along shear planes in highly altered andesite which was dull brownish red due to the presence of much hematite; also as disseminations throughout the rock in fine grains and patches. It was relatively soft, density 7.16, and was accompanied by abundant yellow and green alteration products.

No. 5, Donaldson Group. Pitchblende in minute fractures and as small irregular patches about 1 mm. in diameter in a highly altered rock, reddish brown due to abundant hematite. Colour dull black, earthy, soft, density 4.50. Yellow alteration products occurred along some fractures.

No. 6, A. B. C. Group. Pitchblende as dull, soft, earthy patches and veinlets in a highly altered, crumbly mafic rock which was brownish red due to abundant hematite. Density 4.10.

The occurrence of pitchblende in the six specimens as tiny veinlets and as fine disseminations, its intimate association with gangue minerals and the presence of abundant alteration products made it difficult to separate enough material for chemical analyses. However, careful crushing, sizing and washing, followed by hand picking under the binocular microscope produced concentrates weighing between 0.4 and 0.8 grams of at least 75% purity. The selected material was dried and ground as finely as possible in an agate mortar in preparation for the chemical analysis.

The separation of hexavalent uranium from tetravalent uranium was based on the relative solubilities of  $UF_6$  and  $UF_4$ . Determination by titration with permanganate solution was not considered feasible due to the presence of iron.

The weighed samples were placed with approximately 15 cc. of concentrated  $H_2F_2$  in covered 20 cc. platinum crucibles into which nitrogen was continuously passed. The attack was allowed to continue for 4 days at a temperature of between 50 and 60° C. The crucibles were not permitted to go dry. At the conclusion of the treatment the contents were filtered, the  $UF_6$  (yellow) being in solution while the  $UF_4$  (green) remained as a residue. This residue was thoroughly washed with cold water and the washings added to the filtrate.

The filtrate and residue were separately dried and converted to chlorides which were then dissolved in a weak solution of HCl in freshly boiled water (to ensure expulsion of  $CO_2$  which would tend to prevent complete precipitation of uranium). The uranium, iron, aluminium, etc., were now precipitated with  $NH_4OH$  and filtered.  $NH_4Cl$  was added to help the precipitation. The precipitate was then washed with a weakly ammoniacal solution, redissolved with HCl and the solution made up to 250 cc. An excess of  $(NH_4)_2CO_3$  was then added to this solution and the precipitation of the iron-aluminium group carried out by the addition of  $NH_4OH$ , the uranium remaining in solution. The precipitate of iron and aluminium hydroxides was filtered off, washed, redissolved and reprecipitated as above. The filtrate from this second precipitation was then added to the first. The precipitation was repeated 3 times where an excess of iron and aluminium was present. The combined filtrates containing uranium were then acidified with HCl and boiled for 2 hours to expel all  $CO_2$ . The solution was then made up to 250 cc. with freshly boiled water and the uranium precipitated with  $NH_4OH$ , as ammonium uranate.  $NH_4NO_3$  was added to help the precipitation. The precipitate

was filtered, ignited and weighed as  $U_3O_8$ . These weights were then calculated to hexavalent or tetravalent uranium and the results for each sample reported as the percentage of hexavalent uranium of total uranium.

Sample No.:	1	2	3	4	5	6
$U^6$ % of total U	17.4	20.2	40.2	60.0	78.5	85.0

Three  $x$ -ray powder photographs were prepared from each sample under the following conditions:

- 1) in the natural state
- 2) after heating in vacuum for  $\frac{1}{2}$  hour
- 3) after heating in air for 5 minutes

The vacuum heatings were conducted in 7 mm. diameter silica glass tubes, the vacuum being maintained during heating by a continuously operating pump. Heating in air was carried out in open silica crucibles. A Meker burner with a flame temperature of near  $1100^\circ$  C. raised the temperature of the sample to about  $900^\circ$  C. For comparison purposes a sample of  $UO_2$  supplied by Eldorado Mining and Refining, Port Hope was photographed under similar conditions.

#### EXPERIMENTAL RESULTS

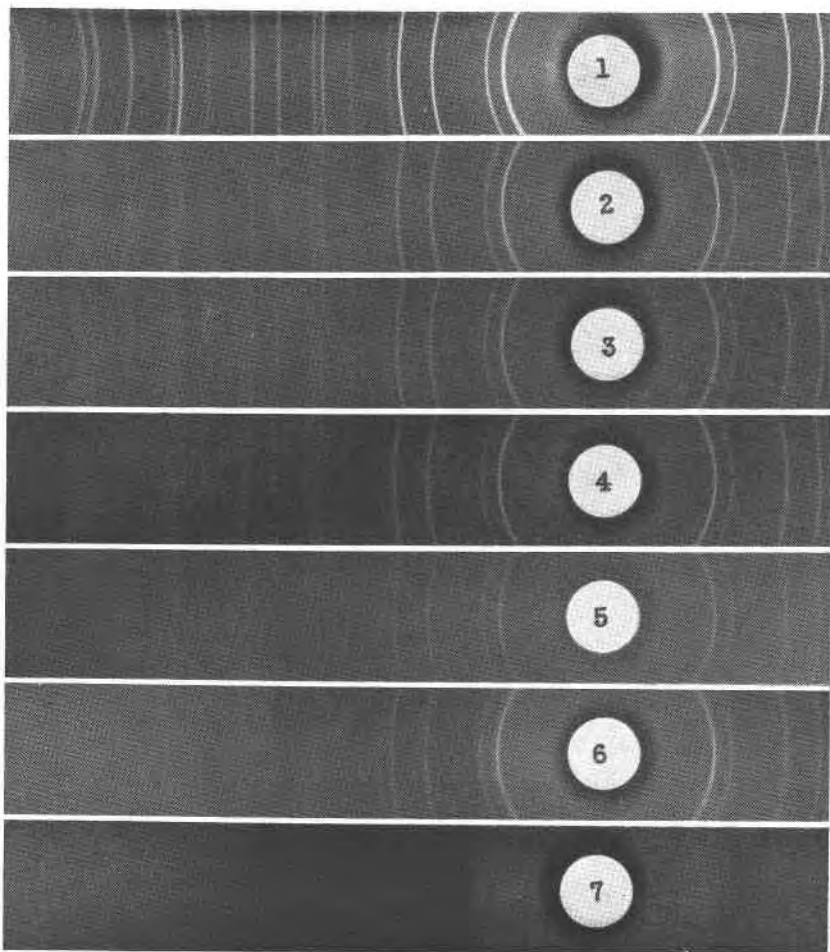
It was at once apparent that the degree of weathering in the 6 samples is an indication of the  $U^6$ /total U ratio, that is to say, to the degree of oxidation. The ratio is low for hard, compact material and high for those specimens which are loosely aggregated and consequently soft. The physical disintegration of the specimen which is a consequence of weathering, and the resulting finely divided products of weathering, are largely responsible for the decrease in density (Table 1).

The interpretation of the  $x$ -ray powder photographs is presented in Table 1. All samples except No. 6 with  $U^6$ /total U = 85.0% gave the typical pitchblende pattern when photographed in the natural state. A comparison of the prints (Figs. 1-7) shows a fairly regular change in the quality of the pattern with composition. As the ratio  $U^6$ /total U increases, back reflections become weaker and more diffuse, then low angle reflections become weak and diffuse and finally with  $U^6$ /total U = 85.0% none of the characteristic pitchblende diffraction lines appeared within normal exposures times. It is evident from Table 1 that the cell edges decrease as the ratio  $U^6$ /total U increases, from  $a = 5.470$  A for synthetic  $UO_2$  down to  $a = 5.405$  A for pitchblende where  $U^6$ /total U = 78.5%. It appears therefore, that the quality of the powder pattern, the cell edge and the state of aggregation of the specimen are all related to the degree of oxidation.

