

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 42

MARCH-APRIL, 1957

Nos. 3 and 4

MINERALOGY OF URANIUM*

CLIFFORD FRONDEL, *Harvard University, Cambridge 38, Massachusetts*

I

At the present time approximately 70 different minerals are known that contain uranium as an essential constituent. Only a very few of these minerals are important as ores of the element. At the time of the discovery of the element uranium by Klaproth in 1789 only two uranium minerals were known, torbernite, and a mineral, pitchblende, for which the name uraninite is now appropriate. Both of these species had been recognized as distinct entities long before by the miners of Saxony and Bohemia. Torbernite and its analogue autunite were first set forth as clearly defined species in 1823. By 1850 the number of uranium minerals had grown to 6; and by 1900 roughly one-third of the species now known had been recognized.

Advances in the mineralogy of uranium have markedly reflected the discovery of new deposits and of new uses of the element. The application of uranium as a pigmenting material in glass and ceramics toward the middle of the 19th Century inaugurated the mining of uraninite in the Erzgebirge. This activity was accompanied by numerous studies of uranium minerals, chiefly by Austrian and German investigators. Among them may be mentioned Albin Weisbach, who alone described 7 new species. Another period of active research on the mineralogy and geology of uranium accompanied the discovery of radioactivity by Becquerel in 1896 and the isolation of radium by the Curies and Bémont in 1898. The uranium deposits of the Colorado Plateau were first explored and exploited at this time, following the description of the important ore mineral carnotite by Friedel and Cumenge in 1899. The mineralogy of the

* Address of the retiring President of the Mineralogical Society of America at the thirty-seventh meeting of the Society at Minneapolis, Minnesota, Nov. 1, 1956.

Contribution No. 371 from the Department of Mineralogy and Petrography, Harvard University, Cambridge, Massachusetts.

Plateau uranium and vanadium ores was studied during this period by W. F. Hillebrand and F. L. Hess, among others.

Following the discovery of the mineralogically diverse uranium ores of the Belgian Congo in 1915, a large number of new uranium minerals were described. This work was done chiefly by Belgian mineralogists, among whom may be mentioned H. Buttgenbach, J. Thoreau, J. Mélon and, in particular, Alfred Shoep. Shoep described 12 of the 24 uranium minerals discovered in the Belgian Congo. No such flood of new species attended the discovery of the rich deposit at Great Bear Lake in 1930, owing primarily to the very small extent of surface oxidation at that place.

The discovery of atomic fission in 1937 by Hahn and Strassmann was followed by a great program of work on the uses of uranium and of the trans-uranium elements both as military weapons and as sources of power. This work brought about a large and immediate demand for uranium ores that still continues, and gave a great impetus to the study of the geology, geochemistry, and mineralogy of uranium. It is largely with these recent studies that I shall be concerned here.

II

Until very recently, uranium minerals as a group were very poorly characterized. In many instances, particularly with less common minerals described before about 1880, it was virtually impossible to recognize the mineral with certainty from the existing published information. A few species described in recent years also fall into this category. The difficulties in part stemmed from inadequacies of the older analytical work and, more generally, from the occurrence of the minerals in relatively small amount as very fine-grained aggregates and mixtures.

It was in fact found useful in the past to use a generic term, gummite, to designate various uranium minerals, found chiefly as oxidation products of uraninite, whose true identity was unknown. The term gummite, like its analogues wad and limonite, found its widest use in the days before the advent of *x*-ray diffraction and other techniques suited to the study of fine-grained mixtures. Of the dozen or so uranium minerals that are now known to constitute the traditional gummite, only one species, the silicate uranophane, was known prior to 1890, although all of these minerals had been examined in the form of gummite, if not identified, by the early mineralogists.

In the past seven or eight years, virtually the whole mineralogy of uranium has been re-examined and the known species provided with definitive redescrptions. A particularly profitable approach in this work has been the study of synthetic material, prepared in bulk in pure form

and shown to be identical with the natural mineral in question. Large use also has been made of x -ray and electron diffraction techniques. X -ray powder data offer a convenient and positive means of identification of these minerals, and sometimes are indispensable. One of the first objectives of the work was the preparation of a complete file of standard x -ray patterns. A list of d -spacings for the known species has since been published. Crystal structure studies also have been fruitful. The resolution of some of the standing problems in this field, such as the chemistry and mineralogy of the hydrated uranyl oxides containing lead or other cations, and problems of the uranyl sulfates, is dependent on structural studies. In recent years the U. S. Geological Survey has very profitably carried on structural studies of uranium and vanadium minerals in conjunction with studies of the solution-chemistry of these elements, particularly with regard to complex-formation in solution.

