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THE ROLE OF LEAD AND EXCESS OXYGEN IN URANINITE*

Robert Morris Berman, 1929-

UNITED STATES GEOLOGICAL SURVEY

OPEN-FILE RELEASE

57-11

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*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

c1957

"The ancient philosophers, who considered our globe as the center of the material universe; and the sun, on the contrary, merely as a planet destined, like the others, to a periodical circumvolution round the earth, flattered themselves that they had discovered a great mystery of Nature, in the agreement of the seven celestial bodies, which they assumed for planets, with the seven metals known in those times . In consequence of the various hypotheses which they founded on this supposed mystery, they alloted to each metal a certain planet, by whose astral effluvia its generation and maturatio were to be promoted. In like manner, they took from these planets their names and symbols, to designate the metals subordinated to them. But as the above number of metals has long since been increased by later researches, and as the discovery of new planets has not kept pace with that of metals, the metals newly found out have been deprived of the honour of receiving their names from planets...... Of late, seventeen metallic substances have been acknowledged as distinct metals, each of a nature peculiar to itself. The design of this essay is to add one to that number."

Klaproth's account of the discovery and
naming of Uranium, 1792. Translated
anonymously into English, 1801.

THE ROLE OF LEAD AND EXCESS OXYGEN IN URANINITE

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ABSTRACT

Analysed samples of uraninite were x-rayed, annealed by heating to 550° and 900° 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 oxygen ions 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_2 ratio; for high ThO_2 and low rare earths, the interstitial oxygens are completely random. 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 the equilibrium point determined by the R.E./ThO_2 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_2 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_3O_8, although they are cubic. They may have crystallized as U_3O_8, then decomposed to the cubic phase and an amorphous phase. This suggests that the stability range of U_3O_8 includes only very exceptional natural conditions.

Vegard's Law calculations, studies of zoning in crystals, differential leaching, polished section textures, and other lines of evidence indicate that lead, including radiogenic lead, is exsolved from uraninite. A study of x-ray line 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 reflections.

CHAPTER I

THE PROBLEM

Uraninite has played a spectacular role in the history of science. From the discovery of uranium itself to the most recent work on age determination, scientists have used the mineral uraninite, or its varietal form pitchblende, as the starting place for many investigations. It is no exaggeration to say that these have affected every branch of science and altered the very course of civilization.

Pitchblende had long been known from the mines of Joachimsthal and Johanngeorgenstadt, in the Erzgebirge, which have been operated since medieval times for silver. The name 'Pechblende', 'blind pitch', is a miner's term, referring to its pitchy lustre and the fact that it yielded no silver. In his systematic mineralogy, Werner described it under iron ores as 'Eisenpecherz (Ferrum ochraceum piceum)'.

In 1789, Martin Klaproth subjected a sample of pitchblende from Johanngeorgenstadt the qualitative analytical procedures of his day. He dissolved the sample in aqua regia and added ammonia, precipitating what is now known to be a mixture of uranium trioxide hydrates. He subjected this bright orange precipitate to a variety of bead tests, obtaining results inconsistent with any known element. He concluded that the substance was new to science, and that the most important constituent of pitchblende was a new element, which he named 'Uran'. However, he thought that UO_2, which he obtained by reduction with carbon, was the free form of the new element; this error persisted in the chemical literature for fifty years until Péligot prepared uranium metal in 1842.

In 1868, J. N. Lockyer, studying the photosphere of the sun spectroscopically, discovered a yellow line which could not be identified with any element known to occur on earth. He named the new element 'helium'. An intensive search for terrestrial helium was finally rewarded with success in 1895, when Ramsay discovered it in Norwegian uraninite. Several years before, Hillebrand (1891) had noted that some uraninite crystals effervesced while dissolving in acid; he believed the gas to be nitrogen. Ramsay showed that it was, to use his word, the "hypothetical" element helium. A somewhat similar case is plutonium, which was found in nature as minute traces in uraninite, after being created artificially in atomic piles.

In 1896, Becquerel discovered radioactivity while investigating the phosphorescence of potassium uranyl sulfate. In a systematic investigation of the periodic table, the Curies found that the radioactivity of uranium minerals, among them uraninite, was many times higher than could be explained by their known constituents. Polonium, radium and radon were isolated and identified from residues of the mill at Joachimsthal.

As the experimental and theoretical investigation of radioactivity progressed, the question arose as to the end product of the radioactive disintegration. Since geologic time is not available for laboratory experiments, it was necessary to have recourse to natural uraninite. Boltwood (1907) studied the available analyses of uraninite and showed conclusively that the end product was lead, rather than barium or bismuth, which had been mentioned as possibilities.

In connection with his study of the radioactive disintegration series, Soddy (1914) proposed the concept of isotopes, as well as the name. He also proposed a crucial experiment for his isotope hypothesis; the lead resulting from the disintegration of uranium should have an atomic weight of 206.0 rather than the accepted value of 207.2 for ordinary lead. Therefore, the lead extracted from uraninite should be significantly lighter than 'common' lead. This was brilliantly confirmed by Richards (1914) and Honigschmid (1914). The first use of radioactive isotopes as tracers was reported by von Hevesy in 1920. He used Radium D, or in modern notation Pb^{210}, to 'label' lead in a study of the diffusion of molten lead through itself. Later he used 'labelled' lead to study the up-take of lead by plants. The Pb^{210} was obtained from the only convenient source, as an inseparable part of the lead extracted from uranium minerals.

Lastly, there are the methods of geologic age determination, which depend on the decay of radioactive elements. It is generally agreed that the determinations on uraninite are by far the most reliable, and provide standards by which new determinations and methods can be judged.

Some of the ablest scientists in history have studied uraninite; and it may seem presumptuous to undertake still another investigation. However, there are still many unsolved problems associated with this mineral, including some rather pedestrian ones.

In the first place, the very formula of the mineral is still open to question. All published analyses of uraninite show a content of U^{6} ranging from 10 to 80% of the total uranium. This has lead to a number of proposed formulae for uraninite such as $(UO_2)_3(UO_3)_2$, which was suggested by Comstock in 1880, and supported by Blomstrand (1884b) and

Schoep (1923). Blomstrand (1884a) also proposed that lead was an essential constituent of certain uraninites, suggesting the formula $U_7Pb(UO_6)_5$. U_3O_7, U_4O_9 and U_2O_5 have also been proposed. Kirsch (1925) was so convinced that oxygen in excess of two atoms per uranium atom was an essential constituent, that he postulated an unoxidized mineral, which he named "ulrichite". Well-crystallized uraninites which showed excess oxygen on analysis were described by him as "uraninite, pseudomorphous after ulrichite". As late as 1951, Katz and Rabinowitch could write, for the presumably authoritative National Nuclear Energy Series, that uraninites were oxidized UO_2, and pitchblendes were U_3O_8. This is not true; all pitchblendes which give discernible x-ray patterns give the cubic UO_2 pattern. U_3O_8 has not been reported as occurring naturally.

Many workers believe that vein and sedimentary pitchblendes are more oxidized than pegmatitic uraninites. This may be true, in a general way; however, it will be shown that both types cover the entire range. The least oxidized sample to be discussed comes from the veins of Joachimsthal.

In addition to varying widely in oxygen content, uraninite varies in composition by including different amounts, up to several percent, of thorium, the rare earths, lead, calcium and vanadium. The extent to which these affect the properties of the mineral, the amount which can be accomodated, and the positions they occupy in the crystal structure (if they are indeed in solid solution) are problems which should be explored.

Uraninite exhibits an extraordinarily great variation in unit cell size. Since it also varies greatly in composition, workers such as

Wasserstein (1954) and Brooker and Nuffield (1953) have proceeded on the assumption that uraninite follows Vegard's Law. This law states that the unit cell size of an isometric solid solution varies as a straight line function of composition, expressed molecularly. These writers assumed that they could substitute an x-ray measurement for the long and difficult chemical analysis of uraninite. Unfortunately, the data were not available to support this assumption. Up to the beginning of this investigation, no one had published the unit cell size of an analysed natural uraninite, or the complete analysis of an x-rayed one. Only the values for synthetic materials were available. It will be shown that the unit cell size depends on other factors in addition to the composition.

Wasserstein (1954) set up three types of uraninite, alpha, beta and gamma, maintaining that the relationship between unit cell size and composition is different in the three types. This work will also divide uraninites into three types, by mode of occurrence; pegmatitic uraninites, vein pitchblendes and sedimentary occurrences. These are not strictly Wasserstein's classes, but certainly each one has its own set of relationships between composition and unit cell size. In his short note, Wasserstein raised other issues, concerning the valence of radiogenic lead, and the original state of oxidation of crystallizing uraninite. These problems need to be re-examined in the light of additional data.

Brooker and Nuffield (1952) have also made a contribution which includes both valuable information and perplexing problems. They heated pitchblendes in air and in evacuated silica tubes. They found that the cell size decreased and the x-ray lines sharpened when the sample was heated in the evacuated tubes at intermediate temperatures. At higher temperatures, the sample decomposed in various ways, depending apparently upon the composition. One of the products could not be identified.

In the laboratory, UO_2 can be oxidized by heating in the atmosphere until $UO_{2.32}$ is obtained. The series is continuous. Any attempt to oxidize beyond $UO_{2.32}$, however, produces phases related to U_3O_8. How is it possible, then, to account for the cubic uraninites with compositions ranging up to $UO_{2.8}$? One suggestion is that the excess oxygen was contributed by the process of auto-oxidation, in which UO_2, by radioactive disintegration, turns to PbO and an extra oxygen, which is available to oxidize additional UO_2 to UO_3. This hypothesis seems plausible, but it has not been sufficiently tested by application to specific analyses of available samples.

There are many other problems still unsolved; whether certain pitchblendes with weak x-ray patterns can correctly be termed metamict; whether some of the excess U^{+6} is present as an amorphous phase; why U_3O_8, which is so easily formed under laboratory conditions, has not been reported in nature.

In this thesis, thirty-two analysed uraninite samples and synthetic UO_2 will be studied in an attempt to clarify, if not to solve, some of these problems, for it is clear that additional data is badly needed.

The author wishes to acknowledge the help and advice, firstly, of Prof. Clifford Frondel, his thesis advisor; of Mrs. Alice Weeks, who directed the work as part of a project for the United States Geological

Survey; of George Switzer, of the United States National Museum, who lent chips from a sizeable proportion of the reliably analysed samples of the literature; of the chemists, Harry Kramer of the U. S. Geological Survey and Jun Ito of the University of Tokyo and Harvard; of the spectroscopist, Katherine Valentine of the U. S. Geological Survey; of Michael Fleischer, Loren Stieff, Thomas Stern and George Phair of the U. S. Geological Survey; of Prof. Robert Garrels and Prof. Cornelius Hurlbut; and of Richard Collette and Ivan Barnes, without whose help and experience the author would still be trying to get his inert-atmosphere furnace to work.

THIS STUDY IS PART OF A PROGRAM CONDUCTED BY THE U.S. GEOLOGICAL SURVEY ON BEHALF OF THE DIVISION OF RAW MATERIALS, OF THE U.S. ATOMIC ENERGY COMMISSION.

CHAPTER 2

THE URANIUM-OXYGEN SYSTEM

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 chapter is intended as a partial synthesis of the data available in the chemical literature on this system.

U-UO

Uranium metal was first prepared by Péligot (1842) who reduced UCl_4 with potassium metal. Previously, it was believed that UO_2, which had been prepared by Klaproth, was the native element.

There are three different forms of uranium metal in the solid state; an α-form, which is orthorhombic, a tetragonal β-form and a cubic γ-form. The transitions are gradual over several degrees, occurring at different temperatures on heating and on cooling, and affected not only by impurities but also by the past history of the working of the metal. In α-extruded uranium, the transitions are somewhat delayed, both on heating and on cooling. In γ-extruded uranium, they begin without delay.

Katz and Rabinowitch (1952) give a table of determinations of the transition points. The results of Dahl and Van Dusen (1947) are close to the average and are reproduced in table 1.

Table 1. Transition points of Uranium (Dahl and Van Dusen, 1947)

$\alpha \rightarrow \beta$	667°C.
$\beta \rightarrow \gamma$	772
$\gamma \rightarrow \beta$	764
$\beta \rightarrow \alpha$	645

A wide variety of values have been quoted for the melting point. Perhaps the most reliable determination is that of Dahl and Cleves (1949) at the National Bureau of Standards. Their value is 1133 ± 2°C.

-uranium is orthorhombic. It is one of the few atypical metals which do not crystallize in cubic or hexagonal closest packing. The lattice parameters are as follows:

Table 2. Unit Cell Dimensions of α-uranium

a_o	2.8482 A. ± 0.01%
b_o	5.8565
c_o	4.9476

The specific gravity of α-uranium is 19.050.

Structures comparable to the β-form of uranium can be studied at room temperature by means of uranium-chromium or uranium-molybdenum alloys quenched from the β-range. Pure β-uranium cannot be quenched. The structure remained unsolved, however, until Thewlis (1952) succeeded in taking a powder photograph of un-alloyed uranium at 720°C. He determined that the β-form of uranium is tetragonal, with $a_o = 10.759$ A. ± 0.001, $c_o = 5.656$A. ± 0.001.

The density of β-uranium is 18.11 at 720°C., and the unit cell contains 30 atoms.

Table 3. X-ray powder diffraction patterns of α and β-uranium.

α-uranium (Wilson, 1933)

d (A.)	I
2.54	75
2.44	50
2.25	100
1.76	100
1.52	75
1.43	50
1.38	50
1.24	75
1.15	50
1.11	50
1.01	25

β-uranium at 720° (Thewlis, 1952)

d (A.)	I	hkl
2.827	10	002
2.696	4	400
2.649	6	112
2.612	70	410
2.536	53	330
2.500	41	202
2.438	48	212
2.370	100	411
2.313	58	331
2.270	20	222
2.175	19	312
1.712	11	432
1.526	45	413
1.513	40	333,602
1.502	42	612

γ-uranium was studied in a heating camera at 785°C. by a group at Battelle Institute, reported by Katz and Rabinowitch (1951). This form of uranium has a body-centered cubic lattice with a cell edge $a_o \cong$ 3.48 A. at 785°C. Like β-uranium, it cannot be quenched to room temperature if pure.

Solid uranium metal tolerates only infinitesimal amounts of oxygen in solid solution.

UO

UO forms as a gray coating on the surface of uranium metal on prolonged heating at very low pressures of oxygen, on the order of 10^{-9} atmospheres. UO_2 is invariably present, but under prolonged heating in "vacuum", the proportion of UO to UO_2 increases. A preparation that may have been as much as one-third UO was prepared by heating a U-UO powder mixture to 1900°C.

UO has an NaCl-type cubic lattice with a unit cell edge $a_o = 4.91$ A. The extent of variation of oxygen content in this phase is unknown. All data on UO is from Katz and Rabinowitch (1951).

Bivalent U has not been reported in nature, although there are environments, such as those of meteorites and volcanic gases, which are probably sufficiently reducing. However, UO is isostructural and probably isomorphous with CaO and MgO; if bivalent U occurred, it probably would be camouflaged as Ca or Mg.

U_3O_4 $(UO_{1.33})$

Nordenskiold (1879) described a mineral, which he named "cleveite", occurring as lustrous black cubes in Norwegian pegmatites. He advanced the hypothesis, on morphological grounds, that it was a member of the spinel group, with the formula U_3O_4. It has since been shown that cleveite is synonymous with uraninite.

U_4O_7 $(UO_{1.75})$

U_4O_7 was announced by Zachariasen in a still-classified report written in 1947. Katz and Zachariasen (1951) report that he found a cubic phase intermixed with UO_2, but with the somewhat larger cell size $a_o = 5.466$ A. Zachariasen called it $UO_{1.75}$ on the basis of extrapolation of the cell size from UO_2. Katz discusses the possibility of a continuous series between $UO_{1.75}$ and UO_2 in his book (1951). 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.

α-UO_2

UO_2 is usually obtained as a fine, brownish-black powder by reducing U_3O_8 with hydrogen or ammonia. Ebelman (1843) obtained visible crystals by fluxing UO_2SO_4 in $MgCl_2$ in a covered crucible. A variation of this method was used bo produce the synthetic sample discussed later.

α-UO_2 was found by Goldschmidt and Thomassen (1923) to have a fluorite-type structure. Rundle (1948) gives the cell constant as $a_o = 5.4692 \pm 0.0005$ A. at 25° C. The calculated specific gravity is 10.96. UO_2 takes up additional oxygen without changing its structure when heated to 200-300°C. in air. This oxidation has been studied by Biltz and Muller (1927), Grønvold and Haraldsen (1948), Jolibois (1947) and many others, but the most complete and reliable data was 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. This 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. In particular, there will be a discussion of natural uraninites above the laboratory limit. As all experimentation to date has been at pressures of virtually one atmosphere, this is incorporated into the definition. As the series moves from the mid-point toward thoria, the laboratory limit falls from 2.34 to 2.0.

The results of an analysis of $(U_{0.5}Th_{0.5})O_{2.34}$ would normally be reported as follows.

Table 4. Hypothetical analysis of $(U_{0.5}Th_{0.5})O_{2.34}$

UO_2	16.87% wt.
UO_3	34.67
ThO_2	48.46
	100.00

If the Th ions are assumed to be in the +4 oxidation state, the uranium must be present as $UO_{2.68}$. However, the form $(U_{0.5}X_{0.5})O_{2.34}$ expresses more accurately the structural condition of the material.

The effect of increased pressure on the oxidation limit has not been studied. However, 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 stmospheric 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 ~~1.32~~ 2.64 A. wide, just the diameter of the oxygen ion, at the $(^1/_2,0,0)$ and $(^1/_2,^1/_2,^1/_2)$ positions. If all these holes could be filled, the composition would be $UO_{3.75}$. 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 α-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. The bonding to U^{+6} is highly directional in character in many compounds. Zachariasen (1954) showed that, of four coordinating oxygens, one pair tends to move in closer than the other. He also showed, however, that this effect was highly variable from compound to compound, so that it was impossible to assign a generally applicable U-O distance for the uranyl ion. In any case, for UO_2, the effect is randomized so that the material remains isometric. Alberman and Anderson found that, within the limits of error of the measurement, the dimensions of the unit cell did not change 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 shows that the mean molar volume does 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. (See chapter 5)

Under stmospheric 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. The diffraction lines became doublets, except for the 111, 222 and 333 reflections, and the split gradually widened as oxidation proceeded, until the laboratory limit was reached. The lattice parameters of $UO_{2.303}$ are given in table 6. The most easily distinguishable lines, in addition to the regular UO_2 pattern, are given in Table 5.

On heating above 300°C., samples less oxidized than $UO_{2.25}$ decomposed 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", a device which measures the weight of a sample as it is heated in air. As oxygen is absorbed, the sample gains weight. 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. Jolibois obtained an X-ray pattern of the $UO_{2.33}$ and found that it was tetragonal. He concluded that it was a new compound with the stoichiometric composition U_3O_7 , and that it forms a continuous series with UO_2. The observations are not in conflict with the data given by Alberman and Anderson on their tetragonal phase. There is no doubt that the two phases are identical. Since Jolibois gives the spacings of his powder pattern, and Alberman and Anderson do not, the data given in table 5 are for Jolibois' U_3O_7.

Table 5. X-ray diffraction patterns of UO_2, U_4O_9 and the lines of the tetragonal phase in addition to the regular UO_2 pattern. In Angstroms.

d UO_2	hkl	d U_4O_9	I	add'l lines of tetr. phase d	hkl
3.157	111	3.137	10		
2.735	200	2.717	5	2.654	002
1.934	220	1.922	6		
1.649	311	1.639	4	1.609	113
1.579	222	1.569	3		
1.367	400	1.358	2	1.331	004
1.255	331	1.247	1		
1.223	420	1.215	2	1.197	204
1.052	333	1.045	2		
.9667	440				
.9244	531				
.9115	600				
.8647	620				
.8340	533				
.8245	622				

DELTA PHASE

Grønvald and Haraldsen (1948) found that UO_2 oxidizes continuously to $UO_{2.34}$ at 150°C. in air. They noted that splitting of the lines associated with the formation of the tetrogonal phase. When they raised this $UO_{2.34}$ to 200-250°C., they observed a decrease in density and in axial ratio. They names this product the "delta phase". 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 of the spectrum in which a hitherto unknown stability field could be fitted. The range of homogeneity seems narrow not only with respect to composition but to temperature as well. The phase does not form below 200° and it decomposes at 270°.

It is not clear, in the original paper, just how the authors ascertained that further oxidation took place on raising the temperature. It seems strange that Alberman and Anderson, who did a large part of their work between 200 and 250°C., did not find this phase. The following table compares the cell dimensions of Alberman's tetragonal phase at $UO_{2.303}$ and Grønvold's delta phase.

Table 6. Lattice parameters of tetragonal phases.

	a_0	c_0	(A.)
$UO_{2.303}$	5.396	5.564	
Delta Phase	5.37	5.54	

The two are almost certainly the same phase. Grønvold probably did not observe additional oxidation.

β-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 $a_o = 5.435$ A. 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.

Unfortunately, it has not been possible to obtain the new phase pure by heating material with a composition of precisely $UO_{2.25}$. The reasons for this failure are not clear, but there is little doubt that the compositions of the new phase is $UO_{2.25}$.

Alberman and Anderson called it "β-UO_2" in their original paper, and later (1954) refer to it as U_4O_9. In their opinion, it is an ordered phase, with the interstitial oxygens occupying the $(^1/_2, ^1/_2, ^1/_2)$ 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. U_4O_9 has the U_4O_8 unit cell of UO_2 with an extra oxygen in the hole in the middle.