TABLE 1. X-RAY POWDER DATA FROM PITCHBLEND E BEFORE AND AFTER HEAT TREATMENTS<sup>1</sup>

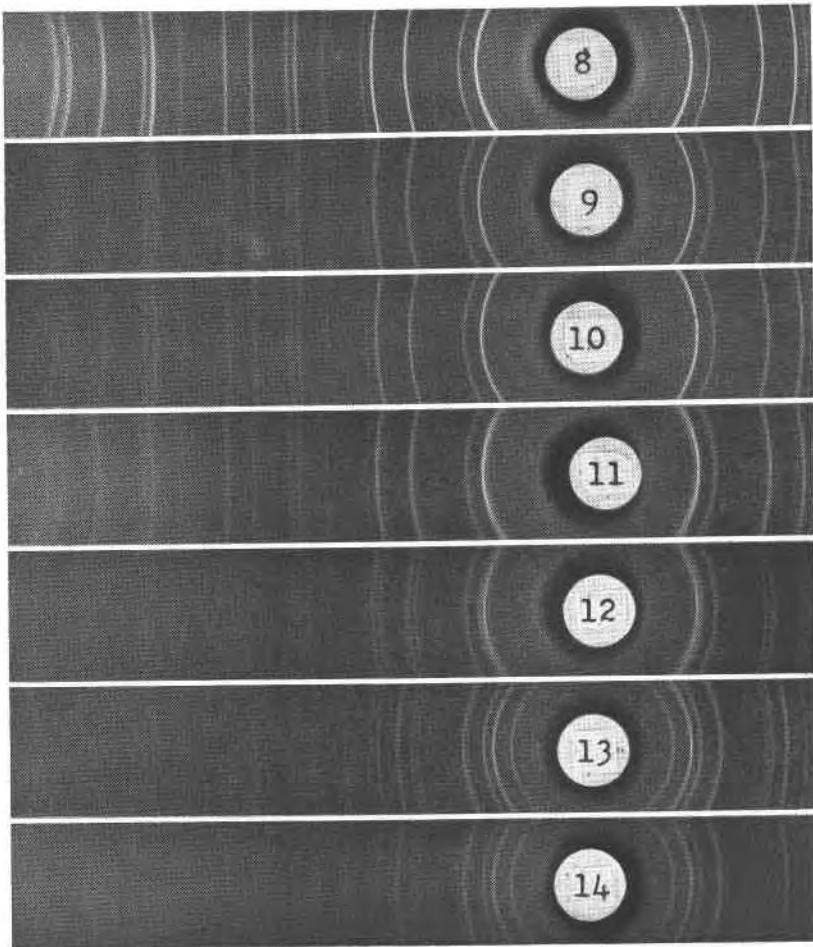
No.	U <sup>6</sup> wt. % of Total U	Dens- ity	Untreated	Heated ½ Hour in Vacuum	Heated 5 Minutes in Air
	Synthetic UO <sub>2</sub>		UO <sub>2</sub> <i>a</i> 5.470	UO <sub>2</sub> <i>a</i> 5.446	U <sub>3</sub> O <sub>8</sub> —two cells sharply defined and of about equal intensity <i>a</i> 3.85, 3.93; <i>c</i> 4.12
1	17.4	8.20	UO <sub>2</sub> <i>a</i> 5.466 plus one faint, un- identified line	UO <sub>2</sub> —clean, sharp <i>a</i> 5.446	U <sub>3</sub> O <sub>8</sub> —intensity relations of two cells anomalous <i>a</i> 3.87, 3.98; <i>c</i> 4.14 plus a few extra, uniden- tified lines
2	20.2	7.12	UO <sub>2</sub> <i>a</i> 5.465 plus one very faint, unidentified line	UO <sub>2</sub> —sharp, strong <i>a</i> 5.416 plus very faint trace of 'X'	U <sub>3</sub> O <sub>8</sub> —intensity relations of two cells anomalous <i>a</i> 3.88, 3.97; <i>c</i> 4.14 plus a few extra, uniden- tified lines
3	40.2	5.55	UO <sub>2</sub> —back reflec- tions very weak and diffuse <i>a</i> 5.435	UO <sub>2</sub> —sharp, strong <i>a</i> 5.406 plus weak 'X' lines but stronger than in #2	'X' essentially, diffuse plus one faint UO <sub>2</sub> line plus faint U <sub>3</sub> O <sub>8</sub> (?)
4	60.0	7.16	UO <sub>2</sub> —back reflec- tions very weak and diffuse <i>a</i> 5.445	'X'—strong plus UO <sub>2</sub> —diffuse and not as strong as 'X' <i>a</i> 5.395	'X'—sharp, strong plus one faint UO <sub>2</sub> line
5	78.5	4.50	UO <sub>2</sub> —back reflec- tions very dif- fuse—low angle reflections dif- fuse <i>a</i> 5.405	UO <sub>2</sub> —sharp, strong <i>a</i> 5.405 plus U <sub>3</sub> O <sub>8</sub> —strong; single cell <i>a</i> 3.94; <i>c</i> 4.17	U <sub>3</sub> O <sub>8</sub> essentially; inten- sity relations of two cells anomalous; two cells not well defined <i>a</i> 3.94, 4.04; <i>c</i> 4.17
6	85.0	4.10	no pattern	U <sub>3</sub> O <sub>8</sub> —strong; sin- gle cell <i>a</i> 3.92; <i>c</i> 4.17 plus UO <sub>2</sub> —sharp, very weak <i>a</i> 5.405	U <sub>3</sub> O <sub>8</sub> —single cell <i>a</i> 3.92; <i>c</i> 4.17 plus faint UO <sub>2</sub> lines

<sup>1</sup> The error of measurement in the pitchblende patterns ranges from  $\pm 0.002$  to  $\pm 0.005$  Å for the more highly oxidized specimens. The values for U<sub>3</sub>O<sub>8</sub> are considered to be accurate to  $\pm 0.01$  Å.



FIGS. 1-7. X-ray powder contact prints ( $1^\circ \theta = 1$  mm.). Untreated material. Fig. 1. Synthetic  $\text{UO}_2$ . Figs. 2-7. Pitchblende (samples 1-6 of Table 1).