A key problem in the general program has been the procuring of authentic and preferably type specimens for the redefinition of ill-defined species. One of the first steps taken was the preparation by the Trace Elements Laboratory of the U. S. Geological Survey, in 1951, of an inventory of the specimens of uranium minerals contained in the leading reference mineral collections of the United States. It was then found that about 10 per cent of the known species and significant varieties of uranium minerals were not represented by authentic specimens in this country. This deficiency has since been remedied, but after much difficulty. It should be emphasized in this connection that the science of mineralogy in its descriptive aspects is a specimen-science, like botany and entomology, and requires for its practice and progress the preservation and ready availability of type material. Mineralogists who describe new species or significant varieties of known species should ensure that specimens are preserved in the leading reference mineral collections of the world.

This program of work on the mineralogy of uranium was essentially a cooperative effort carried on at a relatively few laboratories in this country. These laboratories included the Trace Elements Laboratory of the U. S. Geological Survey in Washington, the Denver and Grand Junction laboratories of the Atomic Energy Commission and the Survey, Professor Gruner's group at Minnesota, Professor Kerr's group at Columbia, and the Harvard group. Most of the university work was supported by contracts with the Atomic Energy Commission.

Much of this mineralogical research centered about the Trace Elements Laboratory, and brief mention may be made of the work of this organization. The Trace Elements Laboratory was created in 1947 as a unit under the Geochemistry and Petrology Branch of the Geological

Survey. It is supported by funds transferred by the Atomic Energy Commission, which, by statute, has the primary responsibility for the whole program of work on fissionable raw materials. A broadly inclusive but well integrated organization, that at its peak employed about 130 scientific personnel, it carries on laboratory investigations on the mineralogy, chemistry, petrography, geochemistry and nuclear physics of natural radioactive substances. Most of the research done by the Laboratory has been made publically available; of some 270 official research reports made to date, 32 already have been published as Bulletins or Professional Papers of the Geological Survey, and 109 have appeared in scientific periodicals. As one of its duties, the laboratory makes chemical or spectrographic analyses together with radiometric and, in part, x -ray or other study of field samples originating in other branches of the Geological Survey. A total of over one-third of a million such samples have been examined to date. In addition, more or less radioactive samples submitted by the general population have been examined in very large numbers by this and other Government laboratories.

Contributions to the mineralogy of uranium during this general period also were made by a few laboratories in foreign countries. Here may be mentioned work in Canada at the University of Toronto, Queen's University and the Geological Survey, and at establishments of the Atomic Energy Commissions of France and of Great Britain. The Russian contributions to this field are known only from a few recent papers descriptive of new species.

A detailed summary account of the mineralogy of uranium and thorium is in press as a Bulletin of the U. S. Geological Survey.

III

Many problems in the descriptive and interpretive mineralogy of uranium still remain. I shall outline a few of these problems, but first I will briefly characterize the mineralogy of this element in crystallochemical terms.

Uranium occurs in two geologically stable valence states: the four-valent or uranous state, and the six-valent state. In the latter state, the uranium forms a cationic complex-ion, the so-called uranyl ion, composed of a linear group of two oxygen ions with the six-valent uranium ion held between them. This complex ion has a net positive charge of two units. The coordination number with oxygen of the six-valent uranium ion ordinarily is six or eight in different compounds, and the uranyl configuration appears as a distortion of this coordination in which two of the surrounding oxygen ions, diametrically opposed to the central uranium ion, are more closely bound thereto than are the other

oxygens of the coordination group. The uranyl ion is readily complexed in both carbonate and sulfate solutions. The carbonate and sulfate complexes are relatively easily reduced into less soluble uranous compounds, including uranium dioxide and hydrated uranous oxides, and these complexes doubtless play an important role in the transport and deposition of uranium in nature.