UNKNOWN OXIDE X

Brooker and Nuffield (1952) heated natural pitchblende samples to 1000° in evacuated silica tubes. The samples that fell between UO_2 and $UO_{2.25}$ decomposed into UO_2 and "unknown oxide X"; those between $UO_{2.25}$ and $UO_{2.67}$, into "oxide X" and U_3O_8. The unknown oxide X is of course U_4O_9. The x-ray patterns reproduced with the article show the U_4O_9 lines, at a slightly higher Bragg angle than each of the UO_2 lines.

In their attempt to identify the unknown phase, Brooker and Nuffield studied the paper of Alberman and Anderson, and proved experimentally the fact that the tetragonal form was identical to Jolibois' U_3O_7, but that their phase was equivalent to neither. This is not surprising; the tetragonal form is unstable above 300°, and phase X was produced at 1000°.

U_2O_5

U_2O_5 was first described by Péligot (1842). It was also reported by Oeschsner de Coninck (1903), Schwartz (1920), Lebeau (1922) and many others, but the most modern and complete work was done by Rundle, Baenziger, Wilson and McDonald (1948). Most of these workers decomposed compounds such as UO_2Cl_2 at temperatures around 900°C. They obtained a product that would absorb additional oxygen to become U_3O_8. Rundle et al. prepared their samples by mixing appropriate amounts of UO_2 and U_3O_8, packing the mixture in a silica capillary and heating. He then x-rayed the capillary to find if he had a single orthorhombic phase with spacings slightly larger than U_3O_8. Hoekstra et al. (1955) point out, however, that it is very hard to prevent additional oxidation from absorbed and entrapped oxygen after the powders are mixed. The state of oxidation can be determined accurately only by chemical analysis after the heating run. Hoekstra is of the opinion that U_2O_5 probably does not exist, and that most of the reported occurrences are the phase he describes as $UO_{2.6}$.

$UO_{2.6}$

Hoekstra, Siegel, Fuchs and Katz (1955) heated mixtures of UO_2

and U_3O_8 of appropriate composition to 1200°C. for several weeks in evacuated glass tubes, then x-rayed and analysed the products. They found no trace of the fluorite-type pattern above $UO_{2.56}$. Instead, between $UO_{2.56}$ and $UO_{2.65}$, they found a single orthorhombic phase, with the lattice constants $a_o = 6.751$ A., $b_o = 31.76$ A., $c_o = 8.286$ A. They refer to the new product as the $UO_{2.6}$ phase. The cell contains 32 uranium atoms, and the calculated specific gravity is 8.38.

Single crystals of $UO_{2.64}$ were prepared by heating U_3O_8 in air to 1100-1500°C. At the higher temperatures, some volatilization occurred with condensation at the cooler part of the tube. (~1100°C.)

The upper limit of the $UO_{2.6}$ phase is set at $UO_{2.65}$. "Above this", say the authors, "x-ray patterns show line shifts and intensity changes...suggesting that this represents the transitional region to U_3O_8."

Milne (1951) reports that his single crystal study of U_3O_8 showed two slightly different hexagonal unit cells, which he describes as interpenetrating. Milne's hypothesis is not representative of nature. Hoekstra et al. point out that he almost certainly had a mixture of the $UO_{2.6}$ phase and U_3O_8. However, the crystals must have been parallel intergrowths, and this indicates a two-phase region in which both are stable, rather than a continuous transition between $UO_{2.6}$ and U_3O_8. It should be noted that Milne's material had stood for a while.

U_3O_8

U_3O_8 is the uranium oxide in stable equilibrium with the atmosphere at temperatures between 500° and 1100°C. All lower oxides can be converted to precisely stoichiometric U_3O_8 for weighing, simply by heating over a Bunsen burner in an open crucible.

At room temperature, U_3O_8 is orthorhombic, with the following parameters; a_o= 6.717 A., b_o= 11.97 A., c_o= 4.150 A (Hoekstra et al., 1955) The calculated density is 8.39. The x-ray powder diffraction pattern is given in table 7.

The ratio between the axes b/a is 1.782. As the temperature is raised, this ratio decreases until it reaches $\sqrt{3}$ (1.732) at about 400°C. At this point, U_3O_8 becomes hexagonal, and it remains so at higher temperatures. Above 1100°, U_3O_8 begins to lose oxygen; at 2000°C., UO_2 is stable in the atmosphere.

Table 7. X-ray powder diffraction patters of U_3O_8

(General Electric Co., cited in A.S.TM. Card File)

d(A.)	I	d(A.)	I
5.87	10	1.77	60
4.15	100	1.71	20
3.43	100	1.66	10
3.36	50	1.58	30
2.64	90	1.55	10
2.61	40	1.44	20
2.07	40	1.42	30
1.99	20	1.33	10
1.95	40	1.32	20
1.80	20	1.30	20

β-U_3O_8

As mentioned above, Hoekstra et al. (1955) prepared single crystals of $UO_{2.64}$ by volatilizing U_3O_8 at high temperatures. They attempted to prepare single crystals of U_3O_8 by heating the crystals of $UO_{2.64}$ in air to the much lower temperature of 750°. They found that the product did not always give the conventional U_3O_8 pattern; occasionally, they obtained an orthorhombic phase with the cell dimensions a_o = 7.06 A., b_o = 11.42 A., and c_o = 8.29 A. The calculated density is 8.38. They named it β-U_3O_8.

This phase is apparently metastable. It disappeared on reheating the samples to 750°. It could not be obtained simply by heating U_3O_8.

U_3O_8-UO_3

Hexagonal products intermediate between U_3O_8 and UO_3 can be obtained by oxidation of U_3O_8 at 450-600°C. under the pressure of 20-30 atmospheres of oxygen. Their structure is apparently related to U_3O_8, with $b/a = \sqrt{3}$.

The best guide to the complete and utter confusion existing at UO_3 is a paper by Pério (1953). Little more than a list of the various phases can be offered here. First, there is amorphous UO_3, which is most easily prepared by heating $UO_4{:}2H_2O$. Then there is the α-UO_3 of Zachariasen (1948). This was obtained by heating the amorphous phase to 500°C. for 8 hours under a pressure of 20 atmospheres of oxygen. It is hexagonal, with $a_o = 3.963 \pm 0.004$ A., and $c_o = 4.160 \pm 0.008$ A. Pério obtained this phase, and maintains that it is stoichiometric U_6O_{17}, thus adding another interesting ratio to our collection. This phase is listed by Katz and Rabinowitch as UO_3(I).

Next there is the so-called "Mallinkrodt" oxide, produced by the Mallinkrodt Chemical Co. by ignition of uranyl nitrate. This is Katz and Rabinowitch's UO_3(III) and Pério's UO_3(I). It is orthorhombic, with the cell dimensions a_o= 13.00 A., b_o= 10.72 A., c_o= 7.51 A. It is bright yellow in color. Its powder pattern is given in table [illegible]. After the Mallinkrodt oxide has stood for two years in air, Pério found, the lines of a tetragonal phase appear, which Pério called UO_3 (II). The lattice dimensions are a_o= 5.11 A., c_o= 5.83 A. Its identifiable lines are given in Table 8. When amorphous UO_3 is heated to 500-700° in oxygen under pressure, a brick-red phase of unknown structure appears. This is Pério's UO_3(III) and may be Katz and Rabinowitch's UO_3(II). Katz and Rabinowitch mention the possibility of two more phases, without giving details. All of these phases break down to U_3O_8 and oxygen when heated above 400° in the atmosphere.

Zachariasen (1954) showed that it was impossible to give any one value for the length of the U-O bond in the uranyl ion; it varies over a considerable range, in an inverse relation to bond strength. This is undoubtedly one of the factors which make the chemistry of uranium so complicated. But there are others; uranium is a small, heavy ion, and it is difficult, compared to other elements, to apply enough kinetic energy to jar it out of its metastable positions. Its envelope of 92 electrons has a complicated internal structure, giving many energy levels close together. In crystals, where each of these energy levels is broadened into a band, it can be seen that a wide variety of stable and near-stable structures is possible. In some of the investigations of solid phases in uranium chemistry, it seemed that every run produced a new phase, and it was impossible to construct any sort of coherent picture.

Table 8. Powder patterns of UO_3(I) and (II)(Pério, 1953)

UO_3(I, Pério)		UO_3(II, Pério)	
d (A.)	hkl	d (A.)	hkl
6.49	200	5.11	100
4.97	120	3.42	002
4.37	021	2.86	102
3.45	130	2.56	200
3.25	202,400	2.47	112
3.06	321,022	2.04	202
3.02	122		
2.79	420		
2.74	312		
2.62	140		
2.38	113		
2.19	341		
2.10	150		
2.01	620		

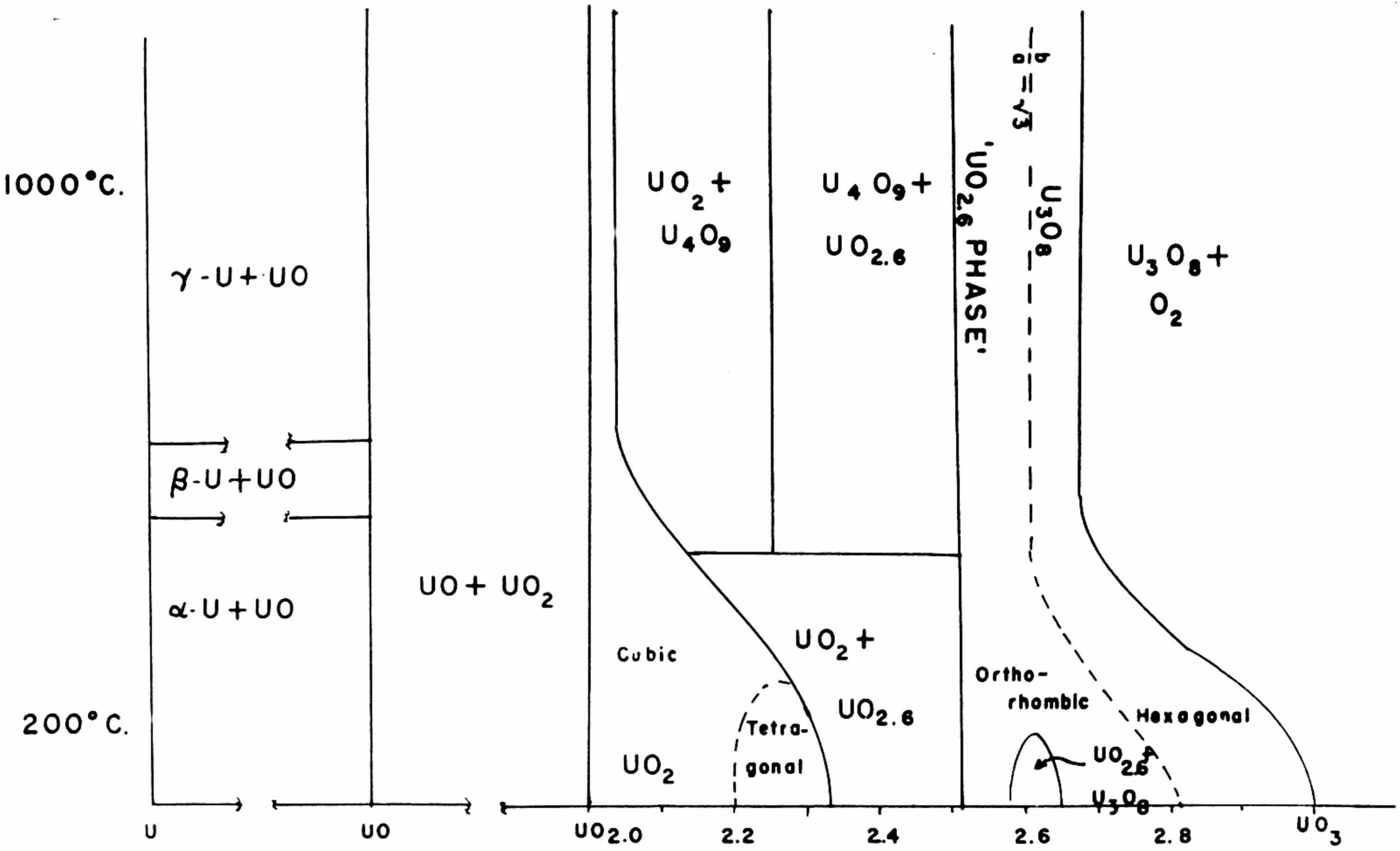

Figure 1. Tentative phase diagram of the U-O system at one atmosphere.

CHAPTER 3

URANINITE AS A MINERAL

Uraninite is a black mineral with pitchy to earthy lustre. Its hardness is 5-6, and the specific gravity ranges from 6.5 to 10.5. It belongs to the isometric system, and is occasionally found in euhedral crystals in pegmatites. The crystal forms most commonly seen are the cube, octahedron and dodecahedron. Uraninite is generally opaque, although occasionally weak brown internal reflections can be seen in polished sections. It has no cleavage, and exhibits a conchoidal fracture. It is rather brittle. Uraninite from veins (pitchblende) sometimes occurs in botryoidal aggregates. Uraninite is soluble in warmed strong acids. In dilute hydrochloric and sulfuric acid, hexavalent uranium may be differentially leached from tetravalent uranium. UO_2 itself is practically insoluble in cold, dilute, non-oxidizing acids.

The most striking diagnostic characteristic of uraninite is its intense radioactivity. Except for some radiocolloid barite, it is the most radioactive mineral.

Chemically, uraninite is UO_2 with varying amounts of additional oxygen. Lead is invariably present, from the disintegration of uranium if from no other source. The typical uraninite might contain 5% lead, although, of course, it is difficult to generalize. In pegmatitic uraninites, up to 13.5% ThO_2 has been reported (anal.65, appendix) and up to 15.01% rare earth oxides (anal.20). Vein and sedimentary pitchblendes contain only trace amounts of ThO_2 and rare earths, but unlike the pegmatitic uraninites, they may contain several percent CaO. In the laboratory, it is possible to make a complete solid solution series between UO_2 and ThO_2, and also between UO_2 and CeO_2; but in nature, the series do not seem to be complete.

The assortment of lustres and textures exhibited by uraninite are rather similar to many exhibited by ordinary coal, and it may be possible to describe them more explicitly by using the terms devised by the coal petrologists for megascopic textures of coal. The four most important terms are defined by Cady (1939) as follows:

Fusain is mineral charcoal. It is dull, soft, and porous.

Vitrain is highly lustrous, vitreous, "jet-like" coal, with a conchoidal fracture. In distinction to fusain, it is a "bright" coal.

Clarain is also a "bright" coal, with a silky lustre. Generally, good conchoidal fractures do not develop.

Durain is a "dull" coal, but in contrast to fusain, it is hard and compact. It breaks unevenly and has a lumpy or matte surface.

In the section in which the specimens used in this study are described, terms such as "vitrain-like" and "durain-like" will be used. It is hoped that these terms will make the descriptions not only shorter and less repetitious, but more nearly exact.

SPECIFIC GRAVITY

Specific gravities of the samples studied were determined on the Berman Balance, using the basket attachment where necessary. The pegmatitic uraninites have specific gravities ranging from 7.32 to 10.25. Vein pitchblendes cover the much smaller range between 6.77 and 7.62. The distribution shows a strong "cluster" in the vicinity of 7.3.

Sedimentary pitchblendes were generally too porous to measure meaningfully, although the value of 6.84 for the Mi Vida sample is probably reliable.

The theoretical density of UO_2, based on a cell edge of 5.4692A. (Rundle, 1948), is 10.96. All measured natural uraninites fall considerably below this. Even the hard, lustrous, compact crystals from pegmatites were seldom much above 9. The analyses show some of the reasons for the discrepancy. The total U, expressed as UO_2, is generally no more than 80%. Thorium would not tend to decrease the specific gravity, and the rare earths would have a comparatively minor effect. But the excess oxygen associated with the presence of U^{+6} would tend to decrease the specific gravity, as would iron, silica, calcium and water (+ and −), which are recorded in most analyses. Furthermore, there are microscopic and sub-microscopic voids, and, as will be shown, amorphous regions of disordered structure which probably have a considerably reduced density.

OCCURRENCE

Uraninite has three main types of occurrence; in pegmatites, veins and in sedimentary uranium deposits.

Uraninite from veins is generally hard, compact, and lustrous. It is often euhedral. The sample from Wilberforce, Ont. included in this study is a single crystal two inches across, showing good dodecahedral faces. These uraninites are associated with the usual pegmatitic minerals; coarse potash feldspar, quartz, muscovite, biotite, zircon, and other, rarer minerals.

The vein pitchblendes occur in either calcareous or siliceous gangue, often with pyrite and galena. Their grain size has been estimated at 10^{-5} cm. from x-ray line breadth studies. (Croft, 1954)

The sedimentary uraninites of the Colorado Plateau occur as sooty deposits in sandstone and limestone. They are associated with coffinite, vanadium minerals, selenides, and other rare species in a very unusual assemblage that has been the subject of much recent study.

The oxidation products of uraninite also form part of all the above associations. Uraninite readily alters to secondary uranium minerals, in which the uranium is in the hexavalent state. The altered material in contact with the uraninite is usually the mixture of orange hydrated oxides formerly known as gummite (Frondel, 1956), which is now known to consist primarily of fourmarierite and vandendriesschite. These in turn alter to yellow and green uranyl silicates, sulfates, phosphates and carbonates. The black uraninite, orange oxides, and yellow or green uranyl compounds form concentric rings in some specimens; elsewhere, the oxidation products invade the main body of the uraninite along innumerable fissures, as at Grafton, N. H., so that it is almost impossible to obtain a pure sample of the uraninite. On the Colorado Plateau, where the primary uranium minerals are porous and the water table low, the primary uranium minerals of entire ore bodies have been completely changed to the vanadium-bearing minerals carnotite and tyuyamunite, which were mined for many years before the primary minerals were discovered. On the Colorado Plateau, uraninite is often associated with organic matter, which may have been the localizing factor in the ore deposition.

THE TERM "PITCHBLENDE"

In this work, the term "pitchblende" will be used as a varietal name, for uraninite from veins and sediments. This follows best current usage.

Many workers have used the terms "uraninite" and "pitchblende" as the names of two separate mineral species. Katz and Rabinowitch (1951) distinguished between them on the basis of chemical composition, maintaining that uraninite was oxidized UO_2, and pitchblende U_3O_8. Ellsworth, Kirsch, and others distinguished between the two on the basis of presence or lack of crystal form; Croft (1954) on the basis of grain size, as revealed by line breadth in x-ray photographs. Rogers (1947) resurrects the old term "mineraloid", meaning an amorphous material of indefinite composition, and applies it to pitchblende in contrast to uraninite. "Mineraloid" is a term suggested by Niedzwiedzki in 1909 to cover such things as limonite and wad.

EXTENT OF OXIDATION

The extent of oxidation of uraninites is one of the main subjects of this study, and detailed data on the samples examined and on the analyses appearing in the literature will be given in later chapters. The degree of oxidation will be defined in terms of the subscript of the oxygen in the formula. The letter "m" will be used to refer to the subscripts of UO_m; "n" will be used for $(U,Th)O_n$; "p" will be used for $(U,Th,R.E.)O_p$; and "q" will be used for $(U,Th,R.E.,Pb)O_q$.

The 35 available analyses of pegmatitic uraninites which distinguish between U^{+4} and U^{+6} have values of m ranging from 2.143 to 2.801:

Only 15 of the 35 fall below the laboratory limit of 2.33. The q values range from 1.963 to 2.458. Only one sample is below 2.00; this case is almost certainly due to non-radiogenic lead. Of the remaining 34, 31 fall in the laboratory range 2.00-2.33.

There are 29 suitable vein and sedimentary pitchblende analyses available which distinguish between U^{+4} and U^{+6}. In these, m varies from 2.000 to 2.850. Only 7 of the 29 fall below the laboratory limit of $UO_{2.33}$. Since many of these analyses are partial, it is possible to give a value of q in only 15 cases. Five out of the fifteen fall in the range 2.00-2.33.

The generalization that pitchblendes are more oxidized than pegmatitic uraninites is unwarranted. The generalization that the degree of oxidation can be estimated by the texture is also very dubious. Most of the pegmatitic uraninites below the laboratory limit are about equally lustrous on comparable surfaces.

All available analyses are given in the appendix.

UNIT CELL EDGE

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 Figure 2.

The cell edges of the 105 pegmatitic uraninites range from 5.415 to 5.560 A. The median is 5.470 A. The 101 vein uraninites have cell edges ranging from 5.370 A. to 5.495 A. The median unit cell size for vein pitchblende is 5.437 A., which is 0.033 A. lower than the median for the pegmatitic uraninites. The unit cell sizes of all 100 pitchblende samples from sediments, virtually all from the Colorado Plateau, range from 5.36 A. to 5.47 A. The highest value is at the median of the pegmatitic uraninite range; the median cell size of the sedimentary uraninites, 5.406 A., is below the bottom of the range of the pegmatitic uraninites.

The high values of the pegmatitic uraninites can in part be explained by the presence of thorium; but these samples contain rare earths as well, and rare earths tend to decrease the unit cell size. The difference between the vein and sedimentary pitchblendes cannot be explained by chemical factors, for there is no essential chemical distinction between them, as far as can be detected from the available analyses.

BEHAVIOR ON HEATING

When uraninite is heated above 400°C. in air, it changes quickly to U_3O_8. Since Th_3O_8 does not exist, Th should decrease the stability field or U_3O_8 in favor of UO_2, and retard the oxidation of high-thorium uraninites. But this is speculative; all samples tested were U_3O_8 after heating to redness in air.

