

# THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 42

NOVEMBER-DECEMBER, 1957

Nos. 11 and 12

## THE ROLE OF LEAD AND EXCESS OXYGEN IN URANINITE<sup>1,2</sup>

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### ABSTRACT

It has long been known that uraninite varies widely in both composition and properties. This paper is an attempt to describe and explain the variation in properties in terms of the variation in composition. Analyzed samples of uraninite were  $x$ -rayed, annealed by heating to 550° C. and 900° C. for various times in a nitrogen atmosphere, and  $x$ -rayed again. A decrease in unit cell size was generally observed. Calculations on the basis of Vegard's Law showed that the ordering of the interstitial oxygens could account for the decrease in cell size on annealing. The interstitial oxygens are not necessarily completely disordered before annealing. The degree of original disorder is dependent on the Rare Earth/ThO<sub>2</sub> ratio; for high ThO<sub>2</sub> and low rare earths, the interstitial oxygens are completely disordered. The degree of disorder apparently depends solely on the composition, and not on the past history of the sample; this implies that the oxygens are being continuously disordered, perhaps by alpha particles, to an equilibrium point determined by the R.E./ThO<sub>2</sub> ratio. The degree of ordering of the interstitial oxygens also accounts for the difference in cell size between vein pitchblendes and those from the sediments of the Colorado Plateau.

A study was also made of the degree of oxidation of uraninites. Although the uranium in many pegmatitic uraninites is more oxidized than can be obtained with the cubic UO<sub>2</sub> phase in the laboratory, if the atoms proxying for uranium are calculated into the structural formula, and the lead is assumed to be radiogenic and calculated as original uranium, almost all pegmatitic uraninites fall into the range of interstitial oxygen content obtainable in the laboratory. This fact supports the auto-oxidation hypothesis.

Many of the vein and sedimentary pitchblendes have compositions close to U<sub>3</sub>O<sub>8</sub>, although they are cubic. They may have crystallized as U<sub>3</sub>O<sub>8</sub>, then decomposed to the cubic phase and an amorphous phase. This suggests that the stability range of U<sub>3</sub>O<sub>8</sub> includes only very exceptional natural conditions.

Vegard's Law calculations, differential leaching, and other lines of evidence indicate that lead, including radiogenic lead, is exsolved from uraninite. A study of  $x$ -ray line

<sup>1</sup> Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 375 This paper is a condensation of a Ph.D. thesis prepared under the direction of Prof. Clifford Frondel. The original thesis contains detailed descriptions of specimens, equipment and technique, and extensive summaries of the literature, which have necessarily been greatly reduced or eliminated in this condensation. Copies of the thesis are available in the Harvard Library.

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intensities indicates that it exsolves as oriented monomolecular layers of orthorhombic PbO (massicot) along cube planes in the uraninite, separating the uraninite crystallites so that the  $x$ -ray reflections interfere destructively to different degrees for different directions.

#### SUMMARY OF RELATIONSHIPS BETWEEN CERTAIN URANIUM OXIDES

At least twenty-two different phases have been reported in the uranium-oxygen system. Quite possibly as many as thirteen actually exist. One is known to occur in nature. This section is intended as a partial synthesis of the data available in the chemical literature on this system.

#### $U_4O_7$ , $UO_{1.75}$

The list of phases pertinent to the present discussion, in order of increasing oxidation, begins with  $U_4O_7$ . Zachariassen announced this phase in a still-classified report issued in 1947. Katz and Rabinowitch (1951) report that they found a cubic phase intermixed with  $UO_2$ , but with the somewhat larger unit cell  $a_0 = 5.488 \text{ \AA}$ . Zachariassen called it  $UO_{1.75}$  on the basis of extrapolation of the cell size from  $UO_2$ . Katz and Rabinowitch discuss the possibility of a continuous series between  $UO_{1.75}$  and  $UO_2$ . Wasserstein (1951) postulated that certain uraninites may have crystallized as  $UO_{1.75}$ , and been oxidized from there. More recently, in a controversy with Wasserstein (1954), Katz and Hoekstra pointed out that the evidence for the existence of  $UO_{1.75}$  rests entirely on  $x$ -rays, that no chemical data are available, and the relationship between composition and cell dimensions in the cubic  $UO_2$  phase is not well established or understood. The extrapolation to  $UO_{1.75}$  is unwarranted, and the existence of this phase is extremely doubtful.

#### $\alpha$ - $UO_2$

$\alpha$ - $UO_2$  is usually obtained as a fine, brownish-black powder by reducing a higher oxide with hydrogen or ammonia. It was found by Goldschmidt and Thomassen (1923) to have a fluorite-type structure. Rundle (1948) gives the unit cell edge as  $a_0 = 5.4692 \pm 0.0005 \text{ \AA}$  at  $25^\circ \text{ C}$ .  $UO_2$  takes up additional oxygen without changing its structure when heated to  $200$ – $300^\circ \text{ C}$ . in air. This oxidation has been studied by Biltz and Muller (1927), Grønfold and Haraldsen (1948), Jolibois (1947) and many others, but the most complete and reliable data were obtained by Alberman and Anderson (1949). They found that pure  $UO_2$  remained cubic as it oxidized, until a composition of  $UO_{2.2}$  is reached. Above  $UO_{2.2}$ , one of the axes gradually became longer than the other two, and the material became tetragonal. The tetragonal phase continued to  $UO_{2.32}$ . Any attempt to oxidize it further at one atmosphere causes the appearance of a second phase, related to  $U_3O_8$ .

When Th is present, the tetragonal phase is suppressed, and the cubic phase continues to  $(U, Th)O_{2.32}$ . The subscript 2.32 remains virtually constant, until Th substitutes for half the U. At the mid-point of the series, it is possible to oxidize to  $(U_{0.5}Th_{0.5})O_{2.34}$ . The rare earths may behave similarly. The highest subscript for the oxygen which can be reached in a laboratory experiment, as the end of a continuous series with  $UO_2$ , will be referred to as the laboratory limit. As the series moves from the mid-point toward thoria, the laboratory limit falls from 2.34 to 2.0.

The effect of increased pressure on the oxidation limit has not been studied. However, R. Collette (pers. comm.) in an attempt to synthesize coffinite, subjected  $U_3O_8$  and silica in a sealed gold capsule to pressures of 4000 atm., and a temperature of about 700° C. The capsule was recovered in a sealed condition; there was no opportunity for hydrogen generated by the steel bomb walls, or any other reducing agent, to affect the sample. The  $x$ -ray pattern of the run showed quartz and a cubic phase which evidently must have had the composition  $UO_{2.67}$ .  $U_3O_8$ , which is stable under atmospheric pressure, cannot react to high pressure by emitting oxygen gas. Increased pressure favors a reaction that decreases volume. The specific gravity of  $U_3O_8$  is 8.39, and that of  $UO_2$  is 10.96.

The excess oxygen is interstitial. The fluorite-type structure has holes approximately the diameter of the oxygen ion, at the  $(\frac{1}{2}, 0, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  positions. If all these holes could be filled, the composition would be  $UO_3$ . However, the interstitial oxygens are surrounded by eight other similarly charged oxygens. The mutual repulsions set up probably represent the structural control that determines the laboratory limit.

In  $\alpha$ - $UO_2$ , the interstitial oxygen has little or no effect on the cell size. The repulsion of the oxygen ions around it is balanced by the shrinkage of the  $U^{+4}$  to the  $U^{+6}$  ion. Alberman and Anderson could not detect any significant change in the dimensions of the unit cell from  $UO_{2.0}$  to  $UO_{2.2}$ . Biltz and Muller (1927) did not use  $x$ -ray diffraction, but their chemical and specific gravity data show that the mean molar volume did not change. And finally, the unit cell size of pegmatitic uraninites can be predicted from the composition if one assumes (among other things) that the state of oxidation does not affect the unit cell size.

Under atmospheric conditions, as the temperature increases above 300° C., the cubic phase will tolerate less and less oxygen. At 1000° C., it departs very little from stoichiometric  $UO_2$ . If the material already has a composition between  $UO_2$  and  $UO_{2.25}$ , and it is heated to 1000° C. in vacuum, it decomposes into  $UO_2$  and  $U_4O_9$ . This was observed in synthetic samples by Alberman and Anderson, and in natural samples by Brooker and Nuffield (1952).