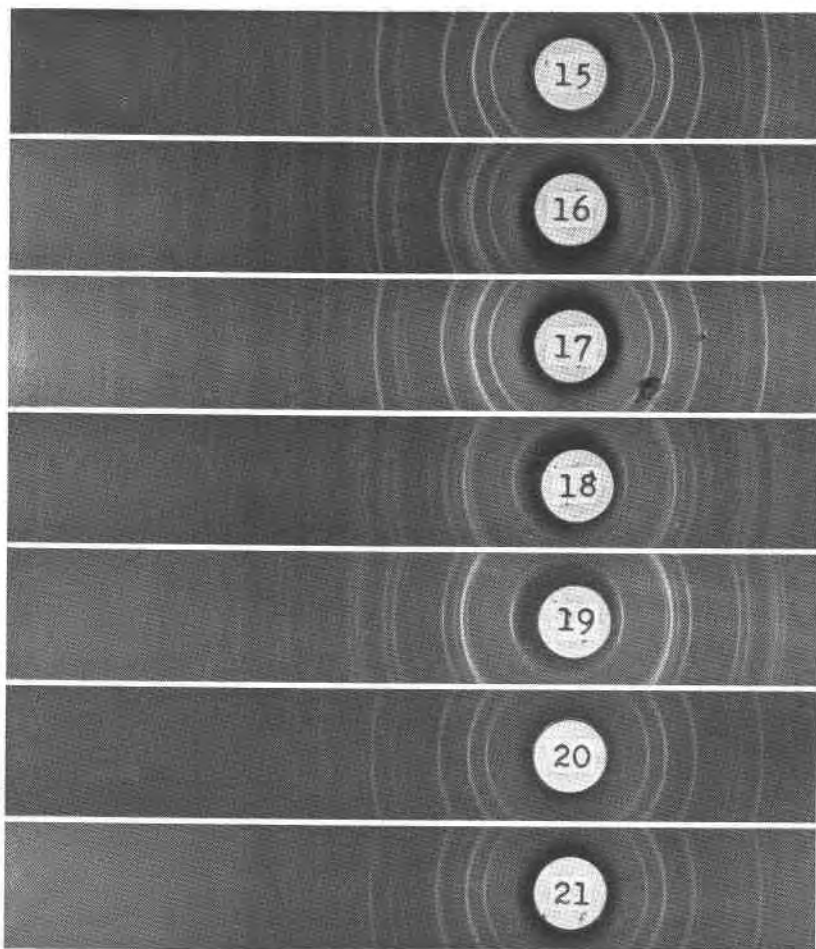
After heating for  $\frac{1}{2}$  hour in vacuum, all the samples now gave the pitchblende pattern (Figs. 8-14) with the diffraction lines somewhat strengthened and sharpened. Furthermore, the cell edges were reduced for all specimens where the cell edge of the untreated material was higher than  $a = 5.405$  A. Synthetic  $\text{UO}_2$  and sample 1 with 17.4%  $\text{U}^6$  of total U gave a clean pattern. The patterns of samples 2, 3 and 4 show extra diffraction lines which are least intense in sample 2 and strongest in sample 4. The compound responsible for this extra pattern has not been identified and will be referred to as compound 'X.' The patterns of samples 5



FIGS. 8-14. X-ray powder contact prints ( $1^\circ \theta = 1$  mm.). Heated  $\frac{1}{2}$  hour in vacuum.  
Fig. 8. Synthetic  $\text{UO}_2$ . Figs. 9-14. Pitchblende (samples 1-6 of Table 1).

and 6 also show extra diffraction lines but are here due to a "one cell" type  $\text{U}_3\text{O}_8$ . This extra pattern is more prominent in sample 6, which has the highest  $\text{U}^6$  content. To summarize: pitchblende low in  $\text{U}^6$  gave after heating in vacuum, only the  $\text{UO}_2$  pattern or with traces of the unidentified oxide 'X.' In pitchblende with a  $\text{U}^6/\text{total U}$  ratio of near  $\frac{1}{2}$ , this extra unknown pattern is strong. Pitchblende relatively high in  $\text{U}^6$  gave a  $\text{U}_3\text{O}_8$  pattern in place of the unknown, along with a  $\text{UO}_2$  pattern.

None of the samples gave a  $\text{UO}_2$  pattern after heating in air for 5 minutes (Figs. 15-21). Synthetic  $\text{UO}_2$  and pitchblende low in  $\text{U}^6$  (samples 1 and 2) and relatively high in  $\text{U}^6$  (samples 5 and 6) gave the  $\text{U}_3\text{O}_8$  pattern,



FIGS. 15-21. X-ray powder contact prints ( $1^\circ \theta = 1 \text{ mm.}$ ). Heated 5 minutes in air.

Fig. 15. Synthetic  $\text{UO}_2$ . Figs. 16-21. Pitchblende (samples 1-6 of Table 1).

the cell edges increasing with increasing availability of  $\text{U}^6$  in the untreated material. All the  $\text{U}_3\text{O}_8$  patterns were of the "two cell" type except that from sample 6 with the highest  $\text{U}^6$  content. Samples 3 and 4 with a  $\text{U}^6/\text{total U}$  ratio of near  $\frac{1}{2}$  again gave the pattern of the unidentified oxide 'X.'

#### DISCUSSION OF THE RESULTS

##### *The $\text{UO}_2$ solid solution series:*

Although it is known that the cubic  $\text{UO}_2$  phase with the fluorite structure exists over a range of composition, there is uncertainty as to the ex-



tent of this range and the constitution of the oxides within it.

Biltz and Müller (1927) found that between  $\text{UO}_2$  and  $\text{UO}_{2.226}$  oxygen is taken up without change in volume of the oxide. Beyond this point the volume increases regularly with no discontinuity at the composition  $\text{UO}_{2.67}$  ( $=\text{U}_3\text{O}_8$ ). They were not able to detect any difference between the  $x$ -ray patterns of  $\text{UO}_{2.226}$  and  $\text{UO}_2$ . Jolibois (1947) established the existence of another phase intermediate in composition between  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$ . He concluded that the oxidation of  $\text{UO}_2$  at  $220^\circ\text{C}$ . ceases at

TABLE 2. CELL SIZES OF CUBIC URANIUM OXIDES

	$\text{UO}_{1.75}$	$\text{UO}_{2.0}$	$\text{UO}_{2.1}$	$\text{UO}_{2.2}$
Rundle, etc. (1948)	—	5.4690	—	—
Alberman & Anderson (1949)	—	5.468	—	5.441
Katz & Rabinowitch (1951)	—	5.4695	5.448	5.444
Zachariasen (in Katz & Rabinowitch, 1951)	5.488	—	—	—

$\text{UO}_{2.33}$  and continues to  $\text{U}_3\text{O}_8$  only above  $300^\circ\text{C}$ . The intermediate compound  $\text{UO}_{2.33}$  (or  $\text{U}_3\text{O}_7$ ) gave an  $x$ -ray diffraction pattern like  $\text{UO}_2$  but with additional lines. Grønvold & Haraldsen (1948) determined the symmetry of this compound as tetragonal with  $a=5.38$ ,  $c=5.55\text{Å}$  and declared that its composition was  $\text{UO}_{2.40}$ . They felt that the cubic phase extends to  $\text{UO}_{2.33}$ . Alberman & Anderson (1949) found that  $\text{UO}_2$  takes up oxygen to  $\text{UO}_{2.19}$  below  $250^\circ\text{C}$ . without change of structure or cell dimensions. At this composition they observed that the symmetry becomes tetragonal, the  $c/a$  ratio increasing progressively from  $\text{UO}_{2.19}$  to  $\text{UO}_{2.3}$ . The low temperature oxides in the range  $\text{UO}_{2.0-2.3}$  were found to be unstable above  $750^\circ\text{C}$ . On annealing at temperatures above  $750^\circ\text{C}$ ., the oxides  $\text{UO}_{2.0-2.19}$  changed in part to a cubic  $\beta$  phase ( $\text{UO}_{2.19}$ ) with a fluorite-like structure having  $a=5.44\text{Å}$  as compared to  $a=5.468\text{Å}$  for pure  $\text{UO}_2$ ; the oxides  $\text{UO}_{2.19-2.3}$  broke down to  $\beta\text{UO}_{2.19}$  and  $\text{U}_3\text{O}_8$ .