In an inert atmosphere, uraninite heated to the vicinity of 550° for several hours undergoes a change that will be called "annealing". The lines of the powder pattern sharpen, and the unit cell size decreases as much as 0.04 A. 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, U_3O_8 lines appear, particularly on long runs. These may actually be the lines of the

$UO_{2.6}$ phase, but Hoekstra et al. (1955) failed to include the powder pattern of $UO_{2.6}$ 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°, more of the samples disproportionate into a cubic phase and an orthorhombic one related to U_3O_8. The results depend on the state of oxidation, and perhaps on the content of thorium and other elements.

The work of Alberman and Anderson (1949) on synthetic material, and that of Brooker and Nuffield (1952) on natural material suggests that, at high temperatures, pitchblendes with no thorium and little excess oxygen should decompose into UO_2 and U_4O_9. This phenomenon was not observed in this study.

STRUCTURE

Goldschmidt and Thomassen (1923) found that UO_2 has a fluoritetype structure. Each uranium ion is surrounded by eight oxygen ions, at the corners of a cube of which the uranium ion occupies the center. Each oxygen is surrounded by four uranium ions, at the corners of a tetrahedron. The other four corners are vacant. The cavities are large enough for an ion with a radius of 1.32 A. Oxygen will just fit it. So will divalent lead.

Table 9 is a list of 47 substances with the fluoritetype structure. They include fluorides of divalent elements, oxides of rare earths and the actinide series, sulfides, selenides, tellurides, and an assortment of 2:1 alloys. Among them are the minerals uraninite, thorianite, cerianite, fluorite, and digenite (high-temperature chalcocite.)

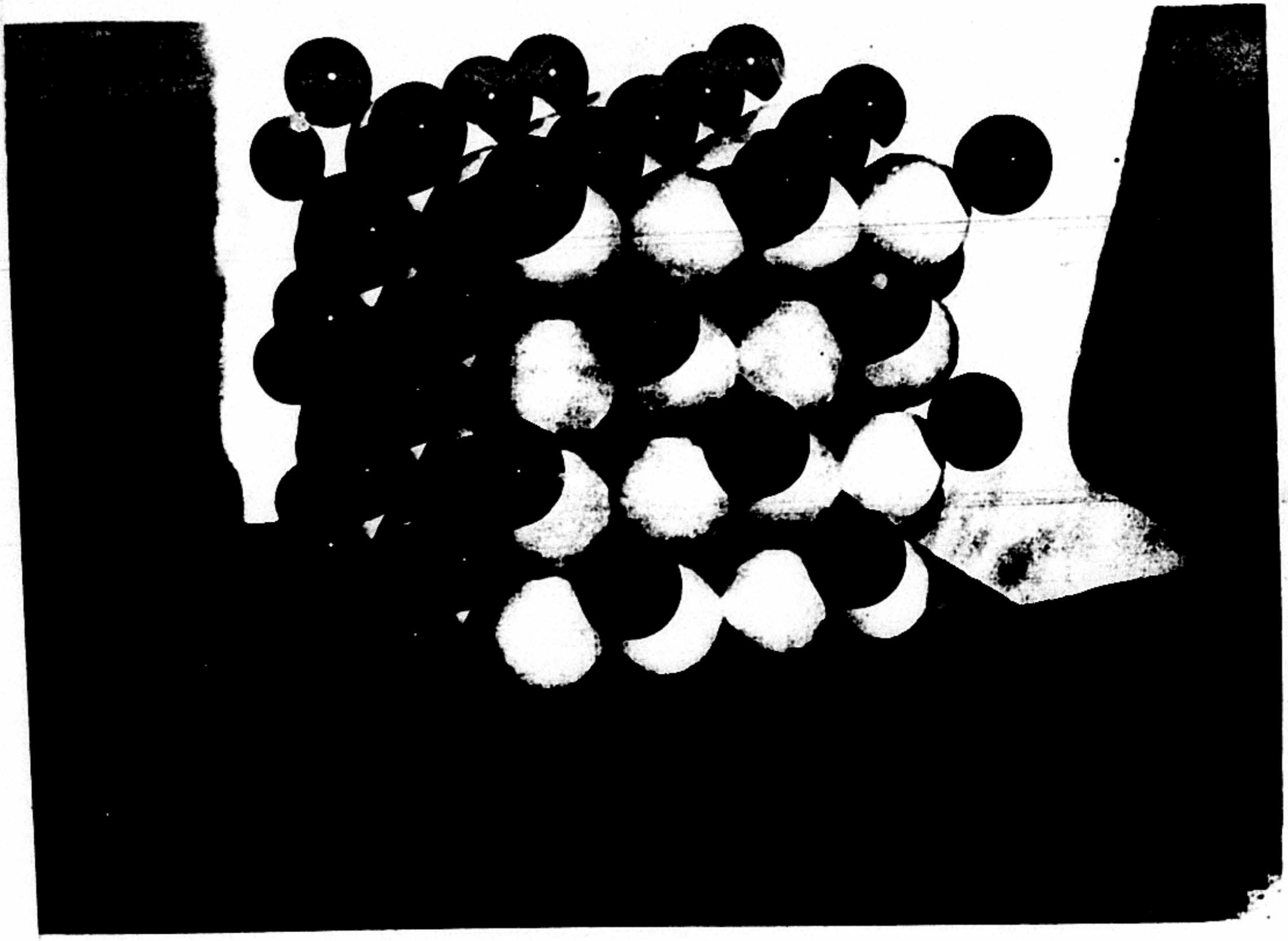

Figure 2. The structure of uraninite. White-oxygen. Dark-uranium.

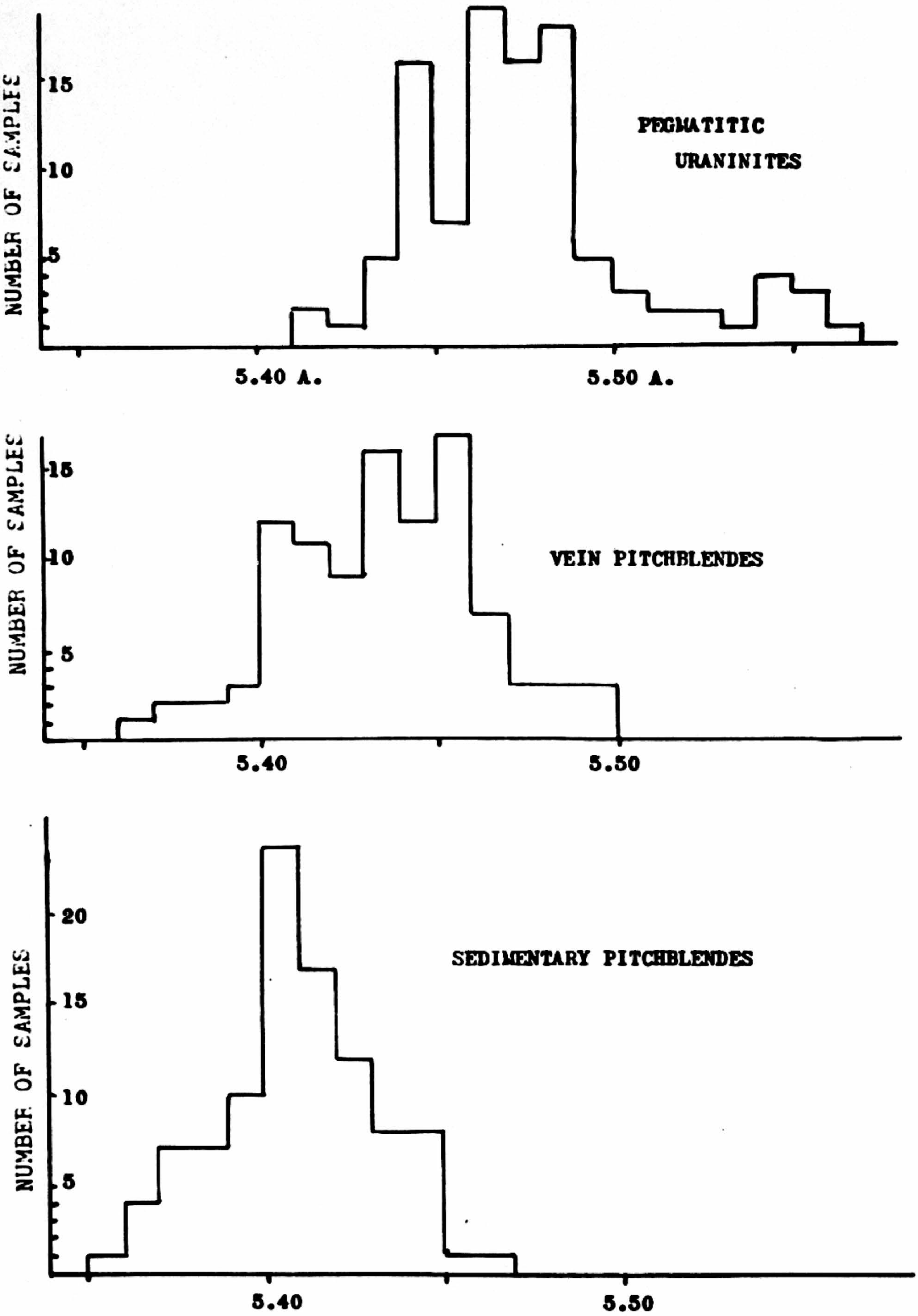

Figure 3. Distribution of unit cell sizes in uraninites, according to occurrence. (In part after C. Frondel.)

Digenite may have a slightly distorted pseudo-cubic structure.

The cubic ZrO_2 listed is not baddeleyite.

Table 9. Substances with fluorite-type or anti-fluorite structures.

Halides	Oxides	Sulfides	Alloys, etc.
CaF_2 (Fluorite)	Li_2O	Li_2S	Mg_2Si
SrF_2	CeO_2 (Cerianite)	Na_2S	Mg_2Sn
BaF_2	PrO_2	K_2S	Mg_2Pb
RaF_2	Rb_2O	Rb_2S	Mg_2Ge
CdF_2	ZrO_2	Cu_2S(digenite)	$PtAl_2$
PbF_2	HfO_2		$PtGa_2$
CuF_2	AcOF	H_2Se	$PtIn_2$
EuF_2	ThO_2(Thorianite)	Li_2Se	$PtSn_2$
$SrCl_2$	UO_2 (Uraninite)	Na_2Se	$AuAl_2$
Na_2UF_6	NpO_2	K_2Se	$AuGa_2$
	PuO_2		$AuIn_2$
	AmO_2	Li_2Te	Be_2C
		K_2Te	Cu_2Si
			$IrSn_2$
			BiCuMg

In actinium oxyfluoride, AcOF, the fluorine and oxygen occupy equivalent positions. A similar mechanism presumably operates in the alloy BiCuMg, and Na_2UF_6.

This structure permits a number of different mechanisms of solid solution to operate. In some, ions fit into the vacancies with appropriate compensation being affected elsewhere. Fluorite, CaF_2, takes up additional fluorine in the vacancies as Y^{+3} is substituted for Ca^{+2}. The series is continuous from CaF_2 to ~~(Y,Ca)$F_{2.[illegible]}$~~ YF_3, at which point the interstitial vacancies are exhausted. Goldschmit suggested that the uptake of fluorine in yttrofluorite and of oxygen in uraninite were comparable, with compensation being affected by U^{+4} going to U^{+6}. SrF_2 can also take up La^{+3} to ~~(La,Sr)$F_{2.75}$~~ LaF_3. Each of these interstitial fluorines is surrounded by eight other similarly charged fluorines.

The fluorite structure also permits omissions. CaO can be substituted into cubic ZrO_2 up to 40% molar; for every Ca ion included, one oxygen must be omitted. CaO can also be substituted into UO_2 up to 47 molar percent at 1650°C. Here there is a choice of two mechanisms. Either an oxygen can be omitted, or U^{+4} can go to U^{+6}. If calcium is present, the material can contain an equivalent amount of U^{+6} without any of the interstitial positions being occupied by oxygen.

Digenite, $Cu_{2-x}S$, can exist at room temperature if some of the copper positions are vacant. Compensation is presumably by means of cupric ion.

When fluorine or oxygen ions are placed in interstitial vacancies, each one is surrounded in close coordination by eight other similarly charged ions. The mutual repulsion can apparently be overcome by fluorine, which has a charge of -1. The oxygen ion has a charge twice as strong, however, and the mutual repulsion is probably the controlling factor that will not permit the oxygen to occupy all the interstitial vacancies up to $UO_{2.75}$.

When fluorite is subjected to x-rays or radioactive bombardment, either naturally or artificially, it may become purple due to the formation of 'F-centers'-distorted areas or vacancies in the structure in which electrons can be trapped in a metastable state, such that they can absorb energy corresponding to visible light. The x-ray lines are broadened. These effects are removed by heating, under conditions comparable to the annealing of uraninite. In the case of fluorite, there is no question of oxidation being involved; the distortion of the structure is certainly due to radiation. Although the sharpening of lines is similar to that in uraninite, in fluorite there is no decrease of the unit cell on annealing. (Berman, 1957)

DESCRIPTION OF SPECIMENS

Descriptions of the 33 specimens included in this study are given below. Since most of them were taken from museum collections, they already had been assigned Specimen numbers. To avoid confusion, and to ease the task of anyone who wishes to locate these analysed specimens in the future, it was decided not to assign additional numbers (such as 1 to 33). The specimens will be identified by the locality name, sometimes somewhat condensed. Terms such as "Strickland", "Katanga", "Wilberforce" and "Mi Vida" will be used as specimen names. In this way, it is hoped that some referring back and forth in the text can be eliminated, and that a "locality" column can be eliminated from many tables.

URANINITE SPECIMENS FROM PEGMATITES

BOQUEIRAO. This is/ **specimen** 105716 of the Harvard collection. The locality is Boqueirao, Rio Grande do Norte, Brazil. It consists of dense, clarain-like chunks weighing about 130 grams together. The specific gravity is 7.80. The largest piece, about 3X2X1 cm., shows dodecahedral crystal faces with rounded intersections. Weathered surfac are dull, and covered with earthy brownish material. Calcite is present as irregular patches in a fracture. Also, there are some masses, about 5 mm wide, of deep purple fluorite, riddled with cleavages.

BRANCHVILLE. This is a portion of USNM 83567, kindly loaned by George Switzer of the U.S. National Museum. It is from Branchville, Con It consists of chips up to 2 mm. across, weighing together about half a gram. It was described and analysed by Hillebrand in Bulletin 78 of the U.S. Geological Survey (1891). It is listed as analysis VI. Hillebrand states that it was received from G. J. Brush and E. S. Dana of Yale, and was "the residue of the material from which Comstock had taken his for analysis". He further describes this sample as "by far the purest of any material obtained from any locality, the crystals being brilliant and well-defined and almost absolutely free of impurity". Hillebrand gives the specific gravity as 9.733.

ELVESTAD. This is also one of Hillebrand's specimens. It is a portion of specimen 83568 of the National Museum. The locality is Elvestad, near Moss, Norway. This sample is Hillebrand's analysis XIII or XIV in Bulletin 78. It is almost certainly XIII, because XIV contains about 15% insoluble columbite, and this specimen apparently does not. In any case, the analyses are almost identical, except for insolubles. Hillebrand gives the specific gravity of XIII as 9.145; this specimen was measured as 9.13. The sample at Harvard weighs about 3 grams, and consists of durain-like chips of uraninite. It includes a good crystal some 5-6 mm across, with rounded edges. The faces are dodecahedrons. A few chips of quartz, muscovite, and brownish feldspar are included with the sample. Hillebrand obtained the material from Brögger.

GORDONIA (HOLMES). This is Harvard's sample 92341, from Gordonia, South Africa. It was obtained from Hecht, who states that it is the analysed material of Holmes. The analysis was made by E. D. Mountain and quoted in Holmes (1934). About 25 grams of material are available at Harvard. This includes a hopper-shaped cast about 2 cm. X 2 cm., coated with a layer of brownish alteration products. The material is compact and clarain-like on a fresh surface; it has an uneven fracture, but is rather lustrous, Holmes gives the specific gravity as 8.876.

GORDONIA (USNM). This material is from the same locality. It is specimen No. 103596 of the National Museum. About 150 gm. of this material was available. It is similar in texture to Holmes' material, and consists of subhedral crystals up to 1 cm. across, embedded in coarse brown plagioclase. A crystal with a square cross-section, 15 mm. across, is included. The specific gravity is 7.32.

GRAFTON. This is specimen 105756 from the Harvard collection. It is one of several polished slabs, about 20 cm. across, from the Ruggles Mine, Grafton, N. H. The lustrous black uraninite is in patches 2-3 mm. across, riddled by cracks filled with alteration products, chiefly gummite and uranophane. There is also some greenish, brilliantly fluorescent autunite, and cyrtolite. The groundmass is quartz. It was necessary to stage-grind the material to 100 mesh (0.15 mm.) for grain picking. Even after all other permissible separation methods had been tried, less than 2% of the concentrate was suitable for inclusion in the sample. Virtually every grain had specks and fissures of secondary uranium minerals. Acid could not be used; it would have removed the unwanted minerals, but it would also have changed the composition of the uraninite by differential leaching. After a month of work, 400 mg. of sample was collected, and Mr. Jun Ito undertook a partial analysis on this quantity. The analysis does not include a determination of ThO_2.

HALE'S QUARRY. This specimen, No. 83566 from the U. S. National Museum, is from Hale's Quarry, Portland, Conn. It is Hillebrand's analysis I-"which led to all subsequent work"-the sample in which nitrogen, later shown to be partly helium, was first observed, recorded and measured. The original sample was a rounded, distorted cubic crystal about 15 mm. across. About 10 gm. of material was sawed off one end of the crystal for this present work. It has a clarain-like lustre. Hillebrand gives its specific gravity as 9.139. It is associated with reddish feldspar, quartz, yellow muscovite, and columbite.

HUGGENASKILEN. This is a portion of specimen 83570 of the National Museum. It is from Huggenäskilen, near Moss, Norway, and is Hillebrand's analysis XVI. Approximately 5 gm were obtained for study. It has a vitrain-like lustre; it is considerably more lustrous, in a side-by-side comparison, than the Hale's Quarry sample, which is much less oxidized according to the chemical analyses. The sample is in chips about 2 mm across. Hillebrand gives the specific gravity as 8.930. The sample is pure except for a little reddish material on weathered surfaces.

KARELIA. Harvard's specimen 106038 is from Karelia, in the USSR. The label of the Minerals Exchange Bureau, Leningrad, reads "Uraninite in Microcline. Karelia. White Sea". It consists of three tabular chunks, weighing together 15 grams. It is compact and vitrain-like. The specific gravity is 8.41. Except for a little microcline on the surface, the material is pure. Some of the sample was sent to Katz for age determination studies.

MOROGORO. The National Museum's records showed that specimen 93290, of which this is a part, was from East Africa and had been analysed by Marckwald. Apparently, it is from the Morogoro District in the Uluguru Mountains, Tanganyika. There are several analyses, and it is uncertain which one this material represents; but the analyses are very similar, and it was arbitrarily decided to use the one listed in Doelter's Handbuch as No. 41. It is the only Morogoro analysis differentiating between UO_2 and UO_3. This assumption produced good agreement between calculated and measured values in the Vegard's Law calculations.

The crystal is a cube, about 2 cm. on a side, with one face being the cast of a hopper-shaped crystal. The surface is covered with a coating of brownish-yellow alteration products. The texture is durain-like. The specific gravity is 9.09.

NEWRY. This is No. 103038, the finest uraninite specimen in the Harvard collection. It is from Newry, Me. It is an octahedral crystal with the edges truncated by sharp, narrow dodecahedral faces. The crystal is about 2 cm. on an edge, and is embedded in a matrix of gray orthoclase. The lustre is vitrain-like, almost sub-metallic. The specific gravity is 9.58.

PORTLAND. This is No. 16214 of the Harvard collection. The locality is Strickland Quarry, Portland, Conn. The sample consists of several crystal fragments, with faces, weighing about half a gram each. They have a vitrain-like lustre. The specific gravity is 10.15.

SPRUCE PINE. This specimen is about 2X3 cm., and consists of 75 gm. of uraninite from Spruce Pine, N. C. It is No. 105712 of the Harvard collection. It is covered by a brownish crust 2-3 mm. thick, consisting of muscovite, fluorescent autunite, torbernite and brown orthoclase. The uraninite is vitrain-like, with well-developed conchoidal fractures and a bluish iridescence. The specific gravity is very low--6.17.

STRICKLAND. Harvard's specimen 106052 is from Strickland Quarry, Portland, Conn. It is a piece of coarsely crystalline orthoclase 7-8 cm. across. On one surface, there is fairly large crystal of uraninite, about 5 mm. across, embedded in the feldspar, also a somewhat smaller one and a scar from which a third had been plucked. The material is very similar in appearance to the "Portland" sample, which came from the same locality, and the "Hale's Quarry" sample, which was found a mile away. It is unfortunate that so many of the analysed samples come from Portland, Conn. and the vicinity of Moss, Norway.

With the specimen, there is a letter from A. C. Lane, stating that this material was analysed by Hecht, and that the results are given in Foye and Lane (1934). The article gives the microanalysis of one large and two smaller crystals. The analyses are virtually identical except for the state of oxidation. A little material was removed from the larger crystal for this work. Presumably it corresponds to Foye and

Lane's analysis 2.

SUDBURY. This sample was obtained from the Public Sample program of the U. S. Geological Survey, which had assigned it the number RW-5060. Correspondence stated that the material was obtained from a pegmatite in the Sudbury district, Ontario. The sample consists of a kilogram of crushed rock, largely quartz, coarse reddish feldspar and biotite, from which about 35 gm. of uraninite crystal fragments were extracted. They are about 1 mm. across, on the average, vitrain-like, and have a specific gravity of 8.6.

WILBERFORCE. Harvard's specimen 105711 is one of a number of large uraninite crystals from Wilberforce, Cardiff Township, Ontario. Originally, the specimen was about 7 cm. across, and weighed 100 grams. It has a durain-like texture, and is associated with deep purple fluorite and brown, powdery feldspar. The specific gravity is the highest for any of the natural samples studied--10.25. The crystals are pitted, distorted dodecahedrons with rounded edges.