*Tetragonal  $UO_{2.2}$ - $UO_{2.32}$* 

At  $UO_{2.2}$ , Alberman and Anderson found that the cubic form began to develop anisotropy, and became tetragonal. The axial ratio  $c/a$  reaches a value of about 1.04 at the laboratory limit. When this tetragonal phase is heated above 300° C., samples less oxidized than  $UO_{2.25}$  decompose into appropriate amounts of  $UO_2$  and  $U_4O_9$ . Above  $UO_{2.25}$ ,  $U_4O_9$  and Hoekstra's  $UO_{2.6}$  phase appear.

 *$U_3O_7$  ( $UO_{2.33}$ )*

In 1947, Jolibois reported the results of heating  $UO_2$  at various temperatures in a heating balance. He found that  $UO_2$  oxidized to  $UO_{2.33}$  at 210° C. No further oxidation took place until a temperature of 300° was reached, at which a phase related to  $U_3O_8$  began to form. The  $UO_{2.33}$  was tetragonal, and Jolibois concluded that it was a new compound with the composition  $U_3O_7$ . The observations are not in conflict with the data given by Alberman and Anderson for their tetragonal phase. A comparison of the x-ray data given in the original references leaves little doubt that the phases are identical.

*Delta Phase*

Grønvd and Haraldsen (1948) reported a tetragonal 'delta phase' formed by oxidation of  $UO_2$  at 200° C. They noted that it decomposed at 270°, and ascribed to it a "narrow range of homogeneity around  $UO_{2.40}$ ." The subscript 2.40 does not seem to represent a chemical analysis, but rather a blank region in which a hitherto unknown stability field could be fitted. The following table compares the cell dimensions of

TABLE 1. LATTICE PARAMETERS OF TETRAGONAL PHASES

	$a_0$	$c_0$
$UO_{2.303}$	5.396 Å	5.564 Å
Delta Phase	5.37	5.54

Alberman's tetragonal phase at  $UO_{2.303}$  and Grønvd's delta phase, and shows the two are almost certainly the same phase.

 *$\beta$ - $UO_2$  or  $U_4O_9$* 

When the oxidized cubic or tetragonal phase is heated to 1000° C. in an inert atmosphere, it decomposes, and the lines of a cubic phase with a cell edge  $a_0 = 5.435$  Å appear on the x-ray photographs. For compositions above  $UO_{2.25}$ , the  $UO_{2.6}$  phase also appears. Compositions below  $UO_{2.25}$  decompose into the new phase and  $UO_2$ . Alberman and Ander-

son called this new cubic phase " $\beta$ - $\text{UO}_2$ " in their original paper, and later (1954) refer to it as  $\text{U}_4\text{O}_9$ . In their opinion, it is an ordered phase, with the interstitial oxygens occupying the ( $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ) positions only. In this case, the forces of attraction and repulsion do not balance out, as was the case with the randomly distributed excess oxygens of the alpha phase. The unit cell is contracted inward upon itself, while still remaining isometric.  $\text{U}_4\text{O}_9$  has the  $\text{U}_4\text{O}_8$  unit cell of  $\text{UO}_2$  with an extra oxygen in the center. The 'unknown oxide X' of Brooker and Nuffield (1952) is almost certainly  $\text{U}_4\text{O}_9$ .

#### *Phases Related to $\text{U}_3\text{O}_8$*

In an article entitled "The Uranium-Oxygen System:  $\text{UO}_{2.5}$  to  $\text{U}_3\text{O}_8$ ," Hoekstra, Siegel, Fuchs and Katz (1955) describe research leading to conclusions which can be summarized as follows.

1.  $\text{U}_2\text{O}_6$ , which had been reported by many earlier authors, does not exist as a phase.
2. From  $\text{UO}_{2.52}$  to  $\text{UO}_{2.64}$ , there is an orthorhombic phase, with  $b/a$  slightly above  $\sqrt{3}$ .
3. When heated in air, this phase absorbs oxygen and becomes  $\text{U}_3\text{O}_8$ . At room temperature,  $\text{U}_3\text{O}_8$  is orthorhombic; however, on heating, or on further oxidation toward one of the forms of  $\text{UO}_3$ ,  $b/a$  reaches  $\sqrt{3}$ , at which point the phase becomes hexagonal.
4. The transition from the  $\text{UO}_{2.6}$  phase to  $\text{U}_3\text{O}_8$  is apparently continuous at higher temperatures. However, Milne (1951) gives evidence of a mixture of  $\text{UO}_{2.6}$  and  $\text{U}_3\text{O}_8$ , intergrown in parallel position, in a sample that had stood for a while at room temperature.

A tentative phase diagram for the U-O system at one atmosphere is presented as Figure 1.

#### SPECIMENS USED IN THIS STUDY

Reference will be made to individual specimens by means of the capitalized portions of the locality names given below. Most of the specimens were taken from the Harvard collection, or were kindly loaned by Dr. George Switzer of the U. S. National Museum; in these cases, the museum numbers are given. The specific gravity and number of the analysis in the appendix are also included. More complete descriptions are available in the original thesis. Some of the uraninite samples analyzed by Hillebrand (1891) were included in Dr. Switzer's gift. These are indicated below.

#### URANINITE SPECIMENS FROM PEGMATITES

- BOQUEIRAO, Rio Grande do Norte, Brazil. H105716.  $G=7.80$ . Large, rough crystal, with purple fluorite.
- BRANCHVILLE, Conn. USNM 83567.  $G.=9.733$ . Anal. 2. Vitreous. Hillebrand (1891).
- ELVESTAD, Norway. USNM 83568.  $G.=9.14$ . Anal 7. Shows xl. faces. With quartz, muscovite. Hillebrand (1891).
- GORDONIA, South Africa (HOLMES) H 92341.  $G.=8.876$ . Anal 39, quoted in Holmes (1934). Sub-vitreous, with brownish alteration products.

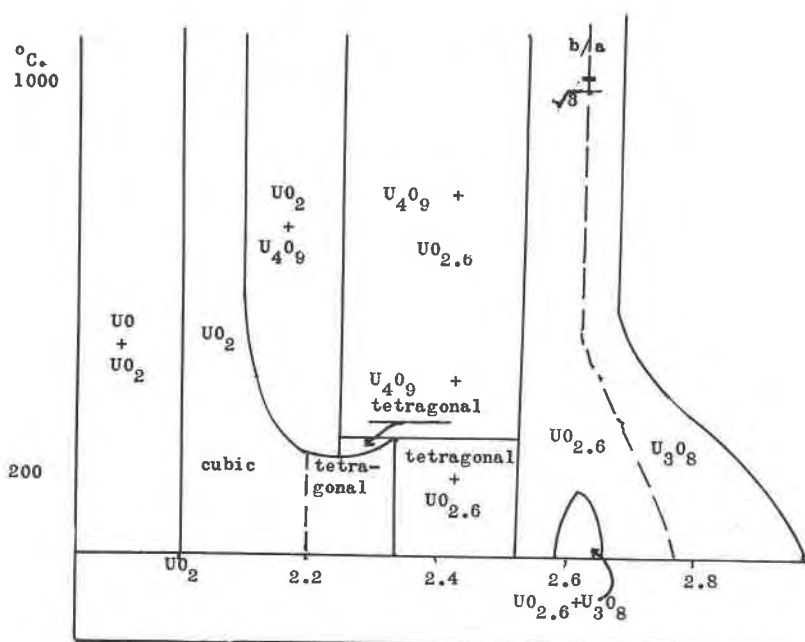


FIG. 1. Tentative phase diagram of the  $\text{UO}_2\text{-UO}_3$  system.

