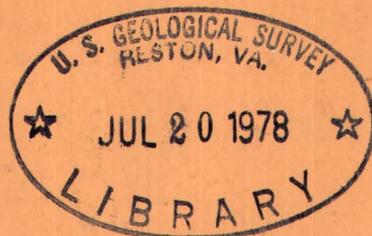


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# Behavior of Colorado Plateau uranium minerals during oxidation

By R. M. Garrels and C. L. Christ



*Trace Elements Investigations Report 588*

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

Geology and Mineralogy

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Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

BEHAVIOR OF COLORADO PLATEAU URANIUM MINERALS DURING OXIDATION\*

By

R. M. Garrels and C. L. Christ

May 1956

Trace Elements Investigations Report 588

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\*This report concerns work done on behalf of the Divisions of Research and Raw Materials of the U. S. Atomic Energy Commission.

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## BEHAVIOR OF COLORADO PLATEAU URANIUM MINERALS DURING OXIDATION

By

R. M. Garrels and C. L. Christ

## ABSTRACT

Uranium occurs as U(VI) and U(IV) in minerals of the Colorado Plateau ores. The number of species containing U(VI) is large, but only two U(IV) minerals are known from the Plateau: uraninite, an oxide, and coffinite, a hydroxy-silicate. These oxidize to yield U(VI) before reacting significantly with other mineral constituents. Crystal-structure analysis has shown that U(VI) invariably occurs as uranyl ion,  $UO_2^{+2}$ . Uranyl ion may form complex carbonate or sulfate ions with resulting soluble compounds, but only in the absence of quinquevalent vanadium, arsenic, or phosphorus. In the presence of these elements in the +5 valence state, the uranyl ion is fixed in insoluble layer compounds formed by union of uranyl ion with orthovanadate, orthophosphate, or orthoarsenate. Under favorable conditions  $UO_2^{+2}$  may react to form the relatively insoluble rutherfordine,  $UO_2CO_3$ , or hydrated uranyl hydroxides. These are rarely found on the Colorado Plateau as opposed to their excellent development in other uraniferous areas, a condition which is apparently related to the semiarid climate and low water table of the Plateau. Uranium may also be fixed as uranyl silicate, but little is known about minerals of this kind. In the present study emphasis has been placed on a detailing of the chemical and crystal structural changes which occur in the oxidation paragenetic sequence.

## INTRODUCTION

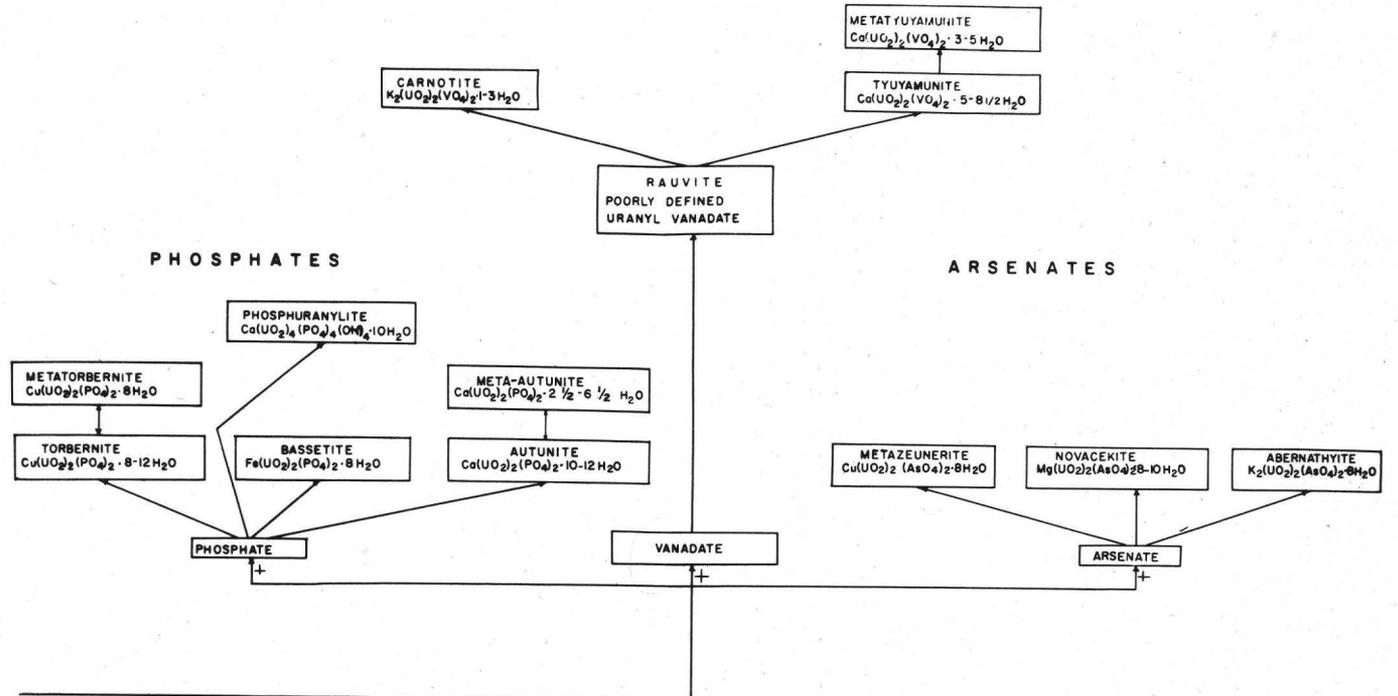
Uranium occurs in two valence states in minerals from the Colorado Plateau uranium ores--as U(VI) and U(IV). The number of species containing U(VI) is large, but only two minerals containing U(IV) have been isolated and characterized. They are uraninite, an oxide, and coffinite, a silicate or hydroxy-silicate. The occurrences of uranium minerals are quite consistent with the view that these two minerals are the progenitors of all the U(VI) phases. That interpretation will be accepted for the purposes of this discussion, and emphasis will be on a detailing of the chemical and structural changes that result in the production of many-hued and chemically diversified later generations from these two parent materials. These relations are shown in figures 1 and 2; the text is best followed by continuous reference to them.

## URANINITE