VEIN PITCHBLENDES

ELDORADO. This is USNM specimen 103183, from the Eldorado mines, Great Bear Lake, N.W.T. A partial analysis was performed by Marble (1937) for age determination purposes. Unfotunately, the sample is badly contaminated with calcium carbonate, and its usefulness was rather limited. It consists of 5 grams of very fine powder.

GREAT BEAR LAKE. This is Harvard's specimen 106051. It is from the 125' level of the east section of the No. 2 vein, Eldorado Mines, Great Bear Lake, N.W.T. The specimen is about 3 cm. across, and weighs 200 grams. It consists mostly of gray and reddish quartz with some carbonate, and with disseminated chalcopyrite throughout the wall rock. One surface of the specimen is covered with a layer of pitchblende up to 1 cm. thick, botryoidal in character with the coalescing, somewhat flattened groups having diameters up to 1 cm. The lustre is vitrain-like. The specific gravity is 7.19.

JOACHIMSTHAL. This was specimen 346 in the collection of A. Berger of Vienna. It is from Joachimsthal, Bohemia. The specimen weighs about a kilogram, and is about 10 cm. across. It exhibits two seams of vitrain-like pitchblende, one about 2 cm. wide, and one averaging 3 cm., extending the length of the specimen. Bordering these, is a "comb structure" of parallel reddish-gray dolomite crystals. Between the pitchblende seams, there are portions of wall rock, a gray mixture of quartz and carbonates with dispersed pitchblende and pyrite. Material from the seams was used. Its specific gravity is 7.28.

KATANGA. Specimen 94710 of the National Museum consists of 15 grams of durain-like pitchblende, seamed with ochre-yellow alteration products, apparently mostly becquerelite. The only locality information available is "Katanga"; it is presumably from the mines at Shinkolobwe. The material is somewaht porous, and a good specific gravity determination could not be made.

PIED DES MONTS. This is 105713 of the Harvard collection, from Lac Pied des Monts, Quebec. It consists of 50 grams of powder on which some person had begun an analysis. The analysis was completed by Harry Kramer of the U. S. Geological Survey. The powdered sample contained a considerable amount of calcium carbonate.

PRZIBRAM. This is 105714 of the Harvard collection. It is from Przibram, Bohemia. It consists of a specimen, 4X6 cm, with one side polished, weighing 110 grams. The polished side shows clearly that the specimen is made up of vitrain-like botryoidal groups of pitchblende up to 8 mm. in diameter, with galena along cracks and concentric shells. Pyrite and galena fill the space between botryoidal groups. The specific gravity is 7.82.

RIX ATHABASKA. This is specimen 105717 from the Harvard collection. It is from the Rix Athabaska mines, Athabaska Lake, Saskatchewan. The specimen is about 15 cm. long. About half of it, by volume, is brecciated reddish limestone wall rock. Pitchblende fills the space between the fragments. It has a somewhat greasy lustre, and shows pisolitic groups up to 1 mm. in diameter on some surfaces. The specific gravity is 7.33.

SCHMIEDEBERG. This is Harvard specimen 104907, from the Bergfreiheits mine, near Schmiedeberg, Silesia. It is about 15 cm. long. It consists of a vein of vitrain-like uraninite in cleavable pink calcite. The vein is irregular, averaging about 3 cm. wide, and extends the length of the specimen, replacing the calcite along cleavage planes. The uraninite shows some botryoidal aggregates about 3 mm. in diameter. The specific gravity is 7.46.

THEANO POINT. This is Harvard specimen 105710, from Theano Point, Algoma District, Ontario. It consists of clarain to vitrain-like uraninite in tabular veins up to 1 cm wide, in somewhat calcareous reddish quartzite. The wall rock has irregular powdery coatings and stainings of canary yellow uranophane. The specific gravity of the pitchblende is variable and extremely low--about 5.

WOLSENDORF. This specimen, weighing about 200 grams, consists of "fetid" purple fluorite and pink quartz, with a seam of grayish durain-like uraninite about 6 mm. wide extending the 10-cm. length of the specimen. It is from Wölsendorf, Bavaria. The fluorite has been described as sample F-1 in an earlier paper by the author. (Berman, 1957) ~~in press)~~

WOOD MINE. Sample 100453 of the National Museum is from the Wood Mine, Central City, Colo. It consists of 200 gm. of gray, fusain-like, porous, pulverulent uraninite, with small grains of pyrite. Washing with water reveals that part of the sample is reasonably compact; this is the portion that was used in the present work. The specific gravity of the compact material is 6.77.

SEDIMENTARY PITCHBLENDES

BIG INDIAN. Harvard specimen 106050 is from the Continental Uranium Co. Mine, Big Indian Wash, San Juan Co., Utah. It consists of two seams of grayish, fusainlike material permeated by calcite, which shows as reflecting cleavages in the pitchblende. The seams are 1/2 and 1 cm. wide, and separated by a 2 cm. band of gray, sandy limestone.

HAPPY JACK. This sample, from Happy Jack Mine, White Canyon, Utah, was part of a sample analysed for Stieff and Stern of the U. S. Geological Survey. They kindly lent the author a few hundred milligrams. The material was in the form of a fine black powder.

MI VIDA. This sample, No. 106040 of the Harvard collection, is from the Mi Vida Mine, San Juan Co., Utah. It is a nearly solid mass of charcoal-like uraninite, weighing nearly a kilogram. There is a small seam of calcite, and a few grains of chalcopyrite. The uraninite is high in vanadium, which may be present as a separate phase. The specific gravity is 6.84.

SHINARUMP NO. 3. Sample 106039 of the Harvard collection is from Shinarump No. 3 mine, Sevenmile District, Grand Co., Utah. It is about 6 cm. across, and consists of dull, pulverulent pitchblende in gray sandy limestone. Orange-yellow alteration products occur at one corner of the specimen. Cleavages of permeating calcite are visible in the pitchblende.

ROYAL CLAIMS. Sample 106037 of the Harvard collection was found at the Royal Claims, Indian Creek, San Juan Co., Utah. It consists of grayish, fusain-like uraninite permeated with light gray calcite.

SYNTHETIC SAMPLE

UO_2 crystals were prepared synthetically following the method of Ebelman (1842) with a few modifications, largely for convenience. 7 grams of anhydrous $MgCl_2$ and 2 grams of $(UO_2)(NO_3)_2 \cdot 6H_2O$ were ground and mixed, and packed into a carbon crucible, which was then covered and heated for half an hour in a forced gas flame. The results, after cooling, consisted of a crust of coarse magnesium chloride crystals. Between the crystals and next to the carbon were dendritic groups of cubic UO_2 crystals, black and very lustrous, with the largest cubes about half a millimeter across. The measured specific gravity is 10.75.

Table 10. Summary of Samples Used.

Name Location	Collection Number	Sp. Gr.	Anal	Chem	Remarks
PEGMATITIC URANINITES					
BOQUEIRAO **Brazil**	H 105716	7.80		TE	Large, rough xl
BRANCHVILLE Conn.	USNM 83567	9.733	2	Hb	xls, vitr.
ELVESTAD Norway	USNM 83568	9.145	7	Hb	
GORDONIA (HOLMES) S. Africa	H 92341	8.876	39	Mountain	
GORDONIA(USNM) S. Africa	USNM 103596	7.32	42	TE	
GRAFTON N. H.	H 105756		36	Ito	altered along cracks
HALE'S QUARRY Portland, Conn.	USNM 83566	9.139	27	Hb	
HUGGENASKILEN Norway	USNM 83570	8.930	10	Hb	vitr.
KARELIA U.S.S.R.	H 106038	8.41		TE	
MOROGORO Tanganyika	USNM 93290	9.09	44	Marckwald	Hoppershaped
NEWRY Me.	H 103038	9.58	33	Ito	vitr., xl
PORTLAND Conn.	H 16214	10.15	32	Ito	xl frags.
SPRUCE PINE N.C.	H 105712	6.17	45	TE	iridescent vitr.,
STRICKLAND Portland,Conn.	H 106052		24	Hecht	

SUDBURY Ont.	RW 5060	8.6	43	TE	vitr.
WILBERFORCE Ont.	H 105711	10.25	65 66	TE	w. purple fluorite

VEIN PITCHBLENDES

ELDORADO Gt. Bear Lake	USNM 103183			Marble	
GREAT BEAR LAKE N.W.T.	H 106051	7.19	52	Ito	botryoidal
JOACHIMSTHAL Czech.	BER 346	7.28	41	TE	w. dolomite
KATANGA Belg. Congo	USNM 94710		40	TE	dull
PIED DES MONTS Que.	H 105713		38	TE	
PRZIBRAM Czech.	H 105714	7.82	67	TE	botryoidal
RIX ATHABASKA L.Athabaska,Sask.	H 105717	7.33		TE	in ls.breccia
SCHMIEDEBERG Silesia	H 104907	7.46	69	TE	vitr.
THEANO POINT Ont.	H 105710	5	55	TE	
WOOD MINE Central City,Colo.	USNM 100453	6.77	68	TE	Porous
WOLSENDORF Bavaria	F-1		37	Ito	w. purple fluorite

SEDIMENTARY PITCHBLENDES

BIG INDIAN Utah	H 106050		35	Ito
HAPPY JACK Utah	TWC 2282		25	TE
MI VIDA Utah	H 106040	6.64	34	Ito
SHINARUMP No. 3 Utah	H 106039			
ROYAL CLAIMS Utah	H 106037			

ABBREVIATIONS

H	Harvard Collection
Hb	Hillebrand
Anal	Number of analysis in appendix
TE	Laboratory of the U.S.G.S. Washington, under contract to AEC
USNM	Collection of the U. S. National Museum

CHAPTER 4

DESCRIPTION OF CERTAIN TECHNIQUES

Most of the techniques used in this study were the orthodox, accepted and recommended methods, and need only be listed. A few will be described in greater detail.

PREPARATION OF SAMPLE

The sample was stage-ground in an agate mortar, first to 0.93 and then to 0.24 mm. No. 000 and No. 6 bolting cloth was used to sieve out coarser particles for regrinding. These correspond roughly to 20 and 75 mesh. In some cases, it was possible to pick the sample from the 20 mesh without further grinding. A piece of bolting cloth was discarded when contamination became likely.

The ground sample was washed in a porcelain casserole with water and Alconox detergent; this removed much of the clinging earthy secondary minerals. If quartz and other light materials were present, they were removed by the use of methylene iodide in separatory funnels. The Frantz magnetic separator was occasionally used to advantage. As mentioned before, acid was not used.

The one-gram sample for chemical analysis was grain-picked from the resulting concentrate. A binocular, dissecting-type microscope which magnified about 10 diameters was used. A piece of paper was placed on its stage; on this, a microscope slide, and on this about half a gram of sample concentrate. Suitable grains were pushed off the edge of the glass slide, on to the paper, with a steel needle. At intervals, the glass slide was lifted off and the grains on the paper were transferred to a small glass vial. The final sample was repicked; this time, the undesirable grains were pushed off the side. Preparing a one-gram sample for analysis was, on the average, four days' work.

The paper used in handling the sample is one of the tools of th druggist's trade, and it should be more widely used by mineralogists. It is glassine powder paper, a translucent material with a hardened, glazed surface specifically designed not to retain any sample. The powder must be dry.

Specific gravity was determined on the Berman balance, using toluene.

X-RAY

Spindles for x-ray powder photography were made with collodion. A small amount of ThO_2 was incorporated into each spindle as an internal standard--roughly 15% of the sample. ThO_2 gives extremely sharp reflections that can easily be measured throughout the film. The unit cell size of this particular batch was determined by means of the symmetrical back-reflection camera to be 5.5977 A ± .0001 at 25° C.

Eastman Type K x-ray film and 114-mm. diameter cameras were used. Exposure was 4 to 8 hours to Ni filtered Cu ra diation. The x-ray tub was run at 45 KV, 20 MA. Development of the film followed the manufacturer's recommendations.

The films showed the sharp cubic pattern of ThO_2, and, at a slightly higher Bragg angle than each ThO_2 line, the corresponding line of the uraninite sample. The distance between the lines was measured to 0.01 mm. At first, a shrinkage correction was applied, but this was found not to affect the final value significantly.

The films were measured on an ARL spectrographic comparator. This machine has a movable carriage with holders for two glass plates. Below the carriage is a light source. Above the carriage, two separate optical systems project the images of the plates on a screen, side by side, enlarged 20 diameters. A contact print of a metric scale on a glass plate was placed in one holder. The film was sandwiched between two x-thin glass plates stripped of emulsion, and inserted in the other holder. The original engraved Metric scale, made by Hilger, is unfortunately too thick for the comparator.

As the carriage is moved, film and scale are translated together across the viewing screen. A transparent vernier is taped directly to the screen; several different designs were used during the course of the work.

The internal intensity distribution of the X-ray diffraction lines is clearly visible, and there is no difficulty in setting the mark scribed on the screen in the center of each line. The mark can be checked for tangency to the film line by translating the film transversely to the length of the carriage. The film is held flat by the glass plates. There is no danger of moving the film by contact with a sliding rider. The rigidly aligned and collimated optical systems virtually eliminate parallax effects, and many other sources of error are eliminated, not the least of these being eyestrain and the limited patience of the operator. Unless otherwise stated, unit cell measurements in this study are accurate to ±0.002 A. In a few cases, the uraninite lines were too broad, or could not be observed at high enough angles, to permit this accuracy.

INERT ATMOSPHERE FURNACE

In order to study annealing and disproportionation effects on analysed samples, it was necessary to have a furnace in which the samples could be heated in vacuum or in an inert atmosphere.

How complete must the exclusion of oxygen be to prevent additional oxidation? The literature provides only a single piece of data. Biltz and Muller (1927) found that $UO_{2.3}$, $UO_{2.6}$ and oxygen at a partial pressure of 10 mm. of mercury were in equilibrium at 1300°C. This is the top of the range at which the laboratory-limit oxide is in equilibrium with the atmosphere at this temperature. From 10 mm., the range of pressure extends down, perhaps several orders of magnitude. If the oxygen partial pressure is anywhere in this range, UO_2 will oxidize to $UO_{2.3}$. Oxides below the laboratory limit will tolerate less than the bottom of the range. At temperatures below 1300°, presumably more oxygen can be tolerated, but the limit is probably not high.

Conybeare and Ferguson (1950) observed some of the annealing and disproportionation effects. They assured a non-oxidizing atmosphere by putting a cover on their crucible. This method is probably inadequate for our present purposes.

Likewise, the method of Brooker and Nuffield (1952) leaves their results open to serious question. Their samples were placed in a silica tube with one end sealed. The other end was attached to a vacuum pump, which evacuated the tube continuously as the tube was placed in a flame. Unfortunately, silica becomes permeable to gases at high temperatures, and the pump may have simply been dragging oxygen over the samples.

Figure 4. Inert atmosphere furnace.

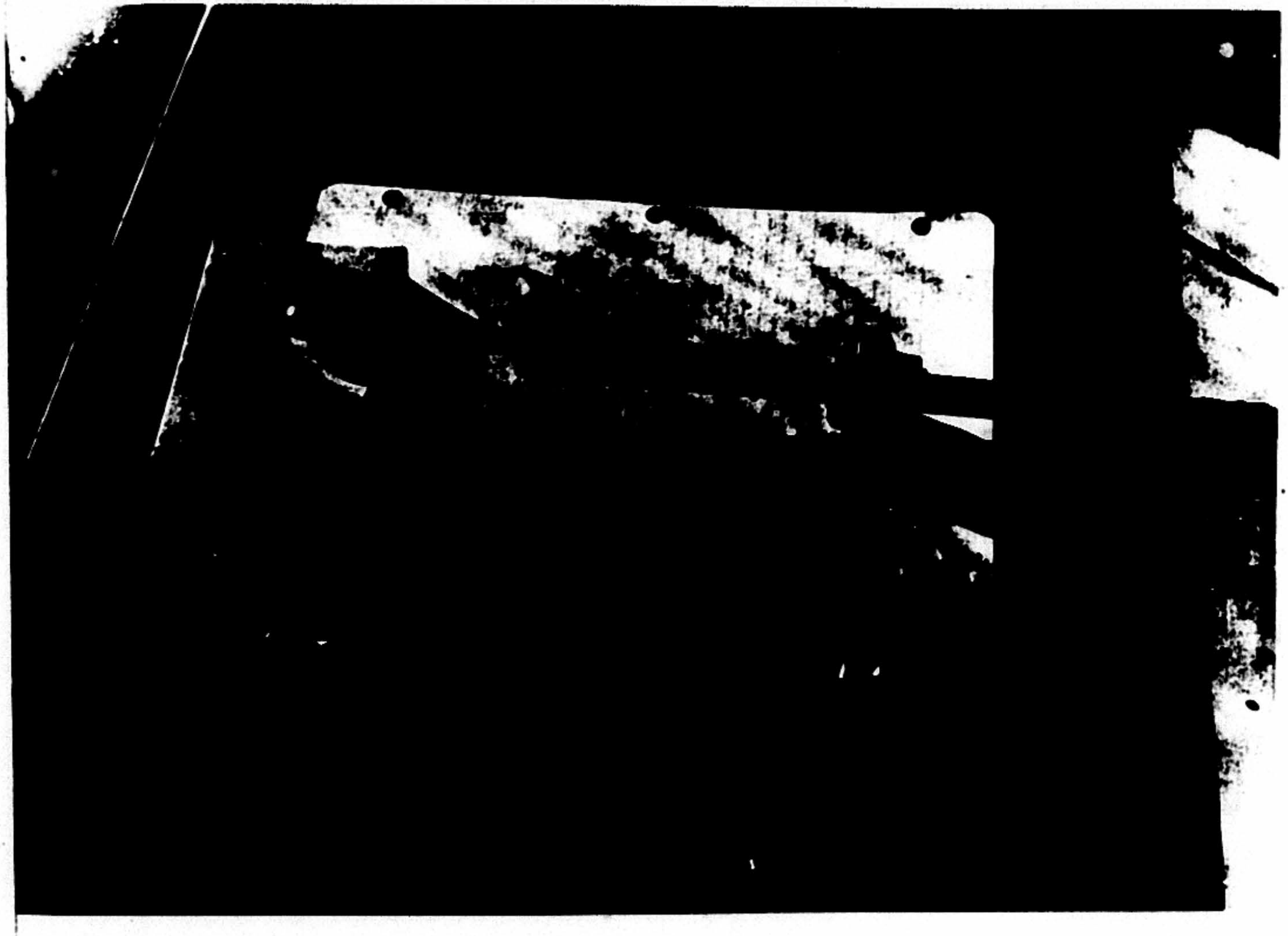

Figure 5. Sample holder and thermocouple for inert atmosphere furnace.

It was decided to heat the samples in pre-purified nitrogen, at a pressure slightly above one atmosphere, so that any leakage in the system would be outward.

The gas was admitted to the system from a 240 cu. ft. tank, through a single-gland reducing valve. It then passed through a 1 1/2" Vycor combustion tube 24 inches long, which was packed, except for the ends, with scrap copper. It was heated to 450° in a muffle furnace. The ends of the tube were sufficiently far removed from the furnace to make it possible to use rubber stoppers. The gas then passed from this purification furnace into a second furnace containing the sample. This furnace was of the 12-inch, hinged-muffle type used in organic combustion trains. It was regulated by a Variac. The internal diameter was 1 3/8", and it was fitted with a sillimanite McDanel combustion tube. A Fisher fitting was attached to the wide end of the tube so that the rubber hose from the purification furnace could be attached. This fitting is made with a cobalt-glass window, which was removed to provide an opening for the thermocouple and the sample holder.

A length of stiff Nichrome wire was wrapped around and through the handle of a large combustion boat in such a way that the boat could be held rigidly in position by the ends of the wire, as by an extension of the handle. The assembly was then attached to the end of a length of half-inch alundum thermocouple tubing by means of other pieces of stiff nichrome wire, which were wound around the boat wires and the tubing, and twisted tight with pliers. A chromel-alumel thermocouple was fitted into the tubing, such that no contact was made with the "structural" wiring, and that the junction was close to the boat. The other end of the thermocouple tubing was marked so that the boat could be kept upright while inserting and removing the assembly from the furnace. The sample was placed in a small combustion boat which fitted inside the large boat. After a sample was inserted in the furnace, wax was used to seal the space between the tubing and the edges of the opening where it leaves the furnace, as well as the openings where the thermocouple wires leave the tubing. The wires are connected to a millivoltmeter from which the temperature may be read directly.

A tube from the rear (small)end of the McDanel tube connects with a gas trap. This consists of two five-liter bottles partially filled with water and connected by a glass-tube siphon. The space above the water in the first bottle is part of the inert gas system; that above the water in the second bottle is open to the atmosphere. The difference in level indicates the pressure in the system, provides a back-pressure to cut the flow from the reducing valve to the minimum necessary, and provides a reservoir in case of valve failure. The trap is an additional safeguard against diffusion back through the system, keeps the amount of nitrogen released into the room at a minimum, and also has safety valve features. The liquid in the trap was boiled distilled water, with a quart-size packet of MQ photographic developer dissolved in it to scavenge any oxygen remaining in the solution or diffusing back through the siphon.

THE 'AVERAGE RARE EARTH'

In many of the analyses, including all those specifically requested for this study, the rare earths are grouped and given as a single quantity, or as cerium and yttrium earths. For many of the calculations, it was necessary to use molar quantities, and for these an atomic weight was necessary. It was assumed that the rare earths in uraninite have the same relative abundance as in granites, although there is some evidence that the yttrium earths are higher in uraninite than this would indicate. The compilation of Green (1953) was most convenient, and on the basis of his tables, an atomic weight of 143 was calculated for the "average" cerium earth, 122 for the "average" yttrium earth, and 130 for the "average" rare earth.