- GORDONIA, South Africa (USNM) USNM 103596.  $G.=7.32$ . Anal 42. Sub-hedral xls, sub-vitreous, imbedded in plagioclase.
- GRAFTON, New Hampshire. H 105756. Anal 36. Altered to secondary mins. along cracks.
- HALE'S QUARRY, Portland, Conn. USNM 83566.  $G.=9.139$ . Anal 27. Sub-vitr. with feldspar, muscovite. Hillebrand (1891).
- HUGGENÅSKILEN, Norway. USNM 83570.  $G.=8.930$ . Anal 10. Vitreous. Hillebrand (1891).
- KARELIA, Soviet Union. H 106038.  $G.=8.41$ . Vitreous. With microcline.
- MOROGORO Dist., Tanganyika. USNM 93290.  $G.=9.09$ . Anal 44. Cube coated with yellowish-brown alteration products.
- NEWRY, Me. H 103038.  $G.=9.58$ . Anal 33. Sharp octahedral faces. Lustre sub-metallic.
- PORTLAND, Conn. H 16214.  $G.=10.15$ . Anal 32. Vitreous lustre.
- SPRUCE PINE, N. Car. H 105712.  $G.=6.17$ . Anal 45. Vitreous. Conchoidal fracture. Bluish iridescence.
- STRICKLAND Quarry, Portland, Conn. H 106052, Anal 24. Small crystals embedded in orthoclase.
- SUDBURY Dist., Ont.  $G.=8.6$ . Anal 43. Vitreous, with quartz, biotite.
- WILBERFORCE, Ont. H 105711.  $G.=10.25$ . Anal 59 and 60. Dull, earthy. With purple fluorite. Pitted crystal faces.

#### VEIN PITCHBLENDES

- GREAT BEAR LAKE, Eldorado Mines, N.W.T. H 106051.  $G.=7.19$ . Anal 52. Botryoidal, on quartz, chalcopyrite.

- JOACHIMSTHAL, Czech. G.=7.28. Anal 41. Vitreous. Seams in dolomite. Conchoidal fracture.
- KATANGA. USNM 94710. Anal 40. Dull matte lustre, with yellow alteration products in cracks and crusts.
- Lac PIED DES MONTS, Que. H 105713. Anal 38. Powder.
- PRZIBRAM, Czech. H 105714, G.=7.82. Anal 61. Vitreous botryoidal groups, with galena, pyrite.
- RIX ATHABASKA mines, Lake Athabaska Dist., Sask. H 105717. G.=7.33. Fills cracks in brecciated reddish limestone.
- SCHMIEDEBERG, Silesia. Bergfreiheits Mine. H 104907. G.=7.46. Anal. 63. Vitreous veinlet in cleavable pink calcite.
- THEANO POINT, Algoma Dist., Ont. H 105710. G.=7. Anal 55. Sub-vitreous, in calcareous redish quartzite. With uranophane.
- WÖLSENDORF, Bavaria. Anal 37. Dull, with purple fluorite.
- WOOD MINE, Central City, Colo. USNM 100453. G.=6.77. Anal 62. Grayish porous chunks. With pyrite.

## SEDIMENTARY PITCHBLENDES

- BIG INDIAN Wash, San Juan Co., Utah. Continental Uranium Co. Mine. H 106050. Anal 35. Grayish, dull material, permeated by calcite.
- HAPPY JACK Mine, White Canyon, Utah. Lent by L. Stieff and T. Stern. G.=9.1. Anal 25. Fine powder.
- MI VIDA Mine, San Juan Co., Utah. H 106040. G.=6.84. Anal 34. Massive, with seam of calcite, few grains chalcopyrite.
- SHINARUMP NO. 3 mine, Sevenmile Dist., Grand Co., Utah. H 106039. Dull, pulverulent, in gray sandy limestone.
- ROYAL CLAIMS, Indian Creek, San Juan Co., Utah. H 106037. Grayish, earthy material permeated with calcite.

Many of the samples had already been chemically analyzed, and analyses were obtained on some of the others. X-ray diffraction patterns were made of all the samples, using a ThO<sub>2</sub> internal standard. The x-ray film was measured on a spectrographic comparator equipped with a metric scale.

C. Frondel and E. Berman have collected the unit cell measurements of many uraninites. To these the author has added his own data, and the resulting distribution bar graphs are shown in Fig. 2. The median value for the pegmatitic uraninites is 5.470 Å. The median for vein uraninites is very considerably lower; 5.437 Å. The median cell size for uraninite from sedimentary occurrences is 5.406 Å, which is smaller than the smallest unit cell of the 105 pegmatitic uraninites measured. Differences in composition cannot fully account for the variation in unit cell sizes. There are apparently three different relationships between composition and cell size for the three modes of occurrence. It is therefore convenient to retain the varietal term 'pitchblende' to refer to the vein and sedimentary occurrences.

In an inert atmosphere, uraninite heated to the vicinity of 550° for

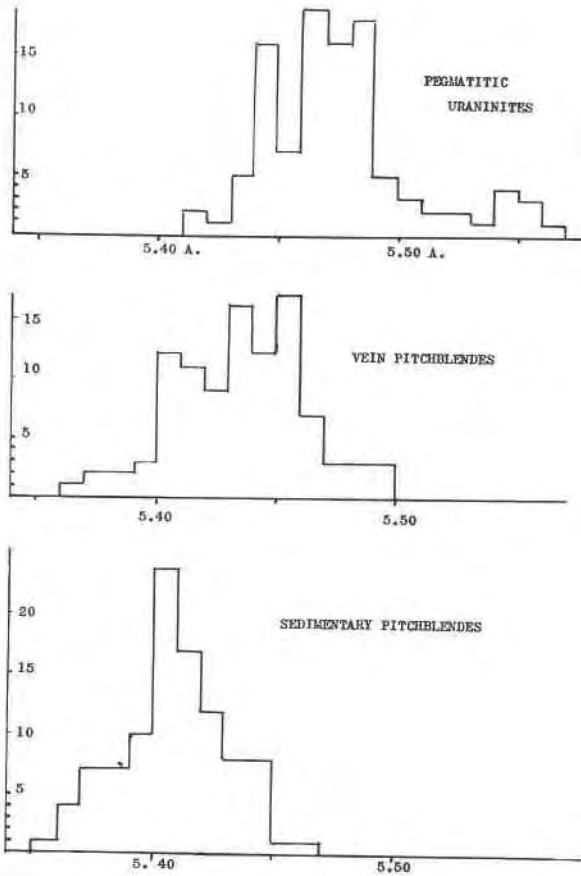


FIG. 2. Distribution of unit cell sizes in uraninites according to occurrence. (In part after C. Frondel.)

several hours undergoes a change that will be called 'annealing.' The lines of the powder pattern sharpen, and the unit cell decreases as much as  $0.04 \text{ \AA}$ . The duration of heating necessary to complete the operation (i.e. until the unit cell stops changing) varies considerably from sample to sample, but 24 hours is usually safely in excess. In certain of the more oxidized samples,  $\text{U}_3\text{O}_8$  lines appear, particularly on long runs. These may actually be the lines of the  $\text{UO}_{2.6}$  phase, but Hoekstra *et al.* (1955) failed to include the powder pattern of  $\text{UO}_{2.6}$  in their original description of the phase, and the criteria are therefore lacking for distinguishing the two phases in an ordinary powder photograph.

When the samples are heated to  $900^\circ$ , more of the samples decompose into a cubic phase and an orthorhombic one related to  $\text{U}_3\text{O}_8$ . The results



depend on the state of oxidation, and perhaps on the content of thorium and other elements. The annealing studies described in this paper were done in a muffle furnace through which a constant stream of prepurified nitrogen was passed.

In certain of the calculations given later, it was necessary to adopt a value for the atomic weight of the 'average rare earth.' A value of 130 was chosen, largely on the basis of the compilation of geochemical data by Green (1953).

#### PEGMATITIC URANINITES

The degree of oxidation was computed for all available pegmatitic uraninite analyses which distinguish between  $U^{+4}$  and  $U^{+6}$ . The degree of oxidation is expressed as the subscript of the oxygen in the formula. The term 'm value' will be used to denote the subscript  $UO_m$ ; 'n' is used for the subscript of  $(U, Th)O_n$ ; 'p' is used for  $(U, Th, R.E.)O_p$ , and 'q' is used for  $(U, Th, R.E., Pb)O_q$ . A distribution bar graph of 'm,' 'n,' 'p' and 'q' is shown as Fig. 3.