All but two of the 70 or so known uranium minerals contain the uranyl ion. All are secondary minerals. It is interesting to note that the mineralogy of the uranyl ion stands quite alone. There are no analogues of these minerals among the minerals formed by other elements. This is due to the unusual dumbbell-like shape of the uranyl ion, which finds no counterpart among the ions of other elements. It is for this same reason that the uranyl ion does not occur in significant amounts as a vicarious constituent in other minerals. The solid solution series in which uranyl compounds do enter in general involve substitution for either the other cations that may be present in the crystal structure or of the anions. The thermal instability of the uranyl ion is an added factor that weighs against its entrance in solid solution into high-temperature igneous and metamorphic minerals.

All this contrasts with the mineralogy of the four-valent or uranous ion. This ion acts as a sphere in crystallochemical regards, with a radius of about 1 Angstrom. The mineralogy of this ion, unlike that of the uranyl ion, has structural analogies with the mineralogy of other elements of the same valence and of comparable ionic radius. Here may be mentioned thorium, zirconium and four-valent cerium. This relation is shown by the nesosilicates of the zircon group, by their hydroxyl-containing analogues of the thorogummite group, and by the fluorite-type dioxides of the uraninite group. Partial or complete solid solution series extend between these isostructural species. The four-valent uranium ion, again in contrast with the uranyl ion, commonly occurs in significant amounts as a vicarious constituent in other minerals. Because of its high valence and relatively large size, however, it is not found in large amounts in substitution for the common cations of rock-forming minerals. The small substitution of four-valent uranium for calcium in apatite, however, is of economic interest because it can be recovered as a by-product. Other minerals in which four-valent uranium occurs as a vicarious constituent that are of interest as sources of uranium include pyrochlore-microlite, brannerite and betafite. In these minerals, coupling mechanisms are available for the housing in solid solution of large, polyvalent ions. Virtually the whole production of uranium, however, presently comes from minerals in which uranium is an essential constituent. Quite the opposite is true of thorium. Monazite, the ore mineral of thorium,

contains this element in solid solution in substitution for cerium and lanthanum.

URANINITE

A great deal of attention has been given to uraninite in recent years, since this is the most important ore mineral of uranium. It is surprising that this long-known mineral, certainly now one of the most important natural substances known to man, should be so little understood. The problem of the chemical composition of uraninite plagued chemists for over 125 years. It still does. The mineral was early considered to have the composition U_3O_8 or U_2O_6 , or to be an orthouranate of uranium and lead. W. F. Hillebrand in his definitive analytical study of uraninite made in the period 1888–1892 disproved these ideas, but could reach no definite interpretation of the composition himself. The problem was largely resolved by Goldschmidt and Thomassen in 1923, when they showed that the crystal structure of the mineral was of the calcium fluoride type and that its ideal chemical composition, at least, was uranium dioxide, UO_2 . The presence of variable and often large amounts of six-valent uranium in the mineral, a puzzling feature that was chiefly responsible for the failure of the earlier interpretations, was ascribed to a non-stoichiometric variation in composition. In this, it was proposed that the six-valent uranium substituted for the normal four-valent uranium ions of the structure, and that valence compensation was effected by the coupled entrance of oxygen ions into vacant interstitial positions. The possibility of intimate admixture of amorphous uranium trioxide, however, cannot be excluded.

This problem of the composition and structure of uraninite requires further study. The mechanism by which the lead atoms formed by radioactive decay are housed within the structure is still not understood, and the coordination with oxygen of any six-valent uranium ions present is an associated problem. If the six-valent uranium ions tend to assume a uranyl configuration, as one might suppose, then this would require a distortion of the normal oxygen coordination. The existence of this distortion and its consequences in natural material have yet to be investigated. It may account for the differences in habit between uraninite and so-called pitchblende. In the synthetic tetragonal phase in the composition range $UO_{2.2}$ to $UO_{2.3}$ structural strain apparently is relieved by a linear arrangement of the uranyl configuration. The entrance of oxygen ions into a vacant position that itself is completely bounded by oxygen ions violates a fundamental rule of crystal chemistry.