CHAPTER 5

URANINITE FROM PEGMATITES

The analyses of uraninites from pegmatites, and tables of their 'm', 'n', 'p', and 'q' subscripts, are given in the appendix. For convenience, the subscript data for the pegmatitic uraninites in this study are tabulated below.

Table 11. Oxygen formula subscripts for pegmatitic uraninites.

Sample	Analysis	m	n	p	q
Boqueirao					
Branchville	2	2.148	2.136	2.136	2.075
Elvestad	7	2.321	2.287	2.282	2.120
Gordonia (Holmes)	39	2.496	2.438	2.384	2.222
Gordonia (USNM)	42	2.777	2.669	2.461	2.224
Grafton	36	2.681			
Hale's Quarry	37	2.261	2.233	2.226	2.176
Huggenaskilen	10	2.436	2.401	2.374	2.215
Karelia					
Morogoro	44	2.530	2.527	2.488	2.349
Newry	33	2.163	2.156	2.156	2.084
Portland	32	2.156	2.149	2.149	2.092
Spruce Pine	45	2.801	2.767	2.607	2.488
Strickland	24	2.156	2.152	2.149	2.092
Sudbury	43	2.389	2.381	2.246	2.048
Wilberforce:					
Outer 4 mm.	65	2.337	2.281	2.248	2.098
Core (>15 mm from (surface)	66	2.400	2.331	2.319	2.155

The distribution of subscripts for all the pegmatitic uraninites for which analyses are available is given by means of bar graphs in Fig. (

The 'm' value, the subscript of UO_m, 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, the rare earth, the lead, and even to some extent the oxygen ion make some adjustment, but the major change as oxygen increases is the reduction in diameter as U^{+4} ions change 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 ($(U,Th,R.E.)O_p$) 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 position. However, if auto-oxidation is the explanation for the uraninites that are oxidized above the laboratory limit, then the 'q' subscript ($(U,Th,R.E.,Pb)O_q$) would indicate the original oxidation state of the uraninite, the oxidation state that was in equilibrium with the environment when the uraninite crystallized. A word of caution is necessary; if non-radiogenic or 'ordinary' 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 uraninites.

In general, the 'm' values are distributed from 2.14 to 2.80, with

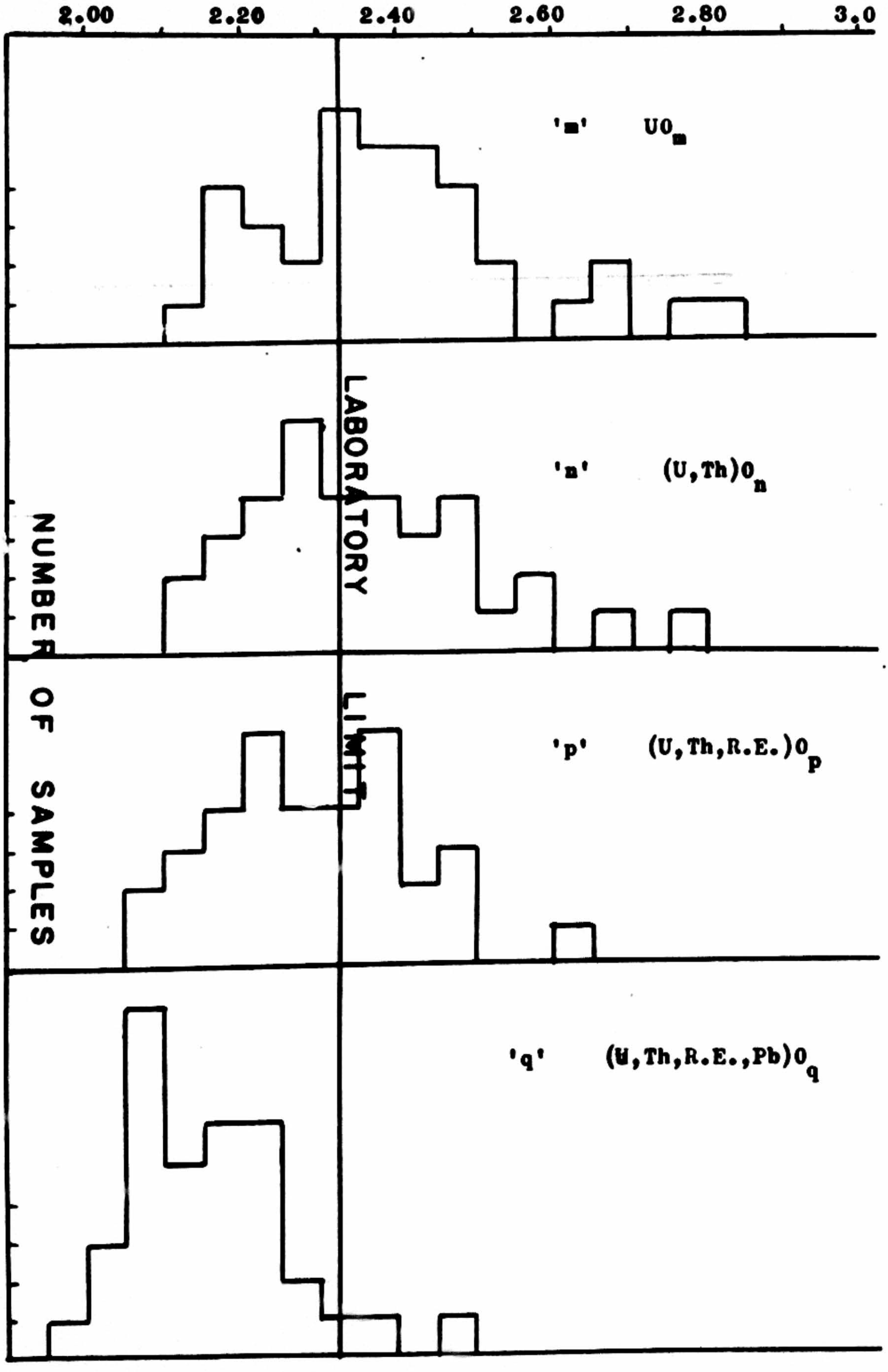

Figure 6. Formula subscripts calculated for available pegmatitic uraninite analyses.

a decrease in frequency of occurrence above 2.30. As mentioned before, a very considerable portion is above the laboratory limit of $UO_{2.33}$. In the calculation of the 'p' values, 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.

Auto-oxidation, therefore, can account satisfactorily for pegmatitic uraninites oxidized above the apparent stability limit. It can be said, cautiously, that a study of the available analyses reveals no great objection to the auto-oxidation hypothesis, and gives it a certain amount of rather negative support.

The 'q' values, the indicies of the original oxidation state, form a bimodal distribution curve with very sharp cutoffs at 2.00 and 2.25, the values for UO_2 and U_4O_9. Of the 34 analyses, 9 fall between 2.05 and 2.10, making a distinct peak on the distribution curve (Fig. 6). The number of samples is not large enough to insure that the peak is significant, but possible explanations suggest themselves. The samples near the $UO_{2.25}$ cutoff may have crystallized as U_4O_9, those of the $UO_{2.05}$ peak as UO_2. The displacement of the $UO_{2.05}$ peak may have been due to environmental oxidation after crystallization.

The distribution of "q" values lends some support to Wasserstein's (1955) hypothesis that uraninites crystallized as UO_2 or U_4O_9, and were auto-oxidized from there. However, it is probably not true of all uraninites.

REGIONAL SIMILARITIES

The unrepresentative concentration of analyses from the Connecticut Valley and from the Moss District, Norway, is unfortunate. However, it provides an opportunity to study the analyses for regional similarities.

The pegmatites of the Connecticut Valley have been assigned ages averaging about 300 million years (Acadian). Those of the Moss District and of Wilberforce, Ontario are approximately 1000 million years old. (Mid-precambrian) The analyses therefore show far more PbO in the Norwegian samples than in those from Connecticut, and the PbO quantities are fairly uniform within the group, averaging about 3% for the Connecticut samples and 9% for the Norwegian samples. Also, as might be expected from auto-oxidation, the Norwegian samples are considerably more oxidized; however, when a correction is made for auto-oxidation (the 'q' values), there seems to have been no great difference between the two groups, although those from Norway may still have been more oxidized originally.

Beyond these similarities, which are imposed by the physics of radioactivity, there are no characteristic features of analyses of one district which clearly distinguish them from those of the other.

Table 12 (Cont)

Analysis	m	q	ThO_2	R. E.	PbO	Locality
			Wilberforce, Ont.			
14	2.439	2.136	10.60	4.02	10.95	Wilberforce
18	2.342	2.067	11.40	4.56	10.40	Wilberforce
65	2.337	2.098	13.5	1.9	9.47	Wilberforce
66	2.400	2.155	13.4	0.7	9.47	Wilberforce

UNIT CELL SIZE BEFORE AND AFTER ANNEALING

X-ray powder photographs were taken of the samples before and aft heating in the inert atmosphere furnace. Runs were continued until sharp lines showed far into the back reflection region; experience indicated that no further change in the unit cell could be expected afte this stage. Table 13 lists the furnace runs and the resulting unit ce size of the cubic phase. If lines belonging to a phase related to U_3O appeared, their intensity is given, relative to the cubic phase.

Table 13. Unit cell sizes of pegmatitic uraninites, before and after furnace runs.

Sample	Time, hr.	Temp., °C.	a_o, A.	U_3O_8 lines
Boqueirao	unheated		5.488	
	12	540	5.474	
	2 1/2	900	5.455	
Branchville	unheated		5.476	
	21	550	5.448	
Elvested	unheated		5.484	
	5 1/2	500	5.465	
	5 1/2	500		
	8	650	5.455	W
Gordonia (Holmes)	unheated		5.491	
	21	550	5.474	
	2	900	5.463	

Sample	Time, hr.	Temp., °C.	a_o, A.	U_3O_8 Lines	Δa_o, A.
Gordonia (USNM)	unheated		5.454		
	2	500	5.438		
	4 1/2	500	5.438		
	10	500	5.438		
	28	500	5.438		
	2 1/2	900	5.435		.019
Grafton	unheated		5.443		
	4	440	5.433		
	20	540		exclusively	
Hale's Quarry	unheated		5.484		
	2	900	5.451		.033
	7	500	5.451		
Huggenaskilen	unheated		5.470		
	6	500	5.454		
	6 +20	500 650	5.447	W	.033
Karelia	unheated		5.491		
	24	540	5.490	W	.001
	4	900	Cubic pattern,	lines too broad	
Morogoro	unheated		5.445		
	24	540	5.435	M	.010
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		
	28	550	5.467		
	2	900	5.460		.026
Mean probable error	± 1/4	20	0.002		

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 A.), the unit cell decreases 0.03 to 0.035 A. 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. An attempt is made to present this information graphically in Fig. 7.

Table 13 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 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 α-UO_2, with random oxygens in the interstices, to β-UO_2, or U_4O_9, in which the interstitial oxygens are ordered. The transition is brought about under the same range of conditions--heating the sample to 1000°C. in an inert atmosphere or vacuum; presumably lower temperatures would be sufficient. The transition is characterized by a contraction of the unit cell of 0.034 A., from 5.469 to 5.435. These values are strongly reminiscent of many of the annealing results.

As a possible hypothesis, it is suggested that natural uraninites correspond to α-UO_2, and on annealing become the ordered phase β-UO_2.

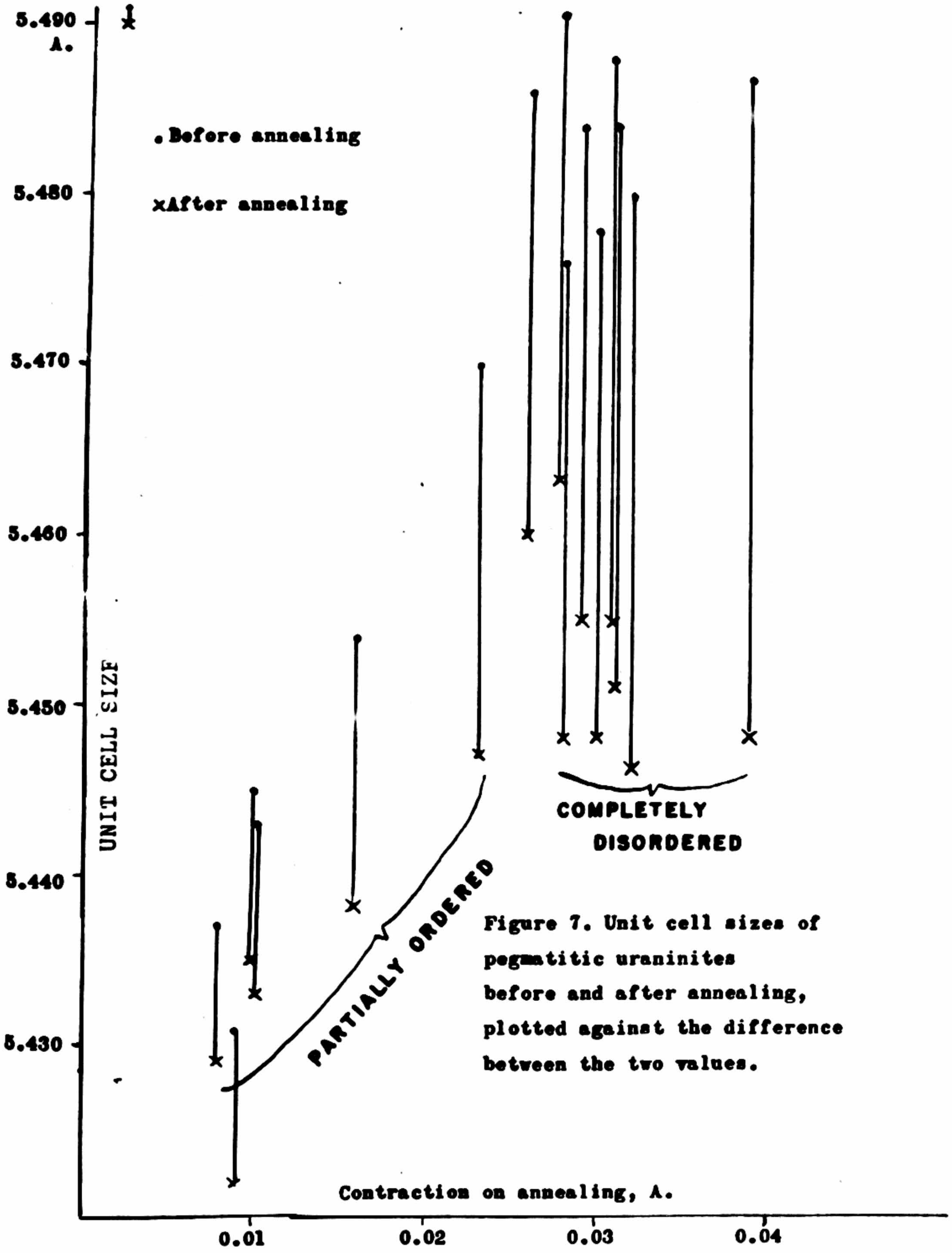

Figure 7. Unit cell sizes of pegmatitic uraninites before and after annealing, plotted against the difference between the two values.

The fact that the unit cell sizes of the natural uraninites do not correspond precisely to those of α and β-UO_2 can be attributed to the other elements that the natural materials contain in solid solution. The hypothesis can be tested by calculating whether these impurities can account for the difference.

Vegard's Law (Vegard and Dale, 1928) provides an empirical method for calculating the unit cell size from the composition. Briefly stated, Vegard's Law maintains that the unit cell size of isotropic substances varies as a straight line function of the composition, expressed molecularly. Zen (1956) has raised objections on theoretical grounds, pointing out that a straight line function can be expected only for very similar substances, or close to one of the end members; however, Vegard's Law will be used in this work as a satisfactory empirical approximation.

Theoretical unit cells sizes will be calculated for each of the analysed pegmatitic uraninites, first assuming that the uranium is present as α-UO_2 , and then as β-UO_2. These calculated unit cell sizes will then be compared to the measured cell sizes before and after annealing.

It is first necessary to fix the values of the end members of the solid solution series. The unit cell size of α-UO_2 is 5.469 A.; that of β-UO_2, 5.435 A. ThO_2 has a cell edge of 5.601 A.

For calculation purposes, it is onee again necessary to assign a value to the "average rare earth". Pure CeO_2 has a cell edge of 5.426 A., but the presence of other rare earths decreases the cell size considerably; ordinary, impure cerium dioxide has a cell size of 5.40 or less.

PrO_2 has a cell edge of 5.372 A. A value of 5.38 A. for the cubic "average rare earth" dioxide was used in these calculations.

Evidence has already been presented that the cell size of α-UO_2 does not change appreciably as oxygen ions lodge in the structural interstices. A similar assumption will be made for β-UO_2, although there is no direct evidence for this. However, it has been observed that the unit cell of U_4O_9 is nearly constant, and unless it is assumed that this phase is restricted to a single fixed composition, it can be inferred that deficiency or excess of oxygen has little effect on the unit cell size. There is apparently a neat balance between the extra oxygen ion, which would tend to expand the structure, and the change from U^{+4} to U^{+6}, which contracts it.

No such mechanism is available in the case of lead. Allowing for lead in the calculations was a problem; it was uncertain which of the various lead oxides to use as an end member. There is even some doubt as to the valence of the lead. Furthermore, none of the oxides are isometric or isostructural with uraninite. Vegard's Law could at best be applied only loosely. However, exploratory calculations showed that it was not necessary to make any correction for the lead; the lead content, like the excess oxygen, apparently has no effect on the unit cell size. The lead was therefore assumed for calculation purposes, not to be in the uranium positions in the structure, although some of it must certainly have come into existence there with the disintegration of the uranium atom. This and several other independent lines of evidence all show that radiogenic lead exsolves. The problem will be discussed further in Chapter 7.

The principal assumptions underlying the calculations can be listed as follows:

1. The validity of Vegard's Law.
2. The cell edges for the pure end members:

α-UO_2, 5.469 A. β-UO_2, 5.435 A. ThO_2, 5.601 A.

3. For the putative end member $(R.E.)O_2$, the cell size, for purposes of calculation, is 5.38 A.
4. Excess or deficiency of oxygen does not affect the unit cell size of α or β-UO_2.
5. Lead, including radiogenic lead, is not in the uraninite structure.

A sample calculation, for the Hale's Quarry specimen, is presented as table 14.

Table 14. Sample Vegard's Law Calculation. Hale's Quarry.

	Hillebrand's Analysis (1891) Wt.%	Relative No. of metal atoms	
UO_2	59.13	21894)	) 29612
UO_3	22.08	7718)	
ThO_2 (CeO_2)	9.09	3442	
$(La,Y)_2O_3$	0.55	357	

	Assuming alpha UO_2			Assuming beta UO_2		
	No. atoms X end member a_o			No. atoms X end member a_o		
U	29612	5.469	161948	29612	5.435	160941
Th	3442	5.601	19279			19279
R.E.	357	5.38	1921			1921
TOTAL	33411		183148			182141

Table 14 (Cont.)

Tot. 33411	183148	33411	182141

$$\frac{183148}{33411} = 5.482 \qquad \frac{182141}{33411} = 5.452$$

Measured unit cell sizes for Hale's Quarry sample

Before annealing	5.484 A.
After annealing	5.451

Table 15 lists the calculated and measured unit cell sizes for the analysed pegmatitic uraninite samples.

Tagle 15. Calculated and measured unit cell size, A.

Sample	Calculated assuming α-UO_2	Measured before annealing	Calculated assuming β-UO_2	Measured after annealing
Hale's Quarry	5.482	5.484	5.452	5.451
Branchville	5.479	5.476	5.446	5.446
Elvestad	5.479	5.484	5.450	5.445
Portland	5.475	5.476	5.442	5.446
Newry	5.475	5.460	5.442	5.446
Strickland	5.474	5.488	5.442	5.446
Wilberforce (outer)	5.467	5.466	5.460	5.460
Huggenaskilen	5.477	5.470	5.446	5.447
Gordonia (USNM)	5.466	5.454	5.436	5.436
Sudbury	5.456	5.437	5.430	5.429
Morogoro	5.460	5.445	5.435	5.435
Gordonia(Holmes)	5.476	5.491	5.450	5.444
Spruce Pine	5.463	5.431	5.434	5.422

The measured value after annealing and the calculated value assuming β-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 β-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 β-UO_2 or U_4O_9 structure, perhaps with an excess or deficiency of oxygens. The annealing process is therefore a disorder-order transformation. It does not reverse on cooling; the disordered state is metastable.

Before annealing, some of the samples have unit cell sizes corresponding to α-UO_2; these are the first group listed in Table 15. Presumably, the interstitial oxygens are completely disordered in these samples. The second group of samples in Table 15, before annealing, have values intermediate between α and β-UO_2. When they are annealed, they complete the rest of the journey to the calculated value for β-UO_2. It is reasonable to assume that these samples reach us in a partially ordered condition.

One index of the degree of ordering is the amount of the decrease of the unit cell size on annealing. In Fig. 7, the cell sizes before and after annealing are plotted against this quantity. They tend to fall along two straight lines (which, of course, diverge; the graph is somewhat tautological). The totally disordered samples fall to the right in this graph; they have contractions of .035 A. or thereabouts on annealing. The partially ordered samples, from the second group of Table 14, contract less on annealing, and fall along the rest of the lines.

The calculations have shown, however, that the cell size of the annealed samples is entirely (for practical purposes) a function of composition. Since the degree of annealing varies as the annealed cell size, it also is a function of composition. The samples which reach us with completely disordered interstitial oxygens have large unit cells even after annealing. This can be explained if they have high thorium compared to rare earths. If the rare earths are higher than usual compared to the thorium, the samples have small unit cells after annealing; these are the samples that are already partially ordered before annealing.