The 'm' value is the best indication of the actual state of oxidation of the uranium atom—that is, to what extent the average uranium atom has adjusted its electron configuration and its ionic radius. Of course, the thorium, rare earth, lead, and even to some extent the oxygen ions make some adjustment, but the major change as oxygen increases is the reduction in ionic radius of uranium ions as  $U^{+4}$  changes to  $U^{+6}$ .

As will be shown, the thorium and rare earth ions occupy uranium positions in the structure. The amount of interstitial space in the structure is indicated by the total amount of uranium, thorium and rare earths. Therefore it is the 'p' value which indicates the stability or the degree of oxygen saturation of the structure, as it indicates the amount of oxygen actually in the interstitial spaces.

It will also be shown that the lead is not in the uranium positions. However, if auto-oxidation is the explanation for the uraninites that are oxidized above the laboratory limit, then the 'q' subscript would indicate the original oxidation state of the uraninite, the oxidation state that was in equilibrium with the environment when the uraninite crystallized. However, if non-radiogenic or previously existing radiogenic lead was incorporated into the sample when it crystallized, the 'q' value will be lower than the original oxidation state—perhaps even lower than 2. Non-radiogenic lead is a more serious problem in pitchblendes than in pegmatitic uraninites.

In general, the 'm' values are distributed from 2.14 to 2.80, with a decrease in frequency of occurrence above 2.50. A very considerable portion is above the laboratory limit of  $UO_{2.33}$ . In the calculation of 'p' values,

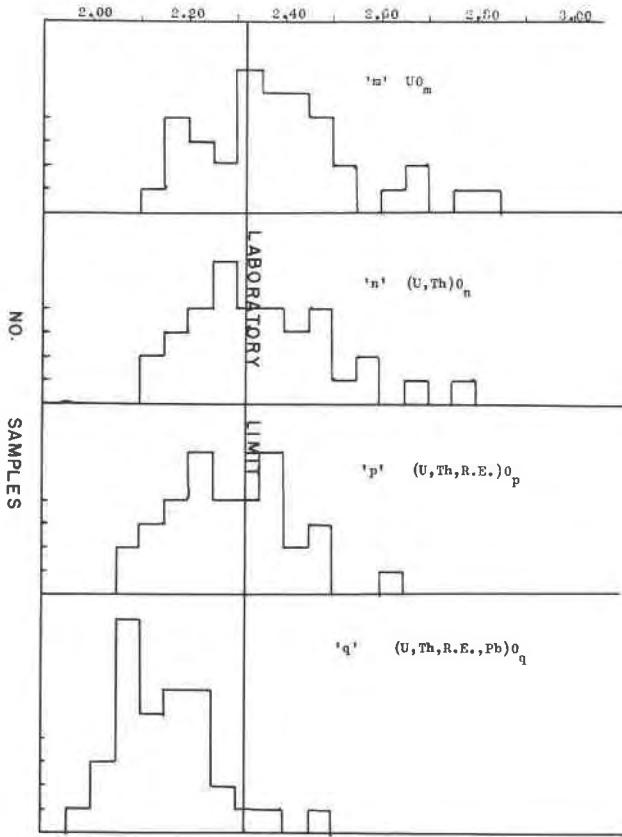


FIG. 3. Formula subscripts calculated for available pegmatitic uraninite analyses.

however, many of the more oxidized samples are shown to be structurally near or slightly above the laboratory limit; only five pegmatitic uraninites out of 34 have 'p' values above 2.40. In other words, as all the impurities proxying for the uranium are taken into account, the subscripts edge closer to permissible values.

The process is virtually completed by the 'q' values. 30 out of 34 pegmatitic uraninite analyses have 'q' values between 2.00 and 2.33, the laboratory stability range. Of the exceptions, one is slightly below the range and two are slightly above. The Spruce Pine sample, with a 'q' value of 2.488, is the only sample that still remains deep in forbidden territory.

Ellsworth (1924) proposed a process, which he called auto-oxidation, to explain the oxidation of uraninites above the laboratory limit. As each  $\text{UO}_2$  formula unit disintegrated to  $\text{PbO}$ , it released an oxygen atom

which was available for oxidizing additional  $\text{UO}_2$  to  $\text{UO}_3$ . The data of the present study indicate that most pegmatitic uraninites crystallized within the limits of the stability field of the cubic form, as outlined in the laboratory. Auto-oxidation can satisfactorily account for the additional oxidation which places some analyses outside these limits.

#### UNIT CELL SIZE BEFORE AND AFTER ANNEALING

X-ray powder photographs were taken of the samples before and after annealing. Table 2 lists the furnace runs and the resulting unit cell size of the cubic phase. If lines belonging to a phase related to  $\text{U}_3\text{O}_8$  appeared, their intensity is given, relative to the cubic phase.

These observations agree in general with those of Brooker and Nuffield (1952) and Robinson and Sabina (1955). They can be summarized as follows: in pegmatitic uraninites with relatively large unit cells (5.47 to 5.49 Å), the unit cell decreases 0.03 to 0.035 Å on annealing in an inert atmosphere. For those with smaller unit cells, the decrease is less, but the difference is not sufficient to wipe out the very considerable range in unit cell sizes.

Table 2 also shows a great disparity in the ease of annealing. The Gordonia (USNM) sample had virtually completed its annealing after 2 hours at 500° C., whereas the Wilberforce sample had not completely annealed after 26 hours at 550° C. The difficulty of annealing seems to vary as the  $\text{ThO}_2$  content, and inversely as the rare earth content.

#### CALCULATED VALUES FOR THE UNIT CELL SIZES

If the uranium-oxygen system, as studied in the laboratory, is examined for behavior comparable to this annealing effect, a striking parallel is found in the transition from oxidized  $\alpha\text{-UO}_2$ , with random oxygens in the interstices, to  $\beta\text{-UO}_2$ , or  $\text{U}_4\text{O}_9$ , in which the interstitial oxygens are ordered. The transition is brought about under the same range of conditions—heating the sample above 500° in an inert atmosphere or vacuum. The transition is characterized by a contraction of the unit cell of 0.34 Å, from 5.469 to 5.435 Å. These values are strongly reminiscent of many of the annealing results.

As a possible hypothesis, it is suggested that natural uraninites correspond to  $\alpha\text{-UO}_2$ , and on annealing become the ordered phase  $\beta\text{-UO}_2$ . Using Vegard's Law (Vegard and Dale, 1928), it is possible to calculate a theoretical unit cell size from the analysis, first assuming that the uranium is present as  $\alpha\text{-UO}_2$ , then as  $\beta\text{-UO}_2$ . Certain other assumptions must be made; they are discussed at some length in the thesis, but here their main justification must be that they work. The assumptions are as follows.

1. The validity of Vegard's Law.

TABLE 2. UNIT CELL SIZES OF PEGMATITIC URANINITES, BEFORE AND AFTER ANNEALING RUNS

Sample	Time, hr.	Temp., ° C.	$a_0$ , Å	$\Delta a_0$ , Å	U <sub>3</sub> O <sub>8</sub> lines	
Boqueirao	unheated		5.488			
	12	540	5.474			
	2½	900	5.455	.033		
Branchville	unheated		5.476			
	21	550	5.448	.028		
Elvestad	unheated		5.484			
	5½	500	5.465			
	{ + 8	5½	500	5.455	.029	Weak
		650				
Gordonia (Holmes)	unheated		5.491			
	21	550	5.474			
	2	900	5.463	.028		
Gordonia (USNM)	unheated		5.454			
	2	500	5.438			
	4½	500	5.438			
	10	500	5.438			
	28	500	5.438			
	2½	900	5.435	.019		
Grafton	unheated		5.443			
	4	440	5.433	.010		
	20	540			Exclusively	
Hale's Quarry	unheated		5.484			
	2	900	5.451			
	7	500	5.451	.033		
Huggenåskilen	unheated		5.470			
	6	500	5.454			
	{ + 20	6	500	5.447	.033	Weak
		650				
Karelia	unheated		5.491			
	24	540	5.490	.001	Weak	
	4	900	Cubic pattern, lines too broad			
Morogoro	unheated		5.445			
	24	540	5.435	.010	Moderate	
Newry	unheated		5.480			
	25	550	5.446	.034		
Portland	unheated		5.478			
	24	550	5.448	.030		
Spruce Pine	unheated		5.431			
	6	500	5.422	.009		
Strickland	unheated		5.488			
	12	570	5.448	.040		
Sudbury	unheated		5.437			
	6	500	5.428			
	23	650	5.429	.008		
Wilberforce	unheated		5.486			
	26	550	5.467			
	2	900	5.460	.026		
Mean probable error, ±	¼	20	0.002			

2. The cell edges of the pure end members:  $\alpha$ - $\text{UO}_2$ , 5.469 Å.  $\beta$ - $\text{UO}_2$ , 5.435 Å.  $\text{ThO}_2$ , 5.601 Å.