These data indicate that the low temperature oxygenation of  $\text{UO}_{2.0}$  in the laboratory is limited by the formation of the tetragonal phase. The upper limits assigned by Jolibois and by Alberman & Anderson to the cubic phase differ by a surprisingly large amount. There appears to be reason to believe that the limits may depend on the physical condition of the sample undergoing oxidation and the laboratory methods employed. The data also clearly establish that solution of oxygen into the  $\text{UO}_2$  structure followed by annealing, reduces the cell size. Table 2 gives cell sizes for oxides of various compositions as determined by different observers.

Rundle and his associates regard the higher cubic oxides as having a uranium-deficient lattice, resulting in a smaller cell and a lower density than has  $\text{UO}_2$ . Alberman & Anderson, in analogy to other anomalous fluorite mixed-crystal systems, favour the view that these oxides have an oxygen-rich lattice, with oxygen occupying interstitial ( $\frac{1}{2}00$ ) positions. A  $\text{U}^4$  cation is simultaneously replaced by the smaller  $\text{U}^6$  cation for each oxygen ion so incorporated. This results in a decrease in cell size and an increase in density. Filling of all the ( $\frac{1}{2}00$ ) positions by oxygen would raise the composition to  $\text{UO}_{2.75}$ . Density measurements by Biltz & Müller of oxides between  $\text{UO}_{1.992}$  and  $\text{UO}_{2.349}$  are not conclusive but are in better agreement with the idea of an oxygen-rich lattice.

The variation in the cell edges of natural pitchblende may be plausibly explained with reference to the above observations on the artificial cubic oxides. Table 1 points conclusively to a close relationship between cell edge and the  $\text{U}^6/\text{total U}$  ratio in the sample. Recent observations by Kerr (1951) have led him to a similar conclusion. He noted that "sooty" pitchblende gives lower lattice constants than hard pitchblende and he surmised that because "sooty" varieties show a higher  $\text{UO}_3$  content, the low lattice constants are connected with the increase in  $\text{UO}_3$ . Our data indicate that the relationship is roughly linear, the cell edge decreasing with increase of the ratio  $\text{U}^6/\text{total U}$ . Evidently, in analogy to the artificial  $\text{UO}_2$  system, oxygen enters interstitial positions in the structure as oxidation proceeds. The consequent change of  $\text{U}^4$  to the smaller  $\text{U}^6$  ions results in a regular decrease in lattice dimensions.

The present data show that the oxidation of pitchblende differs in two respects from the oxidation of artificial cubic uranium oxides in the laboratory.

(1) Low temperature oxygenation has no effect on cell edges within the solid solution limits of the artificial cubic  $\text{UO}_2$  phase. This must represent an anomalous, perhaps metastable condition in the structure since according to the view of Alberman & Anderson, solution of oxygen should result in a smaller cell. Presumably the metastable condition is "corrected" by annealing for the cell edge is reduced from 5.468 to 5.44 Å. Our data indicate that natural pitchblende on the other hand, has a range of cell edges grading from 5.470 through 5.44 to 5.405 Å. A survey of published cell constants for pitchblende shows that the gradation is continuous between the limits. This suggests that when oxidation occurs in the fullness of geological time and at atmospheric temperatures the  $\text{UO}_2$  structure maintains a more stable condition while accommodating interstitial oxygen, than is possible under laboratory conditions of oxygenation. It has been shown in this study that when pitchblende is heated in vacuum, some reduction in cell size usually takes place. This may rep-

resent a final stabilizing of the structure and/or the introduction of additional oxygen which is always available in oxidized pitchblende.

(2) The upper limit of solid solution in the artificial cubic phase, which was given as  $\text{UO}_{2.226}$  (Biltz & Müller),  $\text{UO}_{2.33}$  (Jolibois), and  $\text{UO}_{2.19}$  (Alberman & Anderson) is represented by a cell with dimensions  $a=5.44$  Å after annealing (Table 2). The cells of certain natural uranium oxides reach markedly smaller dimensions. The lowest value recorded in this study, 5.395 Å, is comparable with the lowest recorded in the literature;

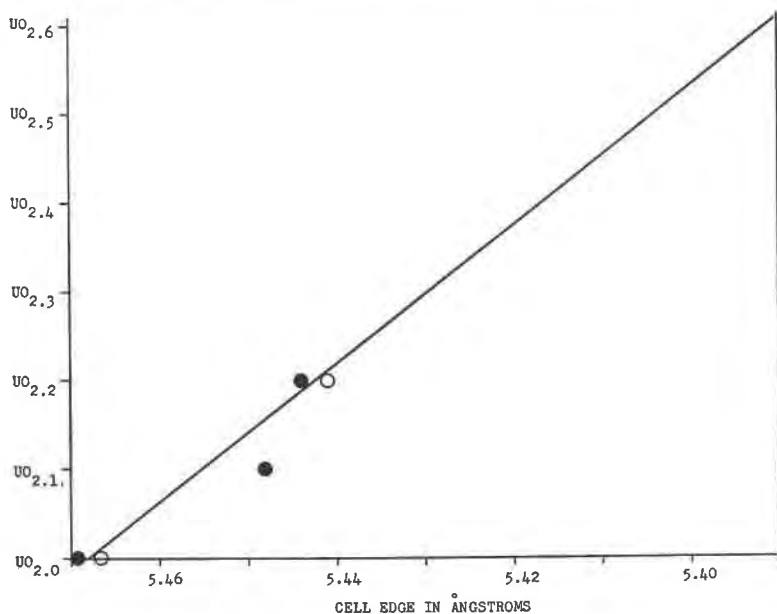


Fig. 22. Cube edge values of Alberman & Anderson, 1949 (open circles) and Katz & Rabinowitch, 1951 (filled circles) plotted against composition and extrapolated linearly to  $a=5.39$  Å.

Kerr<sup>1</sup> (1950) gives 5.3965 Å as the smallest of 33 determinations. This indicates that in nature the solid solution series extends well beyond the upper limits recorded for artificial uranium oxides. In terms of the cell edges of oxides of known composition our lowest values may be extrapolated to represent a composition of near  $\text{UO}_{2.6}$  (Fig. 22). It is a reasonable assumption that certain highly oxidized pitchblende specimens reach the composition  $\text{UO}_{2.75}$  with all of the ( $\frac{1}{2}$ 00) interstitial positions

<sup>1</sup> In a table compiled to show the range of cell constants in pitchblende and uraninite, values are given without designation of the unit of measurement in both kX and Å units.

filled by oxygen. The tetragonal phase has not been discovered in nature. Evidently the slow oxidation of pitchblende in nature at low temperatures permits a more complete saturation of the  $\text{UO}_2$  structure by oxygen than is possible with laboratory methods which invariably result in the formation of the tetragonal phase before the process is half completed.

It should be pointed out that although the measured cell edges of pitchblende furnish a rough estimation of the ratios  $\text{O}/\text{U}$  and  $\text{U}^6/\text{total U}$  in the  $\text{UO}_2$  structure, these ratios are not necessarily representative of the composition of the pitchblende sample as a whole. Heating in vacuum results in the appearance of extra diffraction lines characteristic of the unknown oxide 'X' or of  $\text{U}_3\text{O}_8$  which become more prominent as the  $\text{U}^6/\text{total U}$  ratio of the specimen increases. It may be presumed that there is present an excess of  $\text{U}^6$  perhaps as amorphous or finely crystalline  $\text{UO}_3$ . On heating in vacuum it is reduced in part to the oxide 'X' or to  $\text{U}_3\text{O}_8$ . At the same time as is evidenced by a lowering of the cell edge, oxygen is freed to enter the  $\text{UO}_2$  structure, although the reduction in cell edge may in part be due to a rearrangement of the interstitial oxygen.