In table 16, two quantities are compared. One is the weight percent of rare earths divided by the weight percent ThO_2. The other is the degree of disorder, as indicated by the actual contraction of the unit cell divided by the theoretical (calculated) contraction.

Table 16. R.E./ThO_2 ratio and degree of ordering.

Sample	$\frac{R.E.}{ThO_2}$	$\frac{\text{Actual contraction}}{\text{Theoretical contraction}}$
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		
Huggenaskilen	0.22	0.74
Gordonia (USNM)	0.90	0.53
Sudbury	4.7	0.29
Morogoro	5.0	0.30

The degree of ordering of a sample as it is found in nature is apparently determined by the R.E./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 16 that the past history influences the degree of annealing.

Radioactivity may have the effect of disordering samples, which are completely ordered. The R.E./ThO_2 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. It may be interesting for someone to re-examine the annealed samples several years hence. They are being left with the specimens in the confidence that Harvard will continue its present policy of never throwing anything away. The work was done in the spring and summer of 1956.

Thorium dioxide is an extremely refractory substance. It has a very stable structure, with strong inter-atomic bonds. The presence of thorium in solid solution would, therefore, tend to stabilize the uranium dioxide structure. Furthermore, since the ordered phase Th_4O_9 is unknown, thorium would tend to lodge by preference in the - α -UO_2 structure, and enlarge its stability field. The fact that ThO_2 has a unit cell size more similar to the α than the β form would tend also to increase the stability of the α form, but this effect is probably slight.

The rare earth dioxides, on the other hand, are much less stable than UO_2. They are known in a pure state only for CeO_2 and PrO_2. They have unit cells closer to the beta form. The presence of rare earths would tned to make the alpha structure less stable, and easier to transform into the ordered phase.

The R.E./ThO_2 ratio may control not only the degree of annealing under natural conditions, but also the ease of annealing the sample the rest of the way in the laboratory.

There remain the samples of the small third group of Table 14, whic do not fit the calculated values satisfactorily. A number of possible explanations can be offered; poor analyses, non-uniform samples, and the existence of an amorphous phase with a disproportionate amount of certain elements. In certain of the samples, a very high thorium content may have prevented complete annealing.

CHAPTER 6

PITCHBLENDE

Pitchblende is a varietal term covering the vein and sedimentary occurrences of uraninite. Pitchblende differs from pegmatitic uraninite in having low or absent ThO_2 and rare earths, high CaO, small crystal size and small unit cell size.

Table 17 shows the average ThO_2, rare earth, and CaO content for the pegmatitic uraninite and pitchblende analyses in the appendix. Analyses for which there were indications of serious contamination of $CaCO_3$ were excluded.

Table 17. Average ThO_2, rare earth and CaO content. Wt. %

	ThO_2	R.E.	CaO
Pegmatitic uraninites	6.00	4.05	0.43
Pitchblendes	0.18	0.92	1.96

The possibility of the substitution of Ca in the U positions of UO_2 must therefore be considered. The Ca $^{+2}$ ion has almost the same atomic radius as the U^{+4} ion; for a coordination number of 6, the radius of both is 1.01 A., according to the tabulation in Dana's System (7th ed.). However, the charge differs by two units. There are two possible mechanisms of compensation; either a structural (in contrast to an interstitial) oxygen must be omitted, or a U^{+4} ion must be oxidized to U^{+6}.

Alberman, Blakely and Anderson (1951) have investigated the UO_2-CaO system. Appropriate amounts of UO_2 and CaO were mixed, pelletized, and heated to 1650-2500°C. by a filament in a vacuum furnace. The product was then x-rayed to determine whether the two phases had combined completely. They found that CaO could be incorporated into UO_2 to the extent of 20 molar percent at 1650°C., and up to 47 molar percent at

2080°C. As the CaO content rose, the unit cell decreased somewhat. Table 18 gives the unit cell sizes measured after runs at 2080°C.

Table 18. Change of unit cell with CaO content. 2080°C., presumably measured at room temperature. (Alberman, Blakely and Anderson, 1951)

Mol. % CaO	a_o, A.
0	5.4683
5.4	5.4626
20	5.4427
30	5.4325
40	5.4229
47	5.4202

This decrease is probably due to oxygen vacancies in the structure. The vacuum was probably high enough to prevent, at this temperature, any valence compensation by the oxidation of U^{+4}. Certainly the decrease shown in the figures above is not sufficent to account for the low unit cell sizes of natural pitchblendes. It may be that compensation in natural material is effected by oxidation and contraction of the uranium ion, rather than by oxygen omissions.

DISTRIBUTION OF SUBSCRIPTS

Since pitchblendes contain insignificant amounts of rare earths and thorium, the 'm', 'n', and 'p' subscripts are virtually identical. The q values are known, in many cases, to be influenced by non-radiogenic lead.

In nearly half the cases, only UO_2 and UO_3 determinations are avail able, and therefore only the 'm' value can be calculated. A distributio graph of these 'm' values for the pitchblende analyses in the appendix i given as Fig. 8. Not enough analyses are available to construct a meaningful graph of 'q' values. Table 19 gives the subscripts of analyzed pitchblendes available for study.

Table 19. Subscripts for studied samples.

Anal		m	q
	Vein		
37	Wolsendorf	2.636	2.636
38	Pied des Monts	2.219	2.012
40	Katanga	2.742	2.451
41	Joachimsthal	2.000	1.916
62	Great Bear Lake	2.326	2.196
55	Theano Point	2.667	2.496
67	Przibram	2.610	2.421
68	Wood Mine	2.282	2.266
69	Schmiedeberg	2.311	2.166
	Sedimentary		
25	Happy Jack	2.359	2.345
34	Mi Vida	2.172	2.156
35	Big Indian	2.334	2.314

THE $UO_{2.6}$ 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_3O_8 is $UO_{2.667}$.

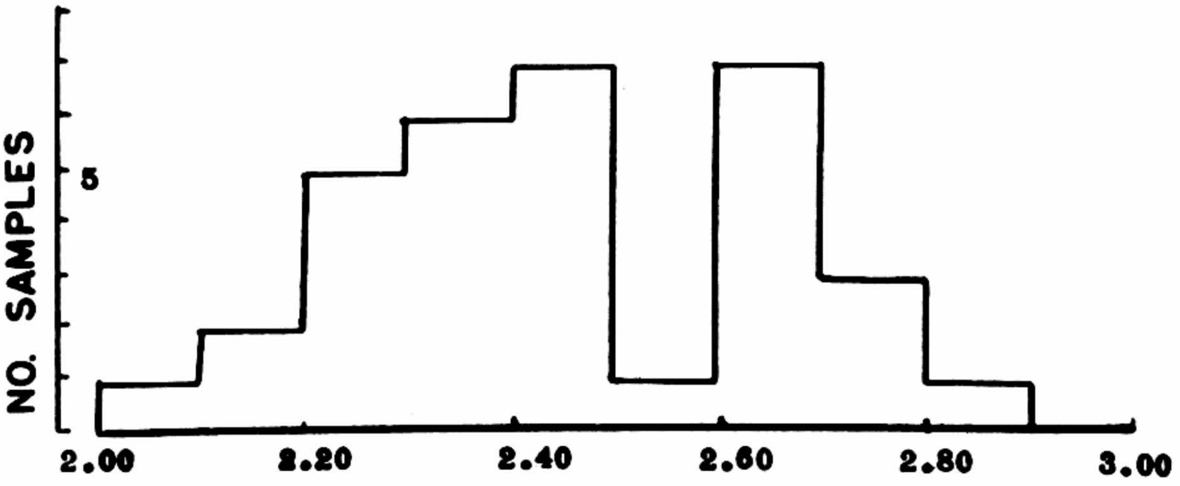

Figure 8. Distribution of 'm' subscripts in analysed pitchblendes.

The samples included in this peculiar cluster are listed in Table 20.

Table 20. Analyses with 'm' values between 2.6 and 2.7.

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

Samples available for study are underlined.

When the author began this project, there was considerable discussion of the possibility that a sample of uraninite might be found with a composition in, or close to, the actual stability field U_3O_8. It now appears that such samples are fairly common; out of the thirty-two pitchblende analyses available, seven fall into this group. 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. ($UO_{2.667}$)

Whatever these samples may have been originally, they are not now U_3O_8. Of the eight samples, including the Grafton sample, those from Wolsendorf, 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 Fig. 5.

None of these patterns show U_3O_8 lines. All except the Wolsendorf sample show somewhat weak and diffuse UO_2 patterns. No pattern was obtainable from the Wolsendorf sample. On annealing, the Theano Point, Martin Lake, Przibram and Grafton samples showed a sharp cubic pattern with a decreased cell size, and, in addition, a strong U_3O_8 pattern. The Wolsendorf sample showed the U_3O_8 pattern exclusively. The other samples were not available for annealing. If these samples crystallized as U_3O_8, they have since dissociated into the cubic phase and an amorphous phase richer in U^{+6}. The cubic phase anneals in the usual manner, while the amorphous phase is crystallized into U_3O_8. The Wolsendorf sample probably represents an incomplete stage in the dissociation, in wh the cubic phase has not yet crystallized in large enough grains to produce a good powder pattern.

'METAMICT' URANINITE

Conybeare and Ferguson (1950) report some 'metamict' pitchblendes from Saskatchewan. As [illegible] metamict zircons or niobate-tantalates, the x-ray pattern was very faint or nonexistent. On heating, a strong pattern developed. As in other metamict minerals, it was not necessarily the pattern of the original material. Like the other metamict minerals, it is strongly radioactive. The Wolsendorf sample is presumably an example of this 'metamict' uraninite.

Is it correct and proper to apply the term 'metamict'? Technically, the Wölsendorf sample falls within the definition, for the definition, quite properly, refers only to observable phenomena and not to mechanisms or causes. (Brögger, cited in Pabst, 1952.) Nevertheless, the author does not believe that the mechanism of the structural disordering of the Wolsendorf sample was analogous to the metamictization of an allanite or a fergusonite.

Metamictization is a process comparable to the disordering of the interstitial oxygens by alpha particles, as suggested in the last chapter. Alpha particles are capable of breaking the weaker interatomic bonds and disrupting some structures. The fact that the structural oxygens remain in place suggests that the uraninite structure itself is not subject to this type of self-disruption. All of the uraninite samples are virtually as radioactive as the Wolsendorf sample, but all the others give x-ray patterns.

The Wölsendorf sample is peculiar not in its radioactivity but in its composition, which indicates that it crystallized with a structure which became unstable under changing conditions. It would be misleading to use the term 'metamict' in this case.

The seven samples of the 'U_3O_8 cluster' have the right composition to form U_3O_8. In the distribution curves, there is evidence that they may have been U_3O_8 at one time. The fact that they 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 conditions 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 volcànic activity; even here, the usual product would probably be hydrated uranyl compounds.

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 21.

Table 21. Unit cell size, A., of pitchblendes before and after furnace runs.

Sample	Time (hr.)	Temp. (°C.)	a_o(A.)	±	Δa_o,A.
Vein Pitchblendes					
Great Bear Lake	unheated		5.425	.005	.019
	14	540	5.406		
Joachimsthal	unheated		5.418	.005	
	20	550	5.418		.000
Katanga	unheated		5.448	.005	
	8	500	U_3O_8		
" leached 40hr in 0.4N H_2SO_4	5	550	5.435		.013
Pied des Monts	unheated		5.468	.005	
	7	500	5.454		
	10	600	5.450		.018
Przibram	unheated		5.413	.005	
	15	540	5.381		.032
Rix Athabaska	unheated		5.431	.002	
	10	550	5.392		.039
Schmiedeberg	unheated		5.430	.005	
	6	500	5.401		.029
Theano Point	unheated		5.405	.005	
	6	540	5.390		.015
Wolsendorf	unheated		no pattern		
	9	540	U_3O_8		
Wood Mine	unheated		5.448	.005	
	8	540	5.413		.035
SEDIMENTARY PITCHBLENDES					
Big Indian	unheated		5.39	.01	
	14	540	5.38	.01	.01

Table 21 (Cont.)

Vein Pitchblendes

Happy Jack		unheated	5.407	.01	
	10	535	U_3O_8		
Mi Vida		unheated	5.399	.005	
	7	540	5.391		.008
Royal Claims		unheated	5.40	.01	
	4	440	5.38	.01	.02
Shinarump No. 3		unheated	5.399	.005	
	7	540	5.391		.008

To summarize, the vein pitchblendes have unit cell sizes of approximately 5.425 A. On annealing, they behave much as the pegmatitic uraninites. The unit cell contracts as much as 0.035 A., resulting in values of 5.39 or 5.40 A. Sedimentary pitchblendes from the Colorado Plateau have significantly smaller unit cells before heating. In these cases, the values are close to 5.40 A. On annealing, they contract comparatively little, about 0.01 A. 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 essential 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.

The same mechanism cannot be used to explain the difference in unit cell size between the pegmatitic and vein types, although the difference is about the same in magnitude. Vein types are not annealed pegmatitic types because they themselves anneal. Once the interstitial oxygens are ordered, they cannot be still further ordered.

An examination of the analyses suggests three chemical components that might explain the small unit cell of pitchblendes; calcium, iron and silicon. Calcium, as has been pointed out, is somewhat higher in pitchblendes than in pegmatitic uraninites. From the data of Table 18, it is possible to derive the unit cell of a hypothetical 'fluorite type CaO end member' for calculation purposes. This hypothetical material would have a unit cell of 5.365 A. This value was applied in Vegard's Law calculations to six pitchblende samples. The results are compared with the measured cell sizes in Table 22.

Table 22. Calculated and measured unit cell sizes, a_o, in A.

Sample	%CaO	Calculated assuming $\alpha\text{-UO}_2$	Calculated assuming $\beta\text{-UO}_2$	Measured before annealing	Measured after annealing
	Vein pitchblendes				
Katanga	0.40	5.466	5.433	5.446	5.435
Joachimsthal	4.28	5.443	5.418	5.418	5.416
Great Bear Lake	5.1	5.443	5.417	5.425	5.406
	Sedimentary pitchblendes				
Happy Jack	2.22	5.457	5.427	5.407	-----
Mi Vida	3.0	5.453	5.424	5.405	5.401
Big Indian	4.4	5.447	5.420	5.39	5.36

It will be shown that the Joachimsthal sample is probably $\alpha\text{-UO}_2$, and therefore the agreement with the calculated $\beta\text{-UO}_2$ value is probably fortituous. Aside from this, and the Katanga specimen which contains little CaO, the measured values are considerably lower than the calculated values. The CaO can account for only a fraction of the lowering of the unit cell size, although usually it is a substantial fraction. The neat agreement between calculated and measured values in the case of pegmatitic uraninites is lacking in the case of pitchblendes, so that it cannot be proven that CaO actually does account in part for the unit cell size. One can say with certainty only that it is not the only factor.

It is possible that there are structural factors other than order and disorder of the interstitial oxygens. The fluorite-type structure itself may be defective in the pitchblendes. Attempts were made to observe a second round of annealing effects by heating at the top of the range of the furnace, 900°C., for several hours. Unfortunately, the equipment was not sufficiently impermeable to prevent additional oxidation under these extreme conditions, and the samples were slowly converted to U_3O_8.

The Joachimsthal sample.

The 7th edition of Dana's System of Mineralogy states, in its article on Uraninite, "Uranium dioxide, UO_2. The natural material always is more or less oxidized, and the actual composition lies between UO_2 and U_3O_8." On the basis of the analyses available in the literature at the time the article was prepared, the least oxidized sample was about $UO_{2.15}$. The statement that natural uraninite always contain U^{+6} reflected the published and unpublished opinion of virtually all workers in the field. It seemed to follow necessarily from the auto-oxidation hypothesis.

On March 6, 1956, Harry Levine, of the U. S. Geological Survey, reported his analysis of the Joachimsthal sample, which is given as analysis 41 in the appendix. According to this analysis, the Joachimsthal sample is not oxidized. UO_2 was reported as 70.2%, and UO_3 as less than 0.1%. This was clearly contrary to all past experience and preconceived notions. The fact that it was a rather dull, greasy-appearing pitchblende rather than a sharp, shiny crystal from a pegmatite reinforced the opinion that the analyst was in error. The problem was discussed in several days of conference with various personnel of the Geological Survey.

Methods of analysis were discussed in relation to this specific sample. The determination of UO_2 and UO_3 takes the form of separate determinations for U^{+4} and total U. For the U^{+4} determination, the sample is dissolved in sulfuric acid, and a known amount of ceric sulfate is added. The U^{+4} is oxidized to U^{+6}, and the Ce^{+4} ion is reduced to Ce^{+3}. The mixture is then titrated with a solution containing ferrous ion, which reduces the remainder of the Ce^{+4} to Ce^{+3}. From the quantity necessary, the amount of Ce^{+4} consumed in oxidizing the U^{+4}, and therefore the amount of U^{+4}, can be calculated. In the case of the Joachimsthal sample, the U^{+4} was found to be almost precisely equal to the total amount of U. If it had been greater than the total U, one might suspect that some other ion beside uranium had been oxidized by the ceric sulfate. It is hardly reasonable to expect it to balance exactly, however.

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 necess 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 analyzed sample reported in th literature. It was the opinion of the chemists that, if the iron was present as pyrite, the reaction with ceric sulfate would be too slow to interfere with the uranium determination.

The author requested that the results be confirmed by a different method. The method of Brooker and Nuffield (1952) depends on the fact that UF_6 is soluble and UF_4 is not. Ordinarily, when uraninite is dissolved in hydrofluoric acid, the UF_4 separates out as a green precipitate which can be weighed. However, the chemists stated that unless the sample contained some U^{+6}, it would not dissolve in the hydrofluoric acid. The test was tried; the Joachimsthal sample remained in hydrofluoric acid on a steam bath for half an hour. It did not dissolve.

Still further evidence is furnished by the behavior on annealing. Before annealing, the unit cell was 5.418 ± 0.005 A. On annealing for 20 hours at 550°C., the lines sharpened somewhat, but there was no change in the cell size. After annealing, the unit cell was 5.418 A. ± 0.002. This is the only sample, with the possible exception of the one from Karelia, which does not contract on annealing. This may mean that the interstitial oxygens are already fully ordered. Or it may mean that there are no interstitial oxygens, as the chemical analys indicates. It is indeed the type of behavior to be expected if the analysis is correct.

During the discussions, the chemists mentioned that they had analyzed a similar sample for Phair of the U. S. Geological Survey. It was a pitchblende from the veins of Jamestown, Colorado, where it occurs with purple fluorite. The sample behaved in the same way and was reported as having no UO_3. Phair doubted the validity of the result, and continues to doubt it. The analysis was never published.

It seems strange that there are no published analyses distinguishing between U^{+4} and U^{+6} for the very important locality at Joachimsthal. Among the samples in the very generous gift from the National Museum were several Joachimsthal specimens marked 'analyzed by Hillebrand'. But the analyses could not be found in Hillebrand's published writings. Instead, in the 1891 reference (P.73) there is a note referring to them as follows. "Owing to the uncertainty of being able to determine with any close approach to the truth the proportions of UO_2 and UO_3 in the presence of sulphides, the compounds of arsenic and vanadium of unknown degree of oxidation, no quantitative analyses have been carried out, but the attempt will yet be made to solve their composition." Once again, analyses were made, but not published. Since the number of available pitchblende analyses is so small, one must be wary of eliminating analyses because of subjective judgment; there is a danger of introducing a serious statistical bias into the available data. Unoxidized pitchblende may be an unexceptional, even a fairly common phenomenon. The fact that they have not appeared in the literature may reflect the limitations, not so much of uraninites, but of scientists.

If this analysis is accepted, how can it be reconciled with auto-oxidation? The author does not know the answer to this question. He, too, has his limitations.

CHAPTER 7

THE ROLE OF LEAD

In chapter 5, it was shown that the unit cell size 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 was 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 Huggenaskilen sample is $(U,Th, R.E.)O_{2.374}$, but $(U,Th, R.E.,Pb)O_{2.215}$. On annealing, it decomposes into U_4O_9 and a smaller amount of U_3O_8. It behaves like $UO_{2.374}$ rather than $UO_{2.215}$. The 'p' subscript, rathan the 'q' subscript, also seems to control the extent of differential leaching of UO_3 from 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 UO_3 and other things that cannot be mad 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.

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. ThO_2 gives extremely sharp diffraction lines. It is a very stable, refractory substance, and it seems reason able to assume that it is entirely crystalline. If, then, it were mixed with a chemically equivalent amount of UO_2, and the 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.

A portion of each of the available analyzed samples was ground fine and weighed. An amount of ThO_2, chemically equivalent to the uranium, thorium, and rare earths, was weighed out and mixed with the sample in a porcelain dish with a steel needle, until the black sample and white ThO_2 appeared as a homogeneous gray powder to the naked eye.

This mixture was tamped into a standard Norelco diffractometer specimen holder with a small hand press. The sample was then run in the vicinity of known pairs of lines, at $1/8^{\circ}$ per minute, at various appropriate settings, depending on conditions. The settings were never changed between a ThO_2 line and the equivalent uraninite line. After the diffractometer run, lines were drawn on the chart representing the local background for each pair of peaks, and any slightly overlapping peaks were divided in such a way that the areas subtended by the normal contour of the peaks were represented. The area under each peak was then measured. At first, a planimeter was used, but it proved easier and more accurate to count the squares in the graph paper of the chart. In some cases, analyses were not ready; these samples were mixed with 80% by weight of ThO_2, and corrected mathematically later.