3. For the putative end member  $(\text{R.E.})\text{O}_2$ , the cell size, for purposes of calculation, is 5.38 Å.

4. Excess or deficiency of oxygen does not affect the unit cell size of  $\alpha$  or  $\beta$ - $\text{UO}_2$ .

5. Lead, including radiogenic lead, is not in the uraninite structure.

In Table 3, the results of these calculations are compared with the measured unit cell sizes of analyzed pegmatitic uraninites, before and after annealing.

The measured value after annealing and the calculated value assuming  $\beta$ - $\text{UO}_2$  agree extremely well. Indeed, considering the complexity of the substance, the difficulties of analysis, and the limitations of x-ray measurement, the agreement could hardly be any closer.

The author therefore maintains that pegmatitic uraninites after annealing are  $\beta$ - $\text{UO}_2$ . The interstitial oxygens, which were more or less randomly arranged, order themselves on heating. The oxygen ions are similarly charged and repel each other. When thermal motion provides the opportunity, they tend to follow Pauling's rule and move as far apart as possible.

The interstitial positions they take up tend to be evenly spaced, so that, perhaps for distances of several unit cells, they can be considered as occupying the middle of the unit cell. The result is the  $\beta$ - $\text{UO}_2$  or  $\text{U}_4\text{O}_9$

TABLE 3. CALCULATED AND MEASURED UNIT CELL SIZES, Å

Sample	Calculated assuming $\alpha$ - $\text{UO}_2$	Measured before annealing	Calculated assuming $\beta$ - $\text{UO}_2$	Measured after annealing
Hale's Quarry	5.482	5.484	5.452	5.451
Branchville	5.479	5.476	5.448	5.448
Elvestad	5.479	5.484	5.450	5.445
Portland	5.475	5.478	5.442	5.448
Newry	5.475	5.480	5.442	5.446
Strickland	5.474	5.488	5.442	5.448
Wilberforce (outer)	5.487	5.486	5.460	5.460
Huggenaskilen	5.477	5.470	5.446	5.447
Gordonia (USNM)	5.468	5.454	5.438	5.438
Sudbury	5.458	5.437	5.430	5.429
Morogoro	5.466	5.445	5.433	5.435
Gordonia (Holmes)	5.478	5.491	5.450	5.474
Spruce Pine	5.463	5.431	5.434	5.422

structure, perhaps with an excess or deficiency of oxygens. The annealing process is therefore a disorder-order transformation.

Before annealing, some of the samples have unit cell sizes corresponding to  $\alpha$ - $\text{UO}_2$ ; these are the first group listed in Table 3. Presumably, the interstitial oxygens are completely disordered in these samples. The second group of samples in Table 3, before annealing, have values intermediate between  $\alpha$ - and  $\beta$ - $\text{UO}_2$ . When they are annealed, they complete the rest of the journey to the calculated value for  $\beta$ - $\text{UO}_2$ . It is reasonable to assume that these samples reach us in a partially ordered condition.

The samples in the second group have smaller cells after annealing than those of the first group; the more ordered a sample is in its original condition, the lower the unit cell after annealing. But the unit cell after annealing is entirely a function of the composition. In Table 4, the degree of disorder, as indicated by the measured contraction of the unit cell divided by the theoretical calculated contraction, is compared to the rare earth/ $\text{ThO}_2$  ratio.

The degree of ordering of a sample as it is found in nature is apparently determined by the R.E./ $\text{ThO}_2$  ratio—in other words, by the composition, and not to any great extent by other factors. One would think, for instance, that the past history of the material would have some effect; surely samples can be annealed naturally. But there is no evidence in Table 4 that the past history influences the degree of annealing.

Radioactivity may have the effect of disordering samples which are

TABLE 4. R.E./ $\text{ThO}_2$  RATIO AND DEGREE OF ORDERING

Sample	R.E./ $\text{ThO}_2$	Actual contraction Theoretical contraction
Completely disordered samples		
Branchville	~0	0.90
Portland	~0	0.90
Newry	~0	1.03
Hale's Quarry	0.06	0.90
Strickland	0.11	1.25
Wilberforce (outer)	0.14	0.96
Elvestad	0.19	1.34
Partially ordered samples		
Huggenåskilen	0.22	0.74
Gordonia (USNM)	0.90	0.53
Sudbury	4.7	0.29
Morogoro	5.0	0.30

completely ordered. The R.E./ThO<sub>2</sub> ratio may fix an equilibrium in the order-disorder scale; samples more disordered than the equilibrium would be annealed as a result of radioactivity, whereas those more ordered would undergo disordering. Here again, it is inconceivable that temperature should not be a factor, but there is no evidence of it in the data. Apparently, equilibrium has been attained under surface or near-surface conditions, and this in turn indicates that geologic time is not required to reach equilibrium.

#### PITCHBLENDES

Pitchblende differs from pegmatitic uraninite in having low or absent ThO<sub>2</sub> and rare earths, high CaO, small crystal size and small unit cell size.

Table 5 shows the average ThO<sub>2</sub>, rare earths, and CaO content for the pegmatitic uraninite and pitchblende analyses in the appendix, excluding a few known to be contaminated with calcite.

Alberman, Blakely and Anderson (1951) investigated the UO<sub>2</sub>-CaO system. They found that CaO could be incorporated into UO<sub>2</sub> to the ex-

TABLE 5. AVERAGE ThO<sub>2</sub>, RARE EARTH AND CaO CONTENT. WT. %

	ThO <sub>2</sub>	R.E. oxides	CaO
Pegmatitic uraninites	6.00	4.05	0.43
Pitchblendes	0.18	0.92	1.96

tent of 20 molar per cent at 1650° C., and up to 47 molar per cent at 2080° C. As the CaO content rose, the unit cell decreased somewhat. Calculations showed, however, that it was not enough to account for the difference in cell size between pegmatitic uraninites and vein pitchblendes. The calcium can at best be one of many contributing factors.

In nearly half the pitchblende analyses, only UO<sub>2</sub> and UO<sub>3</sub> determinations are available, and therefore only the 'm' subscript can be calculated. A distribution graph of these 'm' values for the pitchblende analyses in the appendix is given as Figure 4.

#### THE UO<sub>2.6</sub> CLUSTER

Twenty-one out of thirty-two pitchblende analyses have 'm' values below 2.50. Only one has a value between 2.50 and 2.60; a sample from Rio Branco, Minas Gerais, Brazil has an 'm' value of 2.524. This makes a very sharp saddle in the distribution curve, for 7 samples have 'm' values between 2.60 and 2.70. U<sub>3</sub>O<sub>8</sub> is UO<sub>2.667</sub>. The samples included in

TABLE 6. ANALYSES WITH 'm' VALUES BETWEEN 2.6 AND 2.7

Anal	Locality	'm'
23	Cerro Blanco, Córdoba, Argentina	2.670
37	<i>Wölsendorf</i> , Bavaria	2.636
46	Monument No. 2 mine, Apache Co., Ariz.	2.635
47	Happy Jack mine, San Juan Co., Utah	2.610
55	<i>Theano Pt.</i> , Algoma Dist., Ontario	2.667
68	Martin Lake, Lake Athabaska Dist., Sask.	2.600
61	<i>Przibram</i> , Czechoslovakia	2.610

Samples available for study italicized.

this peculiar cluster are listed in Table 6. In addition, a pegmatitic uraninite, the Grafton sample, may also be included; it has an 'm' value of 2.681. The author suggests that the samples forming this 'high' in the distribution curve crystallized as  $U_3O_8$ .