Further, are the extra oxygen ions distributed through the uraninite structure in a random way or with order? Laboratory study has shown that ordering of the oxygen positions is an important mechanism in the

anhydrous system $\text{UO}_2\text{-UO}_3$, and that this ordering is accompanied by a variety of phase changes that can be followed by *x*-ray means. Strangely, none of the phases that occur in synthetic anhydrous material have been identified in natural material that covers essentially the same range of composition. There is some recent evidence, obtained by study of changes in the unit cell dimensions produced by annealing, that the low temperature uraninite of the sandstone deposits of the Colorado Plateau and of hydrothermal veins may be ordered. There also is the possibility, particularly in the older uraninites, that order originally present among the extra oxygens may have been later destroyed by self-irradiation—a partial metamictization of the structure. The ordered oxide U_4O_9 may come into consideration here.

There is a further problem with uraninite that has important geological implications. It has been generally supposed, since the work of Goldschmidt and Thomassen, that uraninite was originally deposited in nature as unoxidized uranium dioxide, and that the content of six-valent uranium and extra oxygen of the mineral is due to secondary oxidation and weathering. Secondary oxidation unquestionably can and does happen. But it also is true that uraninite can crystallize directly from solution in a more or less oxidized condition. Oxidized uraninite has been synthesized in the laboratory by hydrothermal means over a wide range of temperature. The amount of initial oxidation in general increases with decreasing temperature of synthesis; and also is influenced by the reducing power and pH of the solution. It is in fact difficult to obtain wholly unoxidized material by hydrothermal means. This matter is of interest in connection with recent efforts to use the cell edge of uraninite as a means of age determination.

Increasing oxidation is accompanied by a decrease in the unit cell dimensions. Study by *x*-ray methods of some 300 samples of uraninite from world-wide localities indicates that low temperature natural uraninite, such as that of the Colorado Plateau, has relatively small unit cell dimensions; middle-temperature uraninite, such as that from hydrothermal veins, has an intermediate range of cell dimensions; high temperature uraninite, such as that of pegmatites, when corrected for the content of thorium and rare-earths usually present, has the largest cell dimensions. This correlates with the laboratory observations on initial oxidation as a function of temperature. It also is significant in this connection that no natural uraninite has yet been described that is wholly unoxidized. The smallest content of six-valent uranium so far reported corresponds to the formula $\text{UO}_{2.15}$. Interesting problems thus remain with uraninite, and there is no doubt but that their study will contribute to a further understanding of the geochemistry of uranium.

URANIUM SILICATES

The recent description of coffinite, a silicate of four-valent uranium that is widespread in the unoxidized uranium deposits of the Colorado Plateau, is of interest in connection with the crystal chemistry of the zircon family of minerals. Coffinite is isostructural with zircon. Study of pure, coarsely crystallized material would be desirable, if such material can be found. The available evidence, however, indicates that a considerable part of the (SiO_4) groups of this nesosilicate have been substituted by hydroxyl ions in groups of four. This mechanism of compositional variation is already well-known in the so-called hydrogarnets.

It now appears that the zircon family of minerals may fall into two groups. The zircon group proper includes the anhydrous minerals ZrSiO_4 (zircon), ThSiO_4 (thorite), and the hypothetical but crystallographically possible substances USiO_4 and CeSiO_4 . The two known members are high-temperature, primary minerals. Parallel to each of these known or hypothetical minerals there apparently exist hydroxyl-containing variants. These form at low temperatures, and in part are secondary minerals. This group of minerals, for which the name Thorogummite Group would be appropriate, seemingly includes coffinite as the variant of hypothetical USiO_4 , thorogummite as the variant of thorite, cyrtolite as the variant of zircon, and possibly the ill-defined mineral freyalite as the variant of hypothetical CeSiO_4 . The hydroxyl-containing variants of both zircon and thorite have been synthesized hydrothermally at temperatures as low as 150°C. , and the content of hydroxyl has been verified by infra-red absorption studies. It also has proven possible to recrystallize metamict zircon and thorite by hydrothermal means at moderate temperatures. Apparently this also happens in nature. Further studies of the crystal chemistry of the zircon family would be highly desirable, particularly of zircon itself in view of the use of this mineral in age-determination work.

I have outlined here only a few of the more interesting or more profitable problems that exist in this general field. There are others. In conclusion, I do not wish to convey the impression that these are residual problems, whose resolution will leave clear this small part of our science. It has been said, the greater the sphere of our knowledge, the larger the circumference of our ignorance.