It was expected that the intensity of the uraninite peaks would be a definite proportion -- say 85% -- of the intensity of the equivalent

ThO_2 peaks, and it would therefore be possible to state that the uraninite was 85% crystalline. Unfortunately, this was 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 seemed to be a definite pattern to the 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 ratio between the peaks for (200) and (220) were almost identical. For CuK alpha radiation, the (111) peaks are at 28° 2θ, the (200) are at 33°, and the (220) are at 47°. The measured values are given in Table 23.

Table 23. Area under diffraction peaks, % of area under equivalent ThO_2 peak.

hkl	111	200	220	311
Sample				
Joachimsthal	48	35	36	
Hale's Quarry	54	37	34	34
" " , 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		

Table 23 (Cont.).

Sample hkl	111	200	220	31
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	
Synthetic Sample	117	97	37	26
CALCULATED (SEE TEXT)	69	45	45	69

The 'pattern of non-uniformity' has some structural significanc The intensity of the uraninite lines has been reduced, and some refl tions have been reduced more than others. There seems to be some so of destructive interference which is greater in some directions than others. The author suggests that natural uraninite consists of a mo of crystallites in parallel position. These are separated along cub planes by 'spacers,' monomolecular layers of massicot (orthorhombic 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 ex tents for different directions. The theoretical intensities calcula on these assumptions are given at the bottom of Table 23. There is agreement with the highest of the measured intensities, such as thos the Hale's Quarry sample. The lower intensities of most of the samp can be attributed to a combination of this mechanism and the effect amorphous material. The proposed hypothesis seems fully competent t explain the pattern of intensity variation from line to line.

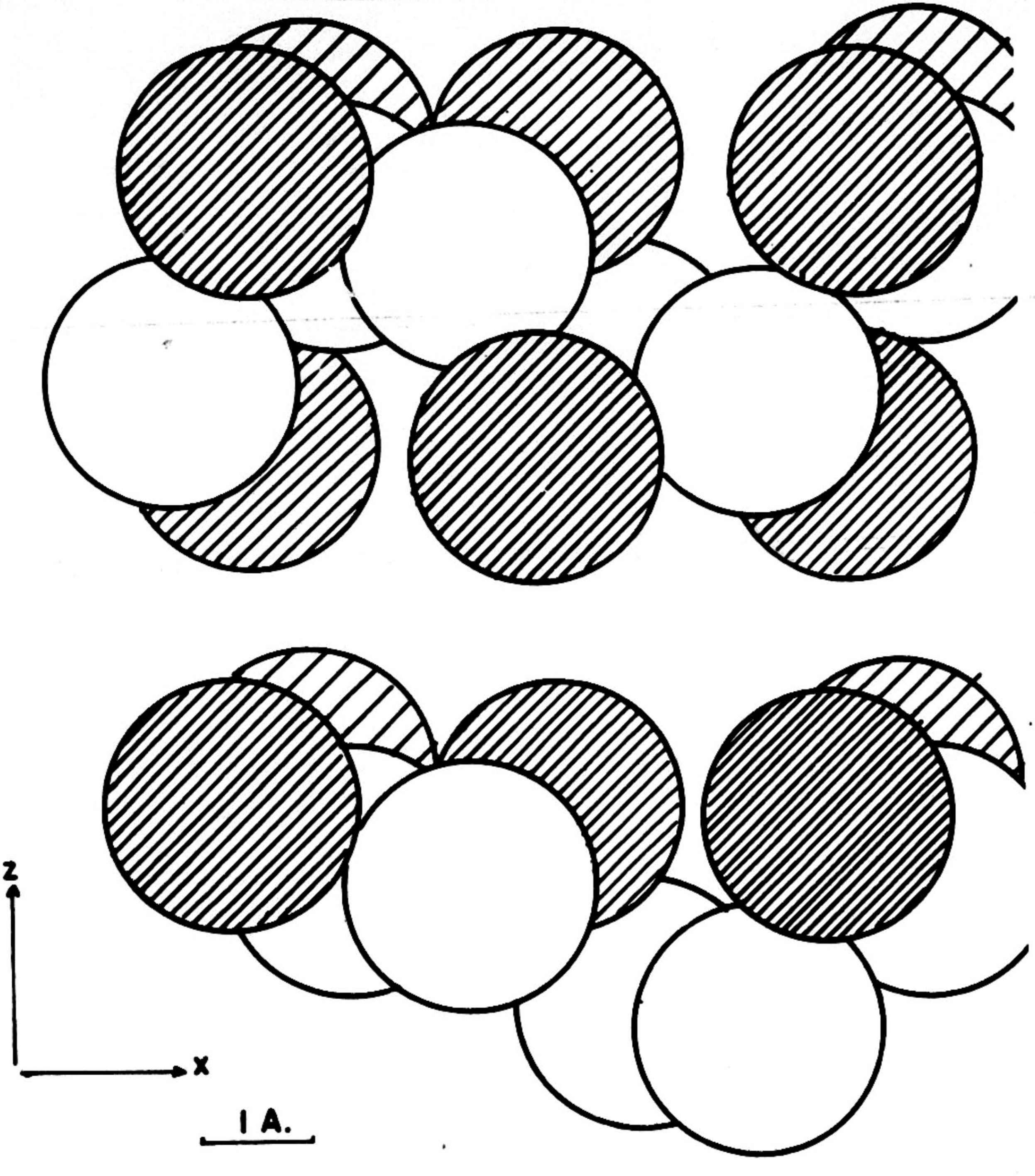

Figure 9. The structure of orthorhombic PbO (Massicot.) Pb- shaded, O- unshaded. From "Structure Reports," Vol.11,p. 239.

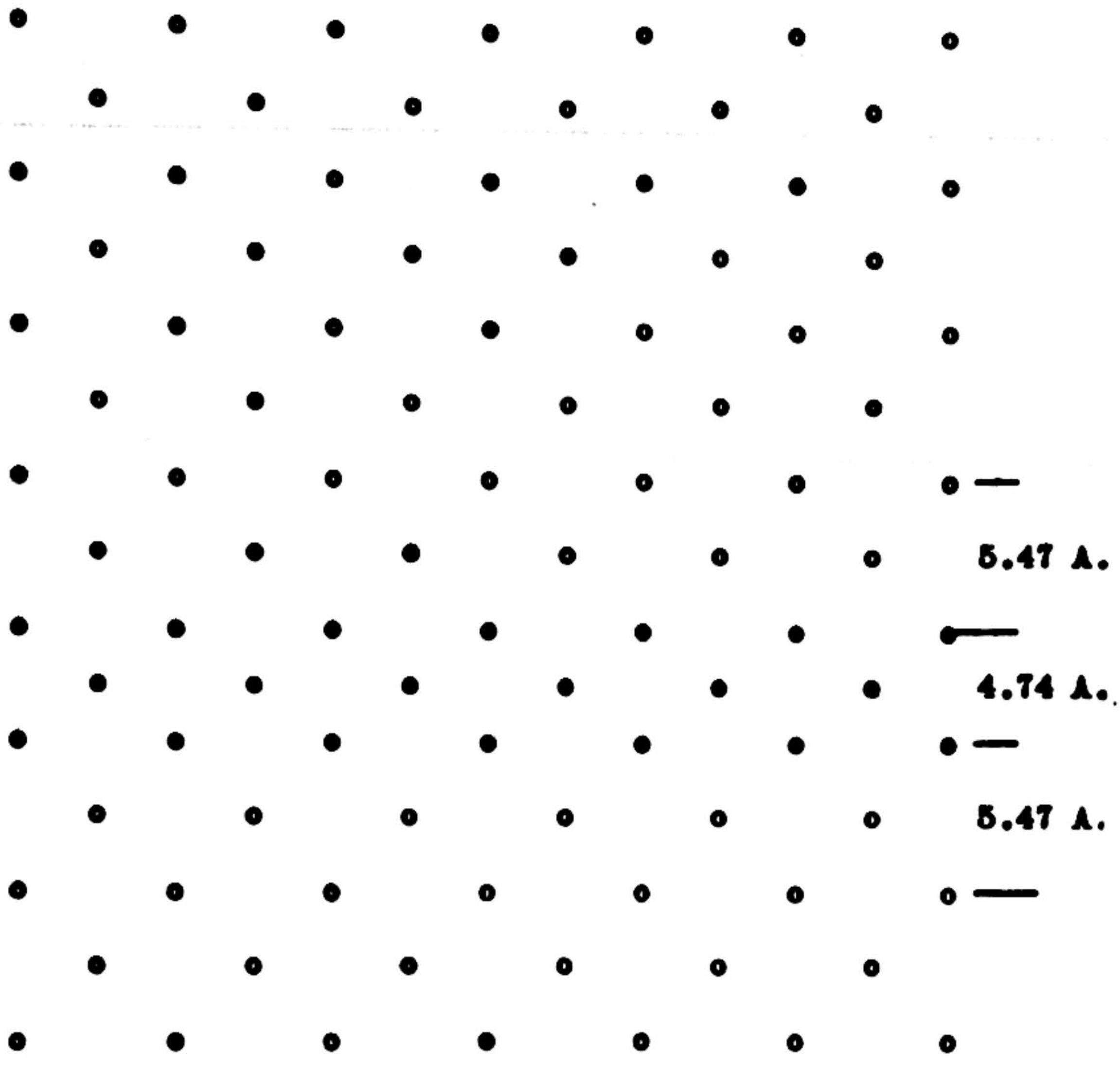

Figure 10. Cation positions of a cube plane through the uraninite structure, showing a 'spacer' of orthorhombic PbO (massicot). o– uranium. ●– lead.

Bystrom (1943) determined the structure of orthorhombic 'yellow' PbO. (Massicot) The cell dimensions are as follows; $a_o = 5.476$ A., $b_o = 4.743$ A., $c_o = 5.876$ A. Except for the b axis, it is similar in size to the UO_2 cell, which is cubic with $a_o = 5.469$ A. If the lead positions only are considered, the cell of orthorhombic PbO is very close to being face-centered. The oxygens are arranged in puckered layers between the lead layers, and these layers decrease the symmetry somewhat. The lead positions in orthorhombic PbO are related to each other almost exactly as the uranium positions in UO_2, except that the 'b' axis of the PbO is compressed. It, therefore, should be able to form an oriented overgrowth on UO_2, such that the Pb positions in the (010) plane fit into the U vacancies on a cube face of the UO_2. The overgrowth is only one cell thick in this case; the UO_2 structure of the next crystallite fits on to the 'back' of the layer in the same way, and continues, so that, among the (100) planes spaced 5.469 A. apart, there is one pair spaced only 4.743 A. apart, and reflections from one side of the 'spacer' are out of phase with those on the other side.

The calculation of intensities assumes two identical crystallites separated by a monomolecular layer of orthorhombic PbO, and compares the results with those for the crystallites joined together without the PbO. If a situation is imagined in which only two crystallites are in the beam in a Debye-Scherrer camera, and the crystallites are not equal in thickness, the intensities at that moment would not be as calculated; but when the spindle revolved 180 degrees, the effect would be precisely reversed, so that the integrated result on the film would justify the simplification. The same would apply to every other pair of crystallites in the beam.

The calculation for the (111) plane is as follows. The displacemen along the cubic axes is (5.469)-(4.743)= 0.726.A. The (111) plane is inclined $54^{\circ} 44'$ to the cube axis, and therefore the (111) planes below th spacer are 'out of step' by (.726) cos $54^{\circ} 44'$, = (.726) (.816) = 0.592

The normal spacing of the (111) planes is 3.158 A. If a (111) pla in the reflecting position is followed at 3.158 A. by another (111) pla the second plane would contribute the full intensity of its reflective power, here arbitrarily set at cos 360° = 1.00, to the intensity of 1 produced by the first plane, making a total intensity of 2. If, however, the second layer is at 3.158-0.592 = 2.566 A., it is at 292.5° rather than 360° in the harmonic cycle set up by the properly placed (111) layers, and its intensity contribution is (cos 292.5) = 0.382. Combined with the contribution of the first layer, the total intensity is 1.382 instead of 2.000, as it would be for the perfect UO_2 structure. The (111) reflection therefore has only 69% of its theoretical intensity. When this calculation is repeated for the (200) and (220) planes, it is found that they are reduced to 45% of their original intensity by the PbO 'spacer'. These values account for the distributio of intensities satisfactorily, and, in combination with the other evidence, would seem to indicate very strongly that PbO has exsolved from the uraninite structure.

Table 22 lists the intensities obtained from the synthetic sample described in Chapter 3. It is plainly not a completely crystalline U as was hoped. No explanation is offered for the anomalous results; t are given for the sake of completeness, and as an example of the sort difficulty often encountered with synthetic uranium compounds.

It would be pleasant to say that, since UO_2 does not accommodate lead in solid solution, all lead found in UO_2 must have originated in it since crystallization. This would make age determinations very much easier, but unfortunately, lead can be absorbed on the surface of a growing crystal as oriented layers of orthorhombic PbO, one or many unit cells thick, and then be incorporated into the crystal as growth continues. Instead of simplifying matters, the exsolution of lead makes it extremely important to obtain fresh, uncontaminated material for age determination, and to purify it mechanically, without recourse to acids.

It should be mentioned that superstructures offer another possible explanation for peculiar distributions of intensity. The explanation advanced above, however, dispenses with the requirement of regularity in the superimposed structure. It would work even if the crystallites varied considerable in size.

ZONING OF LEAD

Variation in lead content between different layers of a uraninite crystal has been recorded by Alter and Kipp (1936) and by Hecht and Kroupa (1936) in crystals from Wilberforce, and by Hecht (1931) in a crystal from Morogoro. These writers analyzed successive layers of their crystals, from the surface inward, dissolving the layers off with acid. They found that the lead increased inward. The use of acid leaves the results open to question, but the increase in lead is probably real, at least in part. Bakken and Gleditsch (1938) used mechanical means -- steel files and forceps -- to pick off successive layers of a uraninite crystal from Auselmyren, Norway. The layers were analyzed by microchemical methods. The results are given in part in Table 24.

Table 24. Analysis of different layers of a crystal from Auselmyren, Norway. (Bakken and Gleditsch, 1938)

Black, fresh-looking material:	UO_2	UO_3	PbO
Core	48.43	32.75	13.02
Middle layer	47.61	33.57	12.86
Outside layer	46.35	34.40	12.66
Alteration products	---	53.22	20.65

The results showed that oxidation increased outward, perhaps due to atmospheric oxidation, although the entire sample is well above the laboratory limit. They also showed that lead decreased significantly outward, until the oxidation products were reached; then it increased sharply. Bakken and Gleditsch offer two possible explanations; selective leaching, and radon leakage. They point out that 90% of the radiogenic helium has diffused out of the specimen. The helium, however, has been diffusing for a billion years. The much heavier radon atom has a half-life of four days, and could hardly have enough time to diffuse out. It is possible that the lead itself has diffused outward. At least, it would have an indefinite length of time to do so. In calculations of the rate of solid diffusion, there is a factor, a function of the difference of chemical potential, representing the tendency of ions to move through an interface in one direction rather than the other. The secondary minerals, in this case, can almost certainly accommodate all the lead necessary, while the uraninite is probably vastly supersaturated. The chemical potential of lead in the alteration products is probably considerably lower than in the uraninite, and solid diffusion of lead from the outer layers of the uraninite into the alteration products may well be sufficient to account for the zoning of the lead. Senftle and Bracken (1955) discuss the possibility of isotopic fractionation of lead by outward diffusion.

An attempt was made to detect zoning in the Wilberforce specimen, which is a large, irregular crystal with dodecahedral faces. The material within 4 mm. of the surface was removed by a diamond saw, and a sample was purified for analysis; this is reported as analyses 65. Material from the core of the specimen, more than 15 mm. from the surface, was used for analyses 66. The results are different from those reported by other workers. The lead content of the two samples is identical. The only significant difference, aside from the rare earths, between the two analyses is the oxidation state of the uranium, and in this case the outside is less, rather than more, oxidized. There were no oxidized alteration products on this specimen; the environment may have been slightly reducing.

DIFFERENTIAL LEACHING

Hillebrand (1891) observed the differential solution of UO_3 in one of his samples from Hale's Quarry (not the one re-examined). A 2-gram portion of the sample was boiled in dilute HCl until 25.5% had dissolved. The analyses before and after leaching are presented below as Table 25. The composition of the material removed has also been calculated.

Table 25. Differential solution in a sample from Hale's Quarry, Portland, Conn. (Hillebrand, 1891)

	Before Leaching	After Leaching	Material Dissolved
UO_2	59.93	66.82	39.78
UO_3	23.03	16.63	41.71
'Earths'	11.10	10.81	11.96
PbO	3.08	3.02	3.25

Steinkuhler (1923) also observed the phenomenon when he leached a specimen of Katanga pitchblende with HCl. He found that the material dissolved had the formula $UO_3.2H_2O$, and he interpreted it as admixed becquerelite. Phair and Levine (1952) also studied a sample from Katanga, as well as one from Great Bear Lake. The Katanga samples showed the effects of differential solution very strikingly. The other samples were less soluble in acid generally, and were differentially leached to a much lesser extent. Since the material leached was substantially amorphous UO_3, the more oxidized samples could be expected to show the effect more strongly.

Differential leaching runs were made on some of the analyzed samples of this study. It was generally not possible to spare sufficient material from the analysed 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 percent, but by means of the state of oxidation, as shown by the 'm' formula subscript.

The samples were ground to pass 200 mesh, and leached for 40 hours in 100 ml of 0.4 N H_2SO_4. The samples were stirred once, about half way through the run. After 40 hours in the acid, the samples were filtered out, washed, dried, and analyzed for UO_2 and UO_3. A CaO analyses was also ordered in certain cases, since the acid also removed any carbonate impurity.

It was apparent, even without analyses, that the acid attacked some 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; in others, virtually colorless acid was decanted at the end of 40 hours. The Mi Vida sample imparted a dark blue, inky color to the acid, due to vanadium.

The 'm' subscripts before and after leaching are given in Table 26. The analyses of leached material were made by Jun Ito.

Table 26. '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	2.262	2.234	-
Pied des Monts	2.219	2.277	-
Mi Vida	2.172	2.108	?
Boqueirao		2.418	
Royal Claims		2.253	
Karelia		2.478	
Rix Athabaska		2.267	

Generally, the results in Table 25 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. It should be remembered that the 'before' and 'after' analyses represent the work of two different persons on two different samples of specimens that were not necessarily homogeneous. However, even if the sample was permitted to oxidize slightly at some stage during the preparation or analysis, the results are still significant.

In the course of the annealing process, the amorphous phase goes to U_3O_8. The disproportionation sometimes observed on heating does not necessarily occur in the furnace; the furnace simply makes it observable. The actual disproportionation may have occurred long before. If it were possible to take into account the lessened amount of uranium in the cubic phase, the agreement between calculated and measured unit cell sizes in the case of pitchblendes might have been closer, in certain oxidized samples.

CHAPTER 8

SUMMARY

Uraninite is UO_2, with thorium, rare earths, additional oxygen, and perhaps calcium in solid solution. UO_2 has a fluorite structure. The thorium, rare earths, and calcium proxy for the uranium ion. The extra oxygen fits into the interstices of the fluorite-type structure, up to about $(U, Th, R.E.)O_{2.33}$, the limit to which the cubic UO_2 phase can be oxidized by heating in the atmosphere. Some samples have oxygen greatly in excess of this, but most of the oxygen above the laboratory limit is contained in an amorphous phase which separates out as the uraninite comes under surface conditions. Under the conditions of formation, there are indications that the cubic phase can crystallize with more oxygen than the laboratory limit. There are also certain indications that some samples have crystallized as U_3O_8, then disproportionated into the cubic phase and the amorphous phase.

When uraninite crystallizes, its state of oxidation is such that it is in equilibrium with its environment and with the other minerals crystallizing at the same time. This can be expressed by stating that the chemical potential of oxygen is the same in all phases; if it were higher in one than in another, oxygen would move out of the first and into the second. One can think of the chemical potential as a measure, a function, of the concentration. The scale is different for each phase, so that all the minerals in an equilibrium assemblage do not have the same amount of oxygen. But, for a given temperature and pressure, for every partial pressure of oxygen, there is a corresponding uranium oxide or oxides.

Where the partial pressure of oxygen is zero, or very low, the phase in equilibrium is metallic uranium. Eventually a single value (about 10^{-182} atm. at 25°C., 1 atm. total pressure) for the concentration is reached, at which both U and UO are in equilibrium with the oxygen. As the potential is increased above this, it enters a range in which only UO is in equilibrium with the oxygen, and tends neither to oxidize nor to decompose. Once again, there is a single concentration of oxygen (also close to 10^{-180} atm.) at which UO and UO_2 can coexist, without one changing into the other. Above this, however, there is a range in which a graph of the formula subscript versus the potential would not be made up of steplike vertical and horizontal lines. There would be a slanted or curved line, representing the fact that, as the potential is raised, the oxygen content of the cubic UO_2 phase increases continuously, until the 'laboratory limit' is reached. Once again, the composition remains constant as the oxygen in the environment increases, until the conditions are reached under which the U_3O_8 phases are stable. It may be that these conditions do not exist for pressures much above one atmosphere, and the slanted curve reaches up above $UO_{2.667}$ without any discontinuity. At 25° C. and 1 atm. total pressure, U_3O_8 will form if the partial pressure of oxygen exceeds 10^{-47} atm.

If one had a complete set of such data, for various temperatures, pressures and compositions, and one could readily measure or control the chemical potential of oxygen, one could predict the oxidation state of the uraninite that is crystallizing out. Once the uraninite has crystallized, it may oxidize further, either by auto-oxidation, resulting from UO_2 going to PbO, or by atmospheric or other environmental oxidation. The resulting material does not correspond to the equilibrium curve.