Whatever these samples may have been originally, they are not now  $U_3O_8$ . Of the eight samples, including the Grafton sample, those from *Wölsendorf*, *Przibram*, *Theano Point* and Grafton were *x*-rayed in the course of this study; the samples from the Happy Jack and Monument No. 2 mines were *x*-rayed by the U. S. Geological Survey in Washington, and the *x*-ray pattern of a seventh, from Martin Lake, Sask., is available in Brooker and Nuffield's (1952) article as their Fig. 5.

The seven samples of the ' $UO_{2.6}$  cluster' have compositions falling in, or close to, the stability range of the phases related to  $U_3O_8$ . In the distribution curves, there is evidence that they may have been  $U_3O_8$  at one time. Except for the *Wölsendorf* sample, however, the available powder patterns showed only the cubic phase. The *Wölsendorf* sample gave no pattern. The fact that these samples are no longer  $U_3O_8$  seems to cast considerable doubt on the possibility of finding this phase as a primary mineral under the temperature, pressure and oxygen availability condi-

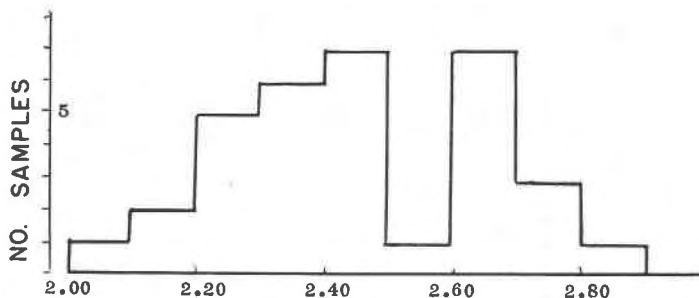


FIG. 4. Distribution of 'm' subscripts in analyzed pitchblendes.



tions of the normal geothermal gradient. High temperatures and low pressures are apparently required.  $U_3O_8$  may possibly occur as a contact metamorphic product in areas of recent volcanic activity; even here, the usual product would probably be hydrated uranyl compounds.

Conybeare and Ferguson (1950) report some 'metamict' uraninites from Saskatchewan, presumably similar to the Wölsendorf sample. This sample was the only one examined in this study which gave no pattern. After heating in an inert atmosphere, it gave the pattern of  $U_3O_8$ . Its radioactivity is not remarkable. This sample is distinguished from most others by its composition, which suggests that it crystallized as  $U_3O_8$  and decomposed. Other 'metamict' vein uraninites should be analyzed; it may be that the destruction of the structure was caused primarily by chemical change rather than by radioactivity. Alpha particles may be capable of disordering interstitial oxygen ions, but the structural oxygens seem to remain in place.

#### UNIT CELL SIZE BEFORE AND AFTER ANNEALING

As with the pegmatitic uraninites, the pitchblendes were  $x$ -rayed before and after heating in an inert atmosphere. The results of the furnace runs are given in Table 7.

To summarize, the vein pitchblendes have unit cell sizes of approximately 5.425 Å. On annealing, they behave much as the pegmatitic uraninites. The unit cell contracts as much as 0.035 Å, resulting in values of 5.39 or 5.40 Å. Sedimentary pitchblendes from the Colorado Plateau have significantly smaller unit cells before heating. In these cases, the values are close to 5.40 Å. On annealing, they contract comparatively little, about 0.01 Å. They behave like partially or almost completely ordered specimens. The vein pitchblendes behave like samples with random or nearly random interstitial oxygens.

After annealing, the unit cell sizes of the two types of pitchblende fall in the same range. The chemical analyses of the two types are also similar, the various determinations covering the same range. It is necessary to call upon some mechanism other than composition to explain the difference in cell size before annealing. The ordering of interstitial oxygens is both necessary and sufficient to explain the difference. When this factor is eliminated by annealing both types, there no longer is a difference. Therefore, it is possible to think of sedimentary pitchblendes of the Colorado Plateau as corresponding to annealed vein types in structure.

Table 7 shows that the Joachimsthal sample does not contract on annealing. The analysis, No. 41 in the appendix, shows that the sample contains no  $U^{+6}$ . The analysis was checked by two independent methods, one based on the reduction of ceric ion, and the other on the solubility of

TABLE 7. UNIT CELL SIZE, Å., OF PITCHBLENDES BEFORE AND AFTER FURNACE RUNS

Sample	Time, hr.	Temp., ° C.	$a_0$ , Å.	±	$\Delta a_0$ , Å
<i>Vein Pitchblendes</i>					
Great Bear Lake	14	unheated	5.425	.005	.019
		540	5.406	.002	
Joachimsthal	20	unheated	5.418	.005	.000
		550	5.418	.002	
Katanga	8	unheated	5.448	.005	
		500	U <sub>3</sub> O <sub>8</sub>		
Katanga leached 40 hr. in 0.4 N H <sub>2</sub> SO <sub>4</sub>	5	550	5.435	.002	.013
Pied des Monts	7	unheated	5.468	.005	
		500	5.454	.002	
		600	5.450	.002	
Przibram	15	unheated	5.413	.005	.032
		540	5.381	.002	
Rix Athabaska	10	unheated	5.431	.002	.039
		550	5.392	.002	
Schmiedeberg	6	unheated	5.430	.005	.029
		500	5.401	.002	
Theano Point	6	unheated	5.405	.005	.015
		540	5.390	.002	
Wölsendorf	9	unheated	no pattern		
Wood Mine	8	unheated	5.448	.005	.035
		540	5.413	.002	
<i>Sedimentary pitchblendes</i>					
Big Indian	14	unheated	5.39	.01	.01
		540	5.38	.01	
Happy Jack	10	unheated	5.407	.01	
		535	U <sub>3</sub> O <sub>8</sub>		
Mi Vida	7	unheated	5.399	.005	.008
		540	5.391	.002	
Royal Claims	4	unheated	5.40	.01	.02
		440	5.38	.01	
Shinarump No. 3	7	unheated	5.399	.005	.008
		540	5.391	.002	

$UF_6$  and insolubility of  $UF_4$  in acid. One possible source of difficulty is the iron. The analysis reported 2.40%  $Fe_2O_3$ , which is rather high for uraninites. But even if all of this iron were  $Fe^{+2}$ , and all of it were oxidized by the ceric sulfate, and the actual amount of  $U^{+6}$  was precisely the quantity necessary to escape detection, there would still be only 4.3%  $UO_3$ , as compared to 66.1%  $UO_2$ . The 'm' value would be 2.058, and the Joachimsthal sample would still be far less oxidized than any uraninite heretofore reported. The annealing behavior seems to indicate that there are no interstitial oxygens to order or disorder. Although it is difficult to reconcile a completely unoxidized sample with the auto-oxidation hypothesis, the author feels compelled to accept the analysis as correct.

#### THE RÔLE OF LEAD

In Table 3, it was shown that the unit cell of pegmatitic uraninites could be calculated from the analyses, if one assumes that lead does not proxy for uranium in the uraninite structure. In itself, this is a powerful piece of evidence. It is reinforced by other, completely independent arguments.

For instance, Eckelmann and Kulp (1956) found that the various isotopic age determinations on samples of pitchblende from Lake Athabaska did not agree, and could be reconciled only if they assumed that the radiogenic lead was exsolved during two separate periods of thermal metamorphism.

Phair and Levine (1952) leached an oxidized pitchblende from Katanga, and a less oxidized sample from Great Bear Lake, in sulfuric acid of various concentrations ranging from 0.17 to 1.84 N. From time to time during the 144-hour run, solution was drawn off and analyzed, and finally the residual samples were analyzed. The results show a marked differential leaching of  $UO_3$  from  $UO_2$ . The effect is much stronger in the more oxidized sample. Aside from this, the results also show a significant differential leaching of  $UO_3$  and  $UO_2$  from lead, which becomes concentrated in the undissolved portion. Of course, it is possible for a solution, solid or otherwise, to be in equilibrium with another solution with a higher, or lower, lead-uranium ratio. Methylene iodide, for instance, containing little acetone, is in equilibrium with water containing much more; therefore water can be used to remove acetone selectively from methylene iodide, even though the acetone is in solution. The mere fact of differential leaching does not prove that the lead is not in solid solution. However, in the 144 hours of Phair and Levine's longest experiment, there could not be enough diffusion in the solid state to be detected. It must be concluded that the acid acted upon an inhomogeneous surface.