Conybeare & Ferguson (1950) have attempted to relate the degree of oxidation of pitchblende samples to the quality of their x-ray powder patterns before and after ignition. They have interpreted their observations on the basis of a statement in Dana (1944) which summarizes the conclusions of Goldschmidt & Thomassen (1923):

"Natural uraninite containing much  $\text{UO}_3$  through oxidation is apparently structurally identical with  $\text{UO}_2$  . . . but on ignition out of contact with oxygen it may recrystallize in part or entirely to  $\text{U}_3\text{O}_8$ , while pure  $\text{UO}_2$  remains unchanged."

Conybeare & Ferguson have assumed that the converse of the statement that refers to pure  $\text{UO}_2$  is true—namely, that pitchblende which gives only the  $\text{UO}_2$  pattern after ignition is pure  $\text{UO}_2$ . Table 1 shows that pitchblende with as much as 17.4%  $\text{U}^6$  of total U gave the present authors a sharp  $\text{UO}_2$  pattern after ignition in vacuum. The results of Conybeare & Ferguson show no relationship between cell dimensions and composition and this can be attributed directly to faulty procedure. To fulfill the condition of ignition in the absence of oxygen, these authors heated their samples in covered crucibles; experience in this laboratory has shown that this favours oxidation and that it is necessary to perform the ignition under continuous evacuation by a pump. It is probable too, that they have overlooked the presence and reducing effect of finely disseminated hydrocarbons which we have found to be extremely common in some of the localities they studied.

Recently Wasserstein (1951) has suggested that "there is a progressive reduction in the size of the unit cell of uraninite-thorianites with time".

Wasserstein has postulated that radiogenic lead, resulting from the decay of uranium, substitutes for uranium in the  $\text{UO}_2$  structure and causes a shrinkage of the cell because the ionic radius of  $\text{Pb}^{4+}$  is smaller than that of  $\text{U}^{4+}$ . The shrinkage was said to range between 0.0025 and 0.0041 Å per hundred million years. Assuming that such substitution occurs and this is by no means certain, its effect if any will be masked by the much more pronounced effect of the introduction of oxygen and change of  $\text{U}^{4+}$  to  $\text{U}^{6+}$ . It is interesting to note that according to Wasserstein's theory, the variation in cell edges (5.466 to 5.405 Å) of the 6 Lake Athabaska specimens studied means that these specimens from the one deposit range in age from  $1 \times 10^8$  to approximately  $20 \times 10^8$  years. Dana (1944, p. 618) gives the calculated age of the Great Bear Lake pitchblende deposits as approximately  $13 \times 10^8$  years.

*"Metamict" Pitchblende:*

The term metamict was originally used by Brögger (1896) to describe the state of non-crystallinity of a number of minerals which however, often showed perfect crystal form. He inferred that a dislocation of the structure had occurred subsequent to crystallization. The disorder did not appear to be connected with weathering since the minerals were glassy, broke with a clean, conchoidal fracture, showed no zoning of the non-crystallinity from the core of a crystal outward and occurred commonly in fresh-appearing, granitic igneous rocks. Subsequent work by various observers has shown that an ordered structure can be produced by ignition either in vacuum or in air. But with the exception of certain specimens of gadolinite the product of ignition is cryptocrystalline and single crystal x-ray studies can therefore not be undertaken. In only a few cases is it assured that the original structure is restored by ignition. One of these exceptions concerns fergusonite; Barth (1926) obtained the same cell constants on ignited, metamict fergusonite as on artificially prepared material. The majority of the metamict minerals have not been prepared artificially and thus there can be little direct evidence that the original structure is restored. However, indirect evidence is not lacking. For example, Arnott (1950) was able to index the powder pattern of euxenite from Mattawan township, Ontario (ignited at  $1000^\circ \text{C}$ . in air) in terms of Brögger's morphological axial ratios on Scandinavian euxenite. The resulting cell dimensions together with the measured density of ignited material gave rational cell contents with the chemical analysis of euxenite from Sabine township, Ontario.

The process responsible for the loss of crystallinity is not fully understood. It is known that the majority of the minerals are multiple oxides of columbium, tantalum and titanium and contain appreciable amounts

of the rare earth elements, uranium and/or thorium. Cation substitution is both complex and abundant. Hence it appears that the disorder is connected with the presence of elements subject to radioactive decay within atomic structures rendered unstable by reason of multiple substitution for few cation positions.

Unfortunately, the casual observer in the field of metamict minerals frequently has acquired little more background than the knowledge that metamict minerals give at best, only weak diffractions. Diffuse and faint diffractions become synonymous with the metamict state. He is inclined to view with suspicion such weakly diffracting substances as opal, which never reached a sufficient degree of crystallinity for strong diffraction, and certain limonites which by the method of their formation as oxidation products of other iron minerals, are too fine-grained for effective diffraction. It is evident from the foregoing paragraphs that in neither case is the term metamict applicable. The term implies a type of crystal imperfection which is not to be confused with fine-crystalline materials that are the products of imperfect crystallization or decomposition.

It might be expected that in view of its high uranium content, pitchblende should exist in the metamict state. In fact Conybeare & Ferguson (1950) having obtained certain weak and diffuse diffraction patterns, have announced the existence of metamict pitchblende. It was mentioned above that the present authors noted a considerable variation in the diffracting power of different pitchblende samples and actually one sample gave no pattern before ignition. However, a direct relationship between the quality of the pattern, its  $\text{UO}_3$  content as determined by chemical analyses, and the state of aggregation was evident. The quality of the pattern declined as the  $\text{UO}_3$  content increased and the specimen itself assumed an ever-increasing weathered appearance. Clearly then, the quality of the patterns of our samples are directly related to the degree of oxidation. Conybeare & Ferguson (1950, p. 404) observed that "all the metamict pitchblendes . . . show varying degrees of oxidation, whereas the specimens from Black Lake and Great Bear Lake are crystalline and differ markedly in their degrees of oxidation." It is certain, therefore, that in the Conybeare & Ferguson samples, oxidation too is responsible for the loss of definition in the diffraction patterns and they are in fact not metamict.

It may be postulated that oxidation will affect the quality of pitchblende  $x$ -ray patterns in one or more of three ways:

1. Surface oxidation and oxidation by solutions (Kerr, 1951) is known by actual observations to affect the state of aggregation of pitchblende by reducing the grain size. Evidently the diffracting units become so small that diffraction occurs over a relatively wide angular range. It is reason-

able to believe that the range may reach such proportions in the highly oxidized specimens that the loss of definition is complete and no diffraction pattern is obtained.

2. Chemical analyses of different zones of a uraninite crystal from Quebec (Ellsworth, 1932) and another from Norway (Dana, 1944, p. 616) clearly show that the  $U^6$  content increases outward from the core. It follows that the O/U ratio in the  $UO_2$  structure and therefore the cell edge, will vary throughout the specimen. To test this,  $x$ -ray powder patterns were obtained of material scraped from the surface of an old laboratory specimen of pitchblende and of fresher material immediately below. The former gave a slightly smaller cell edge. Consequently the average  $x$ -ray powder sample may consist of a range of oxides, each with a characteristic cell edge and hence a different Bragg angle of reflection for each plane resulting in broadened diffraction lines.