The oxygen in the interstitial positions may be in various states of ordering, apparently depending primarily on the composition. When the sample is heated to 550°C. in an inert atmosphere for several hours, the interstitial oxygens become entirely ordered, and the material corresponds to cubic U_4O_9. A contraction of the unit cell takes place. Ordinary uraninite is generally between alpha UO_2, in which the interstitial oxygens are random, and U_4O_9, in which they are ordered. Sedimentary pitchblendes from the Colorado Plateau are almost completely ordered; this accounts in part for their small unit cell.

Lead, even radiogenic lead, does not seem to be in solid solution. The anomalous x-ray intensities suggest that it exsolves as monomolecular layers of orthorhombic PbO, which separate crystallites of uraninite along cube planes.

In drawing this work to a conclusion, the author realizes that he has scarcely dented the mass of problems associated with this mineral. But it is the duty of the laboratory worker to stop work occasionally and render a report.

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APPENDIX A

This appendix contains a compilation of the uraninite analyses used in this work. It includes almost all available analyses starting with Hillebrand's, providing that the analyses distinguish between U^{+4} and U^{+6}. 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 zoning studies, except for the Wilberforce sample, the analysis of the core of the crystal only is given, to avoid distorting the statistics.

	1	2	3	4	5	6	7	8	9	10	11
CaO	0.11	0.18	0.84	0.23	0.37	0.30	0.77	0.37	0.36	0.41	1.00
MnO	--	0.10	0.16	--	--	--	0.06	--	--	--	0.09
PbO	3.08	4.35	0.70	4.53	9.04	8.41	10.06	8.58	9.46	9.44	6.39
MgO	--	--	--	--	--	--	1.10	--	0.97	--	0.17
$(Y,Er)_2O_3$	--	--	--		1.11	2.42	--	--	--	1.03	none
$(Ce,La)_2O_3$	11.10	--	--	3.04	--	0.38	--	--	--	--	--
La_2O_3	--	--	--		0.27	--	0.26	--	0.36	0.23	none
CeO_2	--	--	0.22		0.18	--	0.21	--	0.17	0.20	none
UO_2	59.93	72.25	58.51	46.56	46.13	43.62	50.74	43.03	43.88	43.38	59.30
	--	--	--	--	--	--	--	--	--	--	--
UO_3	23.03	13.27	25.26	44.11	30.63	36.31	25.36	22.04	32.00	35.54	22.33
ThO_2	--	7.20	--	--	6.00	5.64	8.48	8.43	8.98	6.63	none
ZrO_2	--		7.59	--	0.06	--	0.08	--	--	--	--
SiO_2	0.16	0.03	2.79	0.13	0.22	0.81	0.38	0.29	0.53	0.49	0.50
Al_2O_3	--	--	--	--	--	--	--	--	--	--	0.20
Fe_2O_3	0.29	0.11	--	--	0.25	1.40	0.21	0.30	0.09	0.32	0.21
CO_2	--	--	--	--	---	--	--	--	--	--	--
H_2O	0.43	0.68	1.96	n.d.	0.74	0.83	0.73	0.74	0.77	0.79	3.17
Insol.	0.89	0.04	--	0.06	4.42	--	0.45	15.45	1.54	0.42	--
Rem.	2.47	--	1.92	0.25	1.19	--	1.32	1.21	1.03	1.21	4.59
Total	101.49	98.21	99.95	98.91	100.61	100.12	100.21	100.44	100.14	100.09	97.95

	12	13	14	15	16	17	18	19	20	21	22
CaO	0.30	0.69	1.01	0.46	0.72	0.41	0.28	0.58	--	0.42	0.70
MnO	--	0.002	0.03	0.001	--	0.01	0.04	--	--	--	--
PbO	0.40	7.02	10.95	16.42	19.50	11.67	10.40	7.63	1.01	5.71	5.00
MgO	--	0.01	0.08	0.01	--	--	0.19	0.13	--	--	--
$(Y,Er)_2O_3$	3.41	0.35	2.14	1.01	} 5.60	2.19	2.74	0.15	14.60	--	--
$(Ce,La)_2O_3$	--	--	1.88	--		0.98	1.82		0.41	--	--
La_2O_3	1.02	0.155	--	0.80	--	--	--	--	--	--	--
CeO_2	0.71	0.22	--	0.265	--	--	--	--	--	--	--
UO_2	70.09	52.77	39.10	48.87	34.49	53.63	45.18	47.5	55.40	41.94	23.10
	--	--	--	--	--	--	--	--	--	--	--
UO_3	22.69	37.537	32.40	28.582	36.94	26.32	24.90	40.8	22.23	49.21	63.00
ThO_2	0.20	--	10.60	2.15	0.15	3.22	11.40	--	3.86	none	1.67
ZrO_2	--	0.14	--	0.22	--	--	--	--	--	--	n.d.
SiO_2	--	0.095	0.19	0.055	--	0.29	0.43	0.47	0.11	0.92	--
Al_2O_3	0.25	--	0.09	--	} tr.	0.17	--	--	0.44	--	tr.
Fe_2O_3	0.10	0.15	0.43	0.30			0.58	0.15	0.17	0.30	tr.
CO_2	--	0.24	--	--	--	--	--	0.29	0.28	--	--
H_2O	0.41	0.38	0.70	0.44	1.40	0.72	0.61	1.34	0.50	1.22	--
Insol.	--	0.09	0.15	0.15	0.53	0.13	--	--	--	--	0.30
Rem.	0.12	0.50	0.31	0.39	0.23	--	0.35	0.44	0.74	--	5.55
Total	99.70	100.349	100.06	100.123	99.56	99.74	98.92	99.48	99.75	99.72	99.32

	23	24	25	26	27	28	29	30	31	32	33
CaO	tr.	0.30	2.22	2.40	0.08	0.61	0.86		0.32		
MnO	--	--	n.d.	0.22	--						
PbO	5.20	3.94	0.74	1.48	3.14	10.95	10.92	10.16	10.08	4.03	5.16
MgO	--	0.13	--	--	--		0.14				
$(Y,Er)_2O_3$	--	0.28	--	--	0.55	9.05	12.24	11.22	9.46	incl. in ThO_2	
$(Ce,La)_2O_3$	--		--	--							
La_2O_3	--	--	--	--		0.67			2.36		
CeO_2	--	--	--	--	inc. in ThO_2	nil			0.34		
UO_2	28.38	75.41	52.28	42.49	59.13	44.18	23.07	19.89	44.17	74.75	76.12
UO_3	61.12	14.83	31.08	20.58	22.08	26.80	40.60	46.75	20.89	14.65	15.67
ThO_2	0.25	2.59	none	n.d.	9.09	4.15	4.60	7.57	6.69	3.74	3.86
ZrO_2	tr.	--	--	--	--				0.34		
SiO_2	--	0.01	2.87	4.35	1.06	0.50			0.46		
Al_2O_3	tr.	0.53	0.30	1.18	--						
Fe_2O_3	tr.		1.21	1.93	1.21	0.24	1.02	0.58	0.14		
CO_2	--	--	--	--	--						
H_2O	--	0.12	1.27	1.87	0.97	N.D.	4.96	2.54	1.48		
Insol.	1.00	0.58	--	--	0.85	1.19	2.34	1.22	1.47	0.73	0.16
Rem.	2.41	--	5.57	15.84	0.96	1.43			0.54	2.0	0.5
Total	98.36	98.72	97.54	92.34	99.12	99.77	100.75	99.93	98.74	99.90	101.47

	34	35	36	37	38	39	40	41	42	43	44
CaO	3.0	4.4	0.3	8.4	15.9	0.63	0.40	4.28	0.60	2.33	0.5
MnO											
PbO	0.9	1.0	2.3	small	6.10	9.48	11.95	3.91	12.98	12.84	7.2
MgO											
$(Y,Er)_2O_3$					2.29		0.23	2.17	8.23	7.20	2.0
$(Ce,La)_2O_3$											
La_2O_3											
CeO_2						3.20					
UO_2	64.8	52.3	26.0	24.1	38.0	36.42	18.9	70.2	20.9	41.6	38.2
UO_3	14.3	27.8	58.7	44.5	11.3	37.94	57.7	<0.1	41.7	28.1	45.4
ThO_2					0.27	9.32	<0.03	0.08	9.18	1.53	0.4
ZrO_2											
SiO_2	3.0	2.5	0.3	2.0	1.1	0.73	0.85	4.17	1.17	0.70	
Al_2O_3											
Fe_2O_3	0.6	0.8	0.2	3.4	0.5	1.86	nil	2.40	0.65	0.42	0.7
CO_2					12.07						0.8
H_2O						0.82					
Insol.						0.21					3.2
Rem.	~8.	~1.									
Total		not complete	not complete		not complete	100.61	not complete		not complete		98.4

	45	46	47	48	49	50	51	52	53	54	55
CaO	0.50									0.18	13.24
MnO											
PbO	5.41								13.02	8.50	5.25
MgO											
$(Y,Er)_2O_3$	5.90									1.57	0.53
$(Ce,La)_2O_3$											
La_2O_3											
CeO_2											
UO_2	13.6	31.86	31.37	36.43	40.19	36.92	44.77	48.69	42.27	41.20	20.4
UO_3	58.0	58.68	51.95	29.72	29.27	36.51	29.99	49.03	27.00	40.92	43.2
ThO_2	2.93									5.02	
ZrO_2											
SiO_2	0.73									0.77	2.60
Al_2O_3										1.01	
Fe_2O_3											
CO_2											
H_2O										0.52	
Insol.											
Rem.											
Total	not complete		not complete			not complete		not complete		99.69	not complete

		%U / Total U	62	63	64	65	66	67	68	69	70
CaO			5.1	0.31	0.31	0.02	0.02	0.23	0.01	0.54	0.35
MnO											
PbO	56	17.4%	6.4	3.65	3.63	9.47	9.47	6.01	0.82	3.08	8.39
MgO	57	20.2		0.07	0.13						
$(Y,Er)_2O_3$	58	40.2		0.36	0.36	1.9	0.7	3.3		4.1	2.61
$(Ce,La)_2O_3$	59	60.0									
La_2O_3	60	78.5									
CeO_2	61	85.0									
UO_2			48.7	67.13	73.59	44.0	39.5	32.1	60.7	51.1	38.71
UO_3			25.0	23.59	16.62	23.7	27.9	53.2	25.3	24.4	41.33
ThO_2				3.80	3.78	13.5	13.4	<0.01		<0.01	5.03
ZrO_2											
SiO_2			1.4								0.76
Al_2O_3				1.00	1.28						
Fe_2O_3			0.8						2.49		1.24
CO_2											
H_2O											0.85
Insol.											
Rem.											
Total	not complete		not complete	99.91	99.70	not complete	not complete		not complete		99.27

1. Hale's Quarry, Portland, Conn. Hillebrand (1891). Rem. is He 2.41, P_2O_5 0.02, F 0.04.
2. Branchville, Conn. Hillebrand (1891).
3. Vein deposit near Black Hawk, Gilpin County, Colo. Hillebrand (1891). Contains admixed sulfides; average of two analyses. Rem. is ZnO 0.44, FeO 0.32, He 0.15, P_2O_5 0.23, As_2O_5 0.43, $CuFeS_2$ 0.12, FeS_2 0.24.
4. Flat Rock Mine, Mitchell County, N. C. Hillebrand, (1891).
5. Gustavsgruben, Anneröd, Norway. Hillebrand (1891). Rem. is He 1.17, P_2O_5 0.02.
6. Gustavsgruben, Anneröd, Norway. Hillebrand (1891).
7. Elvestad, Norway. Hillebrand (1891). Rem. is He 1.28, P_2O_5 0.04.
8. Elvestad, Norway. Hillebrand (1891). ThO_2 includes rare earths. Rem. is alk. 0.13, He 1.08.
9. Skraatorp, Norway. Hillebrand, (1891).
10. Huggenäskilen, Norway. Hillebrand (1891). Rem. is alk. 0.13, He 1.08.
11. Johanngeorgenstadt, Saxony. Vein deposit. Hillebrand (1892). Rem. is He 0.02, Na_2O 0.31, Bi_2O_3 0.75, CuO 0.17, P_2O_5 0.06, As_2O_5 2.34, (V,W,Mo) oxide 0.75, SO_3 0.19.
12. Placer de Guadalupe, Chihuahua, Mexico. Average of two analyses. Wells (1930). Rem. is TiO_2 0.06, As_2O_5 0.06.
13. Shinkolobwe, Belgian Congo. Vein deposit. Davis (1926). Rem. is He 0.159, N 0.076, O 0.005, BaO 0.06, Alk. 0.01, MoO_3 0.07, As_2O_5 0.09, P_2O_5 0.03.
14. Wilberforce, Halliburton County, Ont. Ellsworth (1930). Rem. is He and other gases. H_2O includes H_2O+ 0.05 and H_2O- 0.65.
15. Ingersoll Mine, Pennington County, So. Dak. Rem. is He 0.08,

BaO 0.08, Alk. 0.02, MoO_3 trace, As_2O_5 0.15, P_2O_5 0.06. Davis (1926).

16. Sinyaya Pala, Karelia, U.S.S.R. Analysis stated to be mean of material from this locality. Nenadkevitch (1926). Rem. is Cl.

17. Parry Sound District, Ont. Ellsworth (1921).

18. Wilberforce, Ont. Todd, analyst, in Walker, (1924). Rem. is He.

19. Shinkolobwe, Katanga, Belgian Congo. Rodden, analyst, in Kerr (1950). Rem. is NiO 0.13, MoO_3 0.31. Vein deposit.

20. Iisaka, Abukama Range, Japan. Iimori (1941). Rem. is Cb_2O_5.

21. Rio Branco, Minas Gerais, Brazil. Florencio and Castro (1943). H_2O is ignition loss.

22,23. Cerro Blanco, Cordoba, Argentina. Rem. is H_2O, He, and in anal. 23 P_2O_5 0.06. Chaudet, analyst, in Ahlfeld and Angelelli (1948).

24. Strickland pegmatite, Portland, Conn. Hecht, analyst, in Foye and Lane (1934).

25. Sedimentary uraninite. Happy Jack mine, White Canyon, Utah. Contains quartz, pyrite, chalcopyrite, and chalcocite as minor impurities. G. Edgington, U.S.G.S., analyst. T. Stern, pers. comm. Rem. is CuO 2.96, (Ba,Sr)O 0.15, V_2O_5 0.54, S 1.70, As 0.005, F 0.21. H_2O includes H_2O- 0.28. Total not corrected for F = O.

26. Sedimentary uraninite. Shinarump No. 1 mine, Sevenmile Canyon, Grand County, Utah. Contains pyrite, quartz, calcite, and barite as minor impurities. G. Edgington, analyst; Weeks, pers. comm. Rem. is Ni_2O_3 0.40, Co_2O_3 0.64, TiO_2 0.29, ZnO 4.09, BaO 5.21, SrO 0.34, V_2O_5 0.22, S 4.35, As 0.013, Se

0.003, F 0.28. H_2O includes H_2O- 0.70. Total not corrected F= O.

27. Hale's Quarry, Portland, Conn. Two analyses combined. Hillebrand (1891). Rem. is Cb_2O_5.

28. Arendal, Norway. Hillebrand (1891). Rem. is MgO 0.04, alk. 0.15, He 1.24.

29. Arendal, Norway. Lindstrom, analyst, in Nordenskiold (1878). H_2O is ignition loss.

30. Baringer Hill, Llano County, Texas. Hidden and Mackintosh (1889). H_2O is ignition loss.

31. Re-analysis of above sample by Hillebrand (1892). Rem. is He 0.54.

32. Strickland Quarry, Portland, Conn. J. Ito, analyst. Rem. not given in detail. ThO_2 includes rare earths.

33. Newry, Me. J. Ito, analyst. Rem. not given in detail. ThO_2 includes rare earths.

34. Mi Vida Mine, San Juan County, Utah. Sedimentary uraninite. J. Ito, analyst; rem. is V_2O_5.

35. Big Indian Wash, San Juan County, Utah. Anal. J. Ito. Rem. is V_2O_5.

36. Ruggles Mine, Grafton, N. H. Analyst, J. Ito.

37. Wölsendorf, Bavaria. Vein deposit. Analyst, J. Ito.

38. Vein deposit. Lac Pied des Monts, Que. Kramer, analyst. Contains $CaCO_3$.

39. Gordonia, South Africa. Mountain, analyst, in Holmes (1934).

40. Shinkolobwe, Katanga, Belgian Congo. Levine, analyst. Vein deposit.

41. Joachimsthal, Czechoslovakia. " " Vein deposit.

42. Gordonia, South Africa. Levine, analyst.

43. Sudbury district, Ont. " "

44. Morogoro, Tanganyika. Marckwald (1911).

45. Spruce Pine, N. C. Levine, analyst.

46. Monument No. 2 mine, Apache County, Ariz. Sedimentary deposit. Sherwood, analyst.

47. Happy Jack mine, San Juan County, Utah. Sedimentary deposit. Sherwood, analyst.

48. School Section 36 mine, San Juan County, Utah. Sedimentary deposit. Sherwood, analyst.

49. School Section 36 mine, San Juan County, Utah. Sedimentary deposit. Sherwood, analyst.

50. Mi Vida mine, San Juan County, Utah. Sedimentary deposit. Sherwood, analyst.

51. La Sal shaft, San Juan County, Utah. Sedimentary deposit. Sherwood, analyst.

52. Hidden Splendor mine, Emery County, Utah. Sedimentary deposit. Sherwood, analyst.

53. Auselmyren, Norway. Bakken and Gleditsch (1938). Core of crystal.

54. Martapoera, Borneo. Chernik (1909). Average of two analyses.

55. Theano Point, Algoma district, Ont. Analyst, Levine.

56. Nicholson mine, L. Athabaska dist., Sask. Vein deposit. Brooker and Nuffield 1952.

57. Nicholson mine, L. Athabaska dist., Sask. Vein deposit. Brooker and Nuffield 1952.

58. Martin Lake, L. Athabaska dist., Sask. Vein deposit. Brooker and Nuffield 1952.

59. Martin Lake, No. 2 flow, L. Athabaska dist., Sask. Vein deposit. Brooker and Nuffield. 1952.

60. Donaldson Group, L. Athabaska dist., Sask. Vein deposit. Brooke and Nuffield 1952.

61. A.B.C. Group, L. Athabaska dist., Sask. Vein deposit. Brooker an Nuffield 1952.

62. Eldorado mines, Great Bear Lake, N.W.T. Vein deposit. Anal. J. Ito.

63,64. Strickland Quarry, Portland, Conn. Hecht, analyst, in Foye and Lane, (1934).

65,66. Wilberforce, Ont. Sherwood, analyst. 65- outer 4 mm. of large xl. 66, core of crystal.

67. Przibram, Czechoslovakia. Vein deposit. Sherwood, analyst.

68. Wood mine, Central City, Colo. Vein deposit. Sherwood, analyst.

69. Schmiedeberg, Silesia. Vein deposit. Sherwood, analyst.

70. Moss, Norway. Chernik (1909).

APPENDIX B. OXYGEN SUBSCRIPTS OF ANALYSED URANINITES

Analysis	m (UO_m) ;	n ($(U,Th)O_n$) ;	p ($(U,Th,R.E.)O_p$) ;	q ($(U,Th,R.E.,Pb)O_q$)
		Pegmatitic uraninites		
1	2.231	2.208	2.199	2.159
2	2.148	2.136	2.136	2.075
4	2.472	2.453	2.453	2.371
5	2.385	2.356	2.329	2.176
6	2.440	2.410	2.355	2.216
7	2.321	2.287	2.282	2.120
8	2.326	2.287	2.287	2.126
9	2.408	2.363	2.356	2.193
10	2.436	2.401	2.374	2.215
12	2.234	2.234	2.218	2.212
14	2.439	2.380	2.307	2.136
15	2.356	2.346	2.310	2.054
16	2.498	2.488	2.365	2.052
17	2.317	2.304	2.250	2.076
18	2.342	2.293	2.218	2.067
20	2.275	2.261	2.059	2.047
24	2.156	2.152	2.149	2.092
27	2.261	2.233	2.226	2.176
28	2.364	2.343	2.172	2.025
29	2.624	2.580	2.293	2.128
30	2.689	2.597	2.375	2.212
31	2.309	2.279	2.089	1.963
32	2.156	2.149	2.149	2.092
33	2.163	2.156	2.156	2.084
36	2.681			
39	2.496	2.438	2.384	2.222

Analysis	m	n	p	q
42	2.777	2.669	2.461	2.224
43	2.389	2.381	2.246	2.048
44	2.530	2.527	2.488	2.349
45	2.801	2.767	2.607	2.488
53	2.390			
54	2.484	2.455	2.421	2.273
63	2.249	2.239	2.234	2.178
64	2.176	2.168	2.164	2.112
65	2.337	2.281	2.248	2.098
66	2.400	2.331	2.319	2.155
70	2.502	2.471	2.421	2.273

Vein pitchblendes

	m	p	q
3	2.290	2.288	2.274
11	2.262	2.262	2.152
13	2.400	2.391	2.270
19	2.448	2.445	2.305
21	2.524	2.524	2.415
22	2.727	2.712	2.600
23	2.670	2.668	2.559
37	2.636	2.636	2.636
38	2.219	2.164	2.012
40	2.742	2.736	2.451
41	2.000	1.975	1.916

Analysis	m	p	q
55	2.667	2.649	2.496
56	2.174		
57	2.202		
58	2.402		
59	2.600		
60	2.785		
61	2.850		
62	2.326	2.326	2.198
67	2.610	2.538	2.421
68	2.282	2.282	2.268
69	2.311	2.240	2.186

Sedimentary pitchblendes

Analysis	m	q	Analysis	m
25	2.359	2.345	47	2.610
26	2.314	2.277	48	2.435
34	2.172	2.156	49	2.407
35	2.334	2.314	50	2.483
46	2.635		51	2.387
			52	2.487