The behavior of certain specimens in this study provides additional evidence that lead does not proxy for uranium in uraninite. For instance, the Huggenäsken sample is  $(\text{U, Th, R.E.})\text{O}_{2.374}$ , but  $(\text{U, Th, R.E., Pb})\text{O}_{2.215}$ . On annealing, it decomposes into  $\text{U}_4\text{O}_9$  and a smaller amount of  $\text{U}_3\text{O}_8$ . It behaves like  $\text{UO}_{2.374}$  rather than  $\text{UO}_{2.215}$ . The 'p' subscript, rather than the 'q' subscript, also seems to control the extent of differential leaching of  $\text{UO}_3$  from  $\text{UO}_2$ . The 'q' value provides a clue to the original state of oxidation of the environment in which the uraninite crystallized, but the 'p' value more truly represents the present structural condition of the material.

Where, then, is the lead? These specimens give the cubic uraninite pattern. There are no lines left over. If the lead is not in the uraninite structure, it seems convenient to consign it to an amorphous phase, along with excess  $\text{UO}_3$  and other things that cannot be made to fit. In order to find if such an amorphous phase actually existed, a study was undertaken of the intensities of  $x$ -ray diffraction lines.

$\text{ThO}_2$  is isostructural with uraninite, and, since its unit cell is only a little larger, corresponding lines have Bragg angles close together. The reflectivity and absorption constants of the thorium and uranous ions are very similar.  $\text{ThO}_2$  gives extremely sharp diffraction lines. It is a very stable, refractory substance, and it seems reasonable to assume that it is entirely crystalline. If, then, it were mixed with a chemically equivalent amount of  $\text{UO}_2$ , and the  $\text{UO}_2$  were entirely crystalline, the  $x$ -ray diffractometer pattern should show pairs of peaks, close together, with almost identical areas under them. If the uraninite peak were less intense, it would indicate that the uraninite sample was not completely crystalline.

An amount of  $\text{ThO}_2$ , chemically equivalent to the uranium, thorium and rare earths, was weighed out and mixed with each analyzed sample. It was expected that the intensity of the uraninite peaks would be a definite proportion—say 85%—of the intensity of the equivalent  $\text{ThO}_2$  peaks, and it would therefore be possible to state that the uraninite was 85% crystalline. Unfortunately, this is not the case. The measured values are astonishingly low, on the order of 25 to 50%, even for pegmatitic crystals with good external faces and sharp  $x$ -ray patterns. Also, the values are not uniform from line to line, so that a single percentage quoted for the whole sample would have little meaning. There seems to be a definite pattern of non-uniformity. In sample after sample, the percentage for the (111) peak was up to half again as high as those for the (200) and (220) peaks. The ratios between the peaks for (200) and (220) were almost identical. The measured values are given in Table 8.

The 'pattern of non-uniformity' has some structural significance. The

TABLE 8. AREA UNDER DIFFRACTION PEAKS, % OF AREA UNDER EQUIVALENT  $\text{ThO}_2$  PEAK

Sample	111	200	220	311
Joachimsthal	48	35	36	
Hale's Quarry	54	37	34	34
Hale's Quarry, annealed	61	42	41	36
Gordonia (USNM)	34	28	26	15
Theano Point	42	33	31	
Sudbury	44	36	33	23
Great Bear Lake	56	50	51	
Elvestad	44	48	35	36
Pied des Monts	27	24	18	19
Spruce Pine	23	22	21	19
Happy Jack	15	16	14	
Mi Vida	17	13		
Boqueirao	75	57	52	55
Wilberforce	63	50	46	
Karelia	39	36	29	
Schmiedeberg	21	22	14	
Wood Mine	49	46	43	
Rix Athabaska	29	27	23	
Calculated (see text)	69	45	45	69

intensity of the uraninite lines has been reduced, and some reflections have been reduced more than others. There seems to have been some sort of destructive interference which is greater in some directions than in others. The author suggests that natural uraninite consists of a mosaic of crystallites in parallel position. These are separated along cube planes by 'spacers,' monomolecular layers of massicot (orthorhombic  $\text{PbO}$ ), the thickness of the layer being the ' $b$ ' axis of the unit cell. The  $x$ -ray reflections from two adjacent crystallites interfere destructively to different extents in different directions. The theoretical intensities calculated on these assumptions are given at the bottom of Table 8. There is good agreement with the highest of the measured intensities, such as those of the Hale's Quarry sample. The lower intensities of most of the samples can be attributed to a combination of this mechanism and the effect of amorphous material. The proposed hypothesis seems fully competent to explain the pattern of intensity variation.

Bystrom (1943) determined the structure of orthorhombic  $\text{PbO}$ . The cell dimensions are as follows:  $a_0 = 5.476 \text{ \AA}$ ,  $b_0 = 4.743$ ,  $c_0 = 5.876$ . Except for the  $b$  axis, it is similar in size to the  $\text{UO}_2$  cell, which is cubic with  $a_0 = 5.469 \text{ \AA}$ . If the lead positions only are considered, the cell of orthorhombic  $\text{PbO}$  is very close to being face-centered. The oxygens are arranged in puckered layers between the lead layers. The lead positions

in orthorhombic PbO are related to each other almost exactly as the uranium positions in  $\text{UO}_2$ , except that the 'b' axis of the PbO is compressed. It should therefore be possible to form oriented overgrowths of PbO on  $\text{UO}_2$ , such that the Pb positions on the (010) plane of the PbO fit into the U vacancies on a cube face of the  $\text{UO}_2$ . The overgrowth is only one cell thick in this case; the  $\text{UO}_2$  structure of the next crystallite fits on the 'back' of the layer in the same way, and continues, so that, among the (100) planes spaced 5.469 Å apart, there is one pair spaced only 4.743 Å apart, and reflections from one side of this 'spacer' are out of phase with those on the other side. Intensities calculated on this assumption agree satisfactorily with measured values, and, in combination with the other evidence, would seem to indicate very strongly that PbO is exsolved from the uraninite structure.

#### DIFFERENTIAL LEACHING

Some of the samples were ground and placed in 0.4 N  $\text{H}_2\text{SO}_4$  for 40 hours in an attempt to study the differential leaching of  $\text{U}^{+6}$  from  $\text{U}^{+4}$ . It was generally not possible to spare sufficient material from the analyzed sample itself; therefore, a two-gram sample was taken from the concentrate from which the analyzed sample was picked. The resulting samples were not pure, but it is reasonably certain that uraninite was the only uranium mineral to survive the leaching process. The comparison between the material before and after leaching will be made, not by means of absolute quantities or weight per cent, but by means of the state of oxidation, as shown by the 'm' formula subscript.

It was apparent, even without analyses, that the acid attacked some

TABLE 9. 'm' SUBSCRIPTS BEFORE AND AFTER LEACHING

Sample	Before	After	Substantial differential leaching
Gordonia	2.777	2.598	+
Katanga	2.742	2.296	+
Grafton	2.681	2.328	+
Przibram	2.610	2.325	+
Morogoro	2.529	2.432	+
Sudbury	2.389	2.330	+
Great Bear Lake	2.327	2.400	?
Wilberforce	2.337	2.372	-
Schmiedeberg	2.311	2.395	-
Wood Mine	2.282	2.234	-
Pied des Monts	2.219	2.277	-

samples to a far greater extent than others. In some cases, the solution showed the yellow color of uranyl ion as soon as the sample settled to the bottom of the beaker; in others, virtually colorless acid was decanted at the end of 40 hours. The 'm' subscripts before and after leaching are given in Table 9. The analyses of leached material were made by Jun Ito.