3. As oxidation proceeds with the introduction of more oxygen in the interstices of the  $UO_2$  structure, it is possible that some distortion of the structure will take place, resulting in some loss of definition of the powder pattern.

It is not our intention to suggest that a metamict form of pitchblende cannot exist. We do feel that the basis of future descriptions must be more substantial than comparisons of powder patterns of materials before and after ignition. It might be expected that metamict pitchblende if it does exist, should be glassy like the typical metamict minerals. But here a word of caution is in order. Certain black, glassy materials from the Lake Athabaska uranium area produce before and after ignition, diffraction patterns which suggest the metamict state. Some of these materials are "thucholite" which has been shown by Davidson & Bowie (1951) to be a hydrocarbon enclosing grains or crystals of pitchblende, often too fine-grained and sparse for effective diffraction. It was observed in this laboratory that heating such material in air has the effect of sharpening the  $UO_2$  pattern, oxidation of the pitchblende being forestalled by the reducing effect of the hydrocarbon. This material could easily be mistaken for metamict pitchblende.

*The  $U_3O_8$  solid solution series:*

$U_3O_8$  is perhaps the most easily prepared of the anhydrous oxides of uranium. Despite this, the compound has not yet been identified as a natural product and as a result, its properties are not as well known as those of  $UO_2$ .

The symmetry of  $U_3O_8$  was originally described as orthorhombic by Zachariassen (1944; in Katz & Rabinowitch, 1951) and by Grønvold (1948) with the cell dimensions:

<i>a</i>	<i>b</i>	<i>c</i>	
6.71	3.99	4.15 Å	Zachariasen (1944)
6.716	3.977	4.144 Å	Grønvd (1948)

Other determinations made at Columbia University (in Katz & Rabinowitch, 1951, p. 271) agree closely with the above values. Grønvd's observations were made on *x*-ray powder photographs only; it is likely that Zachariasen and the Columbia University observers also used the pow-

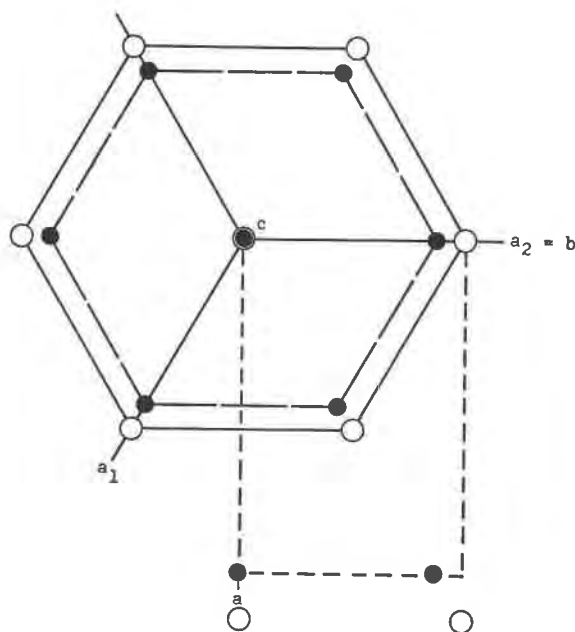


FIG. 23. The relationship between the two hexagonal  $U_3O_8$  cells of Milne (1951) and the unreel orthorhombic cell chosen by earlier observers to account for the multiple *x*-ray powder pattern. The difference in the *a* dimensions of the hexagonal cells has been exaggerated.

der method since no mention of single crystals is made. Milne (1951), working in this laboratory with lath-like crystals obtained sharp Weissenberg films clearly showing hexagonal symmetry. They indicated that the crystals are actually multiple, consisting of two cells oriented with their *a* and *c* directions coinciding and with identical *c* dimensions:

$$a = 3.87, 3.94; c = 4.15 \text{ \AA}$$

Milne noted and this has been confirmed during the present study, that



the majority of  $U_3O_8$  powder patterns show the double cell. It is evident that the previous observers worked with the double pattern for their orthorhombic cell shows the following relationship to the two hexagonal cells:

Orthorhombic	Hexagonal
$d(200)$	$d(10\bar{1}0)$ small cell
$d(020)$	$d(11\bar{2}0)$ large cell
$d(001)$	$d(0001)$ both cells

Fig. 23 depicts the three cells and shows that the orthorhombic cell is not a real one. The orthorhombic elements may be converted to the proper hexagonal ones by the formulae:  $a(\text{hex., small}) = a(\text{orth.})/2\cos 30^\circ$ ;  $a(\text{hex., large}) = b(\text{orth.})$ ;  $c(\text{hex.}) = c(\text{orth.})$ .

Milne's hexagonal cell contains  $\frac{1}{3}[U_3O_8]$ . He suggested that the true hexagonal  $c$  dimension is actually  $3 \times 4.15$  A, the measured value being a strong pseudo-period resulting from the arrangement of uranium atoms in the structure.

Zachariasen (1948; in Katz & Rabinowitch, 1951, p. 277) has described as  $UO_3(I)$  a compound obtained by heating amorphous anhydrous  $UO_3$  to  $500^\circ$  C. for 8 hours under 20 atmospheres of oxygen pressure. It is instructive to compare its cell constants with those of Milne's large hexagonal cell of  $U_3O_8$ :

	Symmetry	$a$	$c$	calc. density
$UO_3(I)$	hexagonal	3.963 A	4.160 A	8.34
$\frac{1}{3}[U_3O_8]$	hexagonal	3.94	4.15 A	8.37

The measured densities of  $U_3O_8$  are distinctly higher than those for  $UO_3$ :

$U_3O_8$	$UO_3$
8.300 (Biltz & Müller, 1927)	6.04 for $UO_{3.07}$ (Biltz & Müller, 1927)
8.34 (Grønvold, 1948)	7.07 for $UO_{2.92}$

They agree well with the calculated values for both  $U_3O_8$  and Zachariasen's  $UO_3(I)$ . The evidence strongly suggests that Zachariasen's amorphous  $UO_3$  was actually reduced to the "single cell" type  $U_3O_8$  phase with the loss of some oxygen during the heating procedure, rather than recrystallized to another form of  $UO_3$ . Highly oxidizing conditions apparently favour production of the "single cell" type; Milne reported that only one sample of  $U_3O_8$ , prepared by heating uranyl nitrate in air

at 220° C. for several days, resulted in a simple structure. In this study only those specimens high in U<sup>6</sup> (samples 5 and 6) produced a "single cell" type U<sub>3</sub>O<sub>8</sub> during heating experiments.

It appears certain that the "single" and "double" type patterns of U<sub>3</sub>O<sub>8</sub> are responsible for the following confusion:

"According to Boule and Domine-Berges (1944) the x-ray diffraction pattern of the comparatively easily-oxidizable preparations of U<sub>3</sub>O<sub>8</sub>, obtained at low temperatures (lower than 350° C.) from oxalate or trioxide, is somewhat different from that of the (practically non-oxidizable) microcrystalline product obtained at high temperatures" (Katz & Rabinowitch, 1951, p. 272).