Generally, the results in Table 9 show that samples above the laboratory limit (2.32) lose a considerable amount of  $U^{+6}$ , so that they approach  $UO_{2.32}$ . They do not move far past this point. Samples below the laboratory limit showed little solubility and very little, if any, differential leaching. The results indicate that samples above the laboratory limit have disproportionated into a cubic phase at the laboratory limit, sparingly soluble in acid, and an amorphous phase, high in  $U^{+6}$  and readily soluble in dilute acid.

In some of the samples, the subscripts appear to increase slightly on leaching. Apparently, the samples were oxidized slightly at some stage of the procedure.

#### ACKNOWLEDGMENTS

This paper is a condensation of a Ph.D. thesis prepared under the direction of Prof. Clifford Frondel of the Department of Mineralogy and Petrography, Harvard University. It is also part of a program conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials, U. S. Atomic Energy Commission. The laboratory facilities were provided by contract AT(30-1)-1403 with the Division of Research, U. S. Atomic Energy Commission. The author also wishes to acknowledge the help and advice of Alice Weeks, Loren Stieff, Thomas Stern, George Phair, Michael Fleischer, Katherine Valentine, Henry Kramer, Harry Levine, and Alexander Sherwood of the U. S. Geological Survey; Professors Cornelius Hurlbut and Robert Garrels of Harvard; George Switzer, of the U. S. National Museum, who made a generous gift of chips of many of the analysed samples of uraninite; Richard Collette, Ivan Barnes, and Eleanor (Berman) Rothman of Harvard, and Jun Ito, of Harvard and the University of Tokyo.

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APPENDIX. ANALYSES OF URANINITE

This appendix contains a compilation of partial analyses of uraninite used in this study. It includes almost all available analyses starting with Hillebrand's, providing that the analyses distinguished between U<sup>4+</sup> and U<sup>6+</sup>. A few were omitted because the samples were stated to contain oxidized secondary uranium minerals. Some duplicate analyses were averaged, or in cases where one analysis was more detailed than another, they were combined, with averaging of comparable items. In the case of analyses performed especially for this study, the partial analysis includes all the information available.

	1	2	3	4	5	6	7	8	9
UO <sub>2</sub>	59.93	72.25	58.51	46.56	46.13	43.62	50.74	43.03	43.88
UO <sub>3</sub>	23.03	13.27	25.26	44.11	30.63	36.31	25.36	22.04	32.00
ThO <sub>2</sub>		7.20	7.81	3.04	1.56	2.80	0.47	8.43	8.98
R.E.									
PbO	3.08	4.35	0.70	4.53	9.04	8.41	10.06	8.58	9.46
CaO	0.11	0.18	0.84	0.23	0.37	0.30	0.77	0.37	0.36
Fe <sub>2</sub> O <sub>3</sub>	0.29	0.11			0.25	1.40	0.21	0.30	0.09
SiO <sub>2</sub>	0.16	0.03	2.79	0.13	0.22	0.81	0.38	0.29	0.53
	10	11	12	13	14	15	16	17	18
UO <sub>2</sub>	43.38	59.30	70.09	52.77	39.10	48.87	34.49	53.63	45.18
UO <sub>3</sub>	35.54	22.33	22.69	37.54	32.40	28.58	36.94	26.32	24.90
ThO <sub>2</sub>	6.63		0.20		10.60	2.15	0.15	3.22	11.40
R.E.	1.46		5.14	0.72	4.02	2.07	5.60	3.17	4.56
PbO	9.44	6.39	0.40	7.02	10.95	16.42	19.50	11.67	10.40
CaO	0.41	1.00	0.30	0.69	1.01	0.46	0.72	0.41	0.26
Fe <sub>2</sub> O <sub>3</sub>	0.32	0.21	0.10	0.15	0.43	0.30	Tr	0.17	0.58
SiO <sub>2</sub>	0.49	0.50		0.09	0.19	0.05		0.29	0.43
	19	20	21	22	23	24	25	26	27
UO <sub>2</sub>	47.5	55.40	41.94	23.10	28.38	75.41	52.28	42.49	59.13
UO <sub>3</sub>	40.8	22.23	49.21	63.00	61.12	14.83	31.08	20.58	22.08
ThO <sub>2</sub>		3.86		1.67	0.25	2.59	none	N.D.	9.09
R.E.	0.15	15.01				0.28			0.55
PbO	7.63	1.01	5.71	5.00	5.20	3.94	0.74	1.48	3.14
CaO	0.58		0.42	0.70	tr	0.30	2.22	2.40	0.08
Fe <sub>2</sub> O <sub>3</sub>	0.15	0.17	0.30	tr		0.53	1.21	1.93	1.21
SiO <sub>2</sub>	0.47	0.11	0.92			0.01	2.87	4.35	1.06
	28	29	30	31	32	33	34	35	36
UO <sub>2</sub>	44.18	23.07	19.89	44.17	74.75	76.12	64.8	52.3	26.0
UO <sub>3</sub>	26.80	40.60	46.75	20.89	14.65	15.67	14.3	27.8	58.7
ThO <sub>2</sub>	4.15	4.67	7.57	6.69	3.74	3.86			
R.E.	9.72	12.24	11.22	9.46	incl. in ThO <sub>2</sub>				
PbO	10.95	10.92	10.16	10.08	4.03	5.16	0.9	1.0	2.3
CaO	0.61	0.86		1.32			3.0	4.4	0.3
Fe <sub>2</sub> O	0.24	1.02	0.58	0.14			0.6	0.8	0.2
SiO <sub>2</sub>	0.50			0.46			3.0	2.5	0.3
	37	38	39	40	41	42	43	44	45
UO <sub>2</sub>	24.1	38.0	36.42	18.9	70.2	20.9	41.6	38.2	13.6
UO <sub>3</sub>	44.5	11.3	37.94	57.7	<0.1	41.7	28.1	45.4	58.0
ThO <sub>2</sub>		0.27	9.32	<0.03	0.08	9.18	1.53	0.4	2.93
R.E.		2.29	3.20	0.23	2.17	8.23	7.20	2.0	5.90
PbO	small	6.10	9.48	11.95	3.91	12.98	12.84	7.2	5.41
CaO	8.4	15.9	0.63	0.40	4.28	0.60	2.33	0.5	0.50
Fe <sub>2</sub> O <sub>3</sub>	3.4	0.5	1.86		2.40	0.65	0.42	0.7	1.01
SiO <sub>2</sub>	2.0	1.1	0.73	0.85	4.17	1.17	0.70		0.73

	46	47	48	49	50	51	52	53	54
UO <sub>2</sub>	31.86	31.37	36.43	40.19	36.92	44.77	48.69	42.27	41.20
UO <sub>3</sub>	58.68	51.95	29.72	29.27	36.51	29.99	49.03	27.00	40.92
ThO <sub>2</sub>									5.02
R.E.									1.57
PbO								13.02	8.50
CaO									0.18
Fe <sub>2</sub> O <sub>3</sub>									1.01
SiO <sub>2</sub>									0.77
	55	56	57	58	59	60	61	62	63
UO <sub>2</sub>	20.4	48.7	67.13	73.59	44.0	39.5	32.1	60.7	51.1
UO <sub>3</sub>	43.2	25.0	23.59	16.62	23.7	27.9	53.2	25.3	24.4
ThO <sub>2</sub>			3.80	3.78	13.5	13.4	<0.01		<0.01
R.E.	0.53		0.36	0.36	1.9	0.7	3.3		4.1
PbO	5.25	6.4	3.65	3.63	9.47	9.47	6.01	0.82	3.08
CaO	13.24	5.1	0.31	0.31	0.02	0.02	0.23	0.01	0.54
Fe <sub>2</sub> O <sub>3</sub>		0.8	1.00	1.28				2.49	
SiO <sub>2</sub>	2.60	1.4							
			64					U <sup>+6</sup>	
			UO <sub>2</sub>	38.71		Analysis		Total U	
			UO <sub>3</sub>	41.33					
			ThO <sub>2</sub>	5.03		65		17.4%	
			R.E.	2.61		66		20.2	
			PbO	8.39		67		40.2	
			CaO	0.35		68		60.0	
			Fe <sub>2</sub> O <sub>3</sub>	1.24		69		78.5	
			SiO <sub>2</sub>	0.76		70		85.0	

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