Milne (1951) has offered two suggestions to account for the "two cell" structure of U<sub>3</sub>O<sub>8</sub>. Both depend upon the introduction of oxygen into the structure. According to Milne this may enlarge the *a* dimension of the cell, with a higher oxide confined to the outer boundaries of grains and crystals where solution of oxygen is most likely. On the other hand, the introduction of oxygen with its consequent change of U<sup>4</sup> ions to the smaller U<sup>6</sup> ions, may result in a shrinkage of the cell as it does in the case of the UO<sub>2</sub> structure. Milne felt that both suggestions called for two similar oxide structures with greater and less oxygen than the resultant U<sub>3</sub>O<sub>8</sub>.

The majority of the U<sub>3</sub>O<sub>8</sub> patterns produced by the heating experiments in this study show the "two cell" effect. Using the powder data given by Milne, the cell sizes were determined from the (20 $\bar{2}$ 0) and the (0003) reflection arcs. Due to the quality of the films, the accuracy of these determinations are no better than  $\pm 0.01$  A. The results show an obvious relationship between the cell sizes and the state of oxidation of the pitchblende:

	<i>a'</i>	<i>a''</i>	<i>c</i>
synthetic UO <sub>2</sub> for 10 min. in air	3.85	3.93	4.12
pitchblende—17.4 % U <sup>6</sup> for 5 min. in air	3.87	3.98	4.14
pitchblende—20.2 % U <sup>6</sup> for 5 min. in air	3.88	3.97	4.14
pitchblende—78.5 % U <sup>6</sup> for 5 min. in air	3.94	4.04	4.17

The unit cells of U<sub>3</sub>O<sub>8</sub> formed by heating samples low in U<sup>6</sup> are distinctly smaller than those formed from pitchblendes that are highly oxidized. These observations support the view that the composition of the U<sub>3</sub>O<sub>8</sub> structure is not constant; that the U<sub>3</sub>O<sub>8</sub> structure exists over a solid solution range. Contrary to the case of the UO<sub>2</sub> structure, solution of oxygen in the U<sub>3</sub>O<sub>8</sub> structure increases the cell size, the expansion being confined largely to the *a* dimension. This was confirmed by the reduction of UO<sub>3</sub> to U<sub>3</sub>O<sub>8</sub> in vacuum:

	$a'$	$a''$	$c$
after heating $\frac{1}{2}$ hour in vacuum	3.91	3.98	4.16
after heating 1 hour in vacuum	3.89	3.98	4.14

The data presented above are in keeping with the results of a tensi-metric analysis by Biltz & Müller (1927) who found that the  $U_3O_8$  structure exists over a solid solution range, the molecular volume increases regularly with oxygen solution. The data also lend support to the first of Milne's suggestions to account for the "two cell" effect: that the introduction of oxygen which may be confined largely to the outer boundaries of grains or crystals, increases the cell size of the higher oxide. Milne's view that the two oxides should have respectively more and less oxygen than the resultant  $U_3O_8$  is not upheld by the new data since it is clear from the variation in cell dimensions given above and from the tensi-metric data of Biltz & Müller that the composition of  $U_3O_8$  may depart considerably from the ideal.

Katz and Rabinowitch (1951, p. 277) have reported that the lattice constants of two samples of partly deoxygenated  $UO_3$  ( $UO_{2.82}$  and  $UO_{2.96}$ ) were not intermediate between those of  $UO_{2.67}$  and  $UO_{3.00}$ . The values as reported are given here in the left hand portion of Table 3. For purposes of comparison, Katz & Rabinowitch have converted the hexagonal ele-

TABLE 3. LATTICE CONSTANTS REPORTED BY KATZ & RABINOWITCH (p. 278)

	Orthorhombic			Hexagonal		
	$a$	$b$	$c$	$a'$	$a''$	$c$
1. $UO_{2.67}$	6.70	3.98	4.14	3.87	3.98	4.14
2. $UO_{2.82}$	6.90	3.91	4.15	3.91	3.98	4.15
3. $UO_{2.96}$	6.90	3.91	4.15	3.91	3.98	4.15
4. $UO_{3.00}$	6.864	3.963	4.160	3.963		4.160

1. Zachariasen from  $U_3O_8$  (p. 271). 2, 3. Fried & Davidson (p. 278). 4. Zachariasen, obtained by heating amorphous  $UO_3$  at  $500^\circ C.$  for 8 hours under 20 atmospheres of oxygen pressure (=  $UO_3(I)$  of Zachariasen) (p. 277).

ments of  $UO_{3.00}$  ( $UO_3(I)$ ) to the orthorhombic setting which was believed to be correct for  $U_3O_8$ . The right hand portion of Table 3 gives the elements in the proper "two cell" hexagonal setting which, on the basis of Milne's single crystal study, is known to be correct. It has already been pointed out that Zachariasen's  $UO_3(I)$  is very likely a "one cell" type  $U_3O_8$ . It is immediately evident that in this setting the lattice constants

of  $\text{UO}_{2.82}$  and  $\text{UO}_{2.96}$  are in fact intermediate between  $\text{UO}_{2.67}$  and  $\text{UO}_{3.00}$ . This lends some support to our contention that the lattice dimensions of the  $\text{U}_3\text{O}_8$  structure increase with solution of oxygen. Actually Katz & Rabinowitch were on insecure footing in this comparison of lattice constants. The compositions of the two intermediate oxides were apparently precisely determined by Fried & Davidson. But in stating that the first sample had the composition  $\text{UO}_{2.67}$ , Katz & Rabinowitch have ignored the tensimetric data of Biltz & Müller which showed that the  $\text{U}_3\text{O}_8$  structure exists over a wide range of composition and have assumed that this particular sample had the ideal composition  $\text{U}_3\text{O}_8$  (or  $\text{UO}_{2.67}$ ). Furthermore, as was stated earlier, the evidence suggests that Zachariasen's  $\text{UO}_3(\text{I})$  is actually a "one cell" type  $\text{U}_3\text{O}_8$  with an O/U ratio of less than 3.

Much research on the  $\text{U}_3\text{O}_8$  solid solution series remains to be done. For example, while it is now known that the cell size increases with the O/U ratio, exact data relating the composition of the structure with the cell size are lacking. The difficulties in supplying this information are obvious. Most  $\text{U}_3\text{O}_8$  samples show the "two cell" effect and chemical analyses of such material will therefore, represent the composition of a mixture of two oxides. The mechanism leading to the "two cell" structure and the physical relations of the two cells to each other require clarification. It was noted in this study that the two cells are sharply defined when prepared by heating synthetic  $\text{UO}_2$  in air. When prepared from some natural pitchblende the doublets representing reflections from similar planes in the two cells appear as continuous bands possibly indicating a gradation of composition between the two cells. At other times intensity anomalies are apparent. Certain planes of the smaller cell may give more intense reflections than do similar planes of the larger cell; on the other hand reflections in the same pattern may indicate that the larger cell is the dominant one.

#### *The unknown oxide "X":*

There is every reason to believe that the unknown pattern produced by heating samples 3, 4 and 5 for  $\frac{1}{2}$  hour in vacuum and samples 4 and 5 for 5 minutes in air, represents an anhydrous oxide of uranium. The results of heating the six samples in vacuum suggest that its O/U ratio is intermediate between the ideal ratios for  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$ . (See next page, top.)

It appears that under these heating conditions, pitchblende low in  $\text{U}^6$  gives only the  $\text{UO}_2$  pattern; with increasing  $\text{U}^6$ , the unknown pattern also appears and this is replaced by the  $\text{U}_3\text{O}_8$  pattern in pitchblendes with an excess of  $\text{U}^6$ .

Two oxides intermediate between  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  are mentioned in the literature:

U <sup>6</sup> % of total U	After heating $\frac{1}{2}$ hour in vacuum
17.4	strong UO <sub>2</sub>
20.2	strong UO <sub>2</sub> plus faint trace of 'X'
40.2	strong UO <sub>2</sub> plus weak 'X'
60.0	strong 'X' plus diffuse UO <sub>2</sub>
78.5	strong UO <sub>2</sub> plus strong U <sub>3</sub> O <sub>8</sub>
85.0	strong U <sub>3</sub> O <sub>8</sub> plus weak UO <sub>2</sub>

1) The existence of a homogeneous phase U<sub>2</sub>O<sub>5</sub> has been suggested by a number of observers, most recently by Rundle, Baenziger, Wilson & McDonald (1948). It was asserted by the latter observers that the compound was formed by heating together equal quantities of UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub>. The new phase gave a somewhat different diffraction pattern than U<sub>3</sub>O<sub>8</sub> but the dimensions of its pseudo-cell are almost identical with those obtained by Zachariasen (in Katz & Rabinowitch, 1951) and Grønvold (1948) for U<sub>3</sub>O<sub>8</sub>:

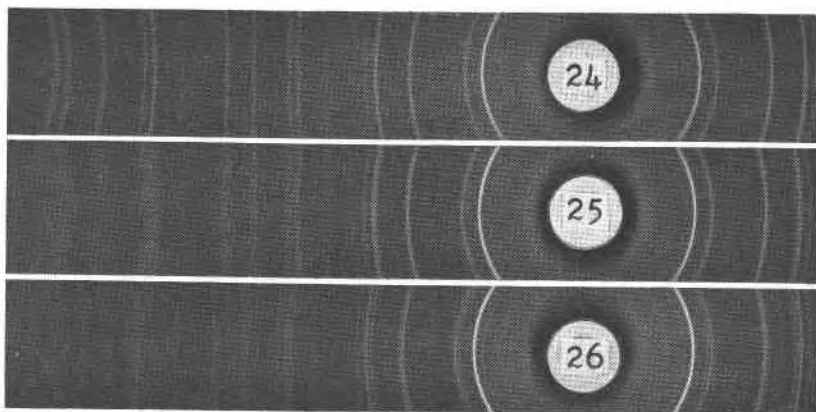
$a=4.135$	$b=3.956$	$c=6.72 \text{ \AA}$	(Rundle, etc.; 1948)
$c=4.14$	$b=3.98$	$a=6.70 \text{ \AA}$	(Zachariasen, 1951)
$c=4.136$	$b=3.969$	$a=6.703 \text{ \AA}$	(Grønvold, 1948)

Our attempts to form U<sub>2</sub>O<sub>5</sub> according to the directions of Rundle, etc., were unsuccessful; an *x*-ray powder pattern showed that a mixture of UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub> was still present. The U<sub>3</sub>O<sub>8</sub> pattern is complex and somewhat obscures the simple UO<sub>2</sub> pattern. Brewer (in Katz & Rabinowitch, 1951, p. 255) has suggested that this may have led Rundle, etc., to regard their product as a single phase. This is supported by the U<sub>3</sub>O<sub>8</sub>-like cell constants which they derived. There is reason therefore, to doubt that these observers produced a phase distinct from UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub>. However persistent reports in the early literature claiming its existence cannot be lightly dismissed and the possibility remains that our compound 'X' is U<sub>2</sub>O<sub>5</sub>.

2) Jolibois (1947) prepared the compound UO<sub>2.33</sub> (=U<sub>3</sub>O<sub>7</sub>) by the low temperature oxygenation of UO<sub>2</sub>. He observed that it gave a diffraction pattern almost identical with that of UO<sub>2</sub> but interpreted it as a new phase, U<sub>3</sub>O<sub>7</sub>. Grønvold & Haraldsen (1948) found that oxidation of UO<sub>2</sub> at 200 to 250° C. gave a tetragonal phase with  $a=5.38 \text{ \AA}$ ,  $c=5.55 \text{ \AA}$ . Alberman & Anderson (1949) have also prepared this compound at temperatures below 300° C. and found that it exists between UO<sub>2.19</sub> and UO<sub>2.30</sub>, the tetragonal character becoming more pronounced with increasing O/U.

We have prepared this phase by heating UO<sub>2</sub> at 250° C. with free access of air for periods ranging up to 6 hours. The effects of heating for  $\frac{1}{2}$  hour were a broadening of the diffraction lines from planes involving

both the  $a$  and  $c$  axes. After 1 hour, the broadened lines had split into two separate lines, the separation becoming more apparent with continued heating. After 6 hours, the tetragonal phase was essentially the same but faint  $U_3O_8$  lines had appeared.<sup>1</sup> This latter pattern gave the cell constants  $a = 5.38$ ,  $c = 5.54$  Å in excellent agreement with the data of



FIGS. 24-26. X-ray powder contact prints ( $1^\circ \theta = 1$  mm.). Fig. 24. Synthetic  $UO_2$ . Fig. 25. Synthetic  $UO_2$  after heating for  $\frac{1}{2}$  hour in air at  $250^\circ$  C. Fig. 26. Synthetic  $UO_2$  after heating for 6 hours in air at  $250^\circ$  C. (= tetragonal phase).

Grønvoold & Haraldsen and Alberman & Anderson. The powder data agree well with those given by Jolibois. This indicates that the various observers were working with the same compound. A comparison of the powder patterns (Figs. 25, 26) with that of our unknown however, shows no similarity.

Alberman & Anderson found that the tetragonal phase is not stable at elevated temperatures, breaking down at temperatures above  $750^\circ$  C. to  $\beta UO_2$  and  $U_3O_8$ . This is in contrast to the compound 'X' which was produced at high temperatures. It is possible that a form of  $U_3O_7$ , stable at high temperatures, can exist but it must be added that the tensimetric data of Biltz & Müller did not indicate the existence of another phase intermediate in composition between  $UO_2$  and  $U_3O_8$ .

The identity of compound 'X' must await further research. For its future recognition the usual  $x$ -ray powder data are given in Table 4.

<sup>1</sup> Jolibois stated that oxygenation of the tetragonal phase below  $300^\circ$  ceased at  $UO_{2.35}$  and continued to  $U_3O_8$  only above  $300^\circ$  C. The present study shows that  $U_3O_8$  is formed at a lower temperature. There is no reason to doubt that  $U_3O_8$  will form at even lower temperatures with prolonged heating.

TABLE 4. COMPOUND 'X'—X-RAY POWDER DATA<sup>1</sup>

<i>I</i>	<i>d</i> meas.	<i>I</i>	<i>d</i> meas.	<i>I</i>	<i>d</i> meas.	<i>I</i>	<i>d</i> meas.
6	5.95	1	2.69	4	1.892	1	1.377
4	3.36	1	2.49	3	1.852	1	1.341
10	3.21	1	2.44	2	1.687	1	1.290
2	3.17	1	2.23	3	1.662	1	1.252
2	3.04	1	2.07	2	1.612		
1	2.95	5	1.989	1	1.568		
5	2.75	2	1.949	1	1.528		

<sup>1</sup> Powder spacings calculated for the wavelength Cu K $\alpha$ =1.5418 Å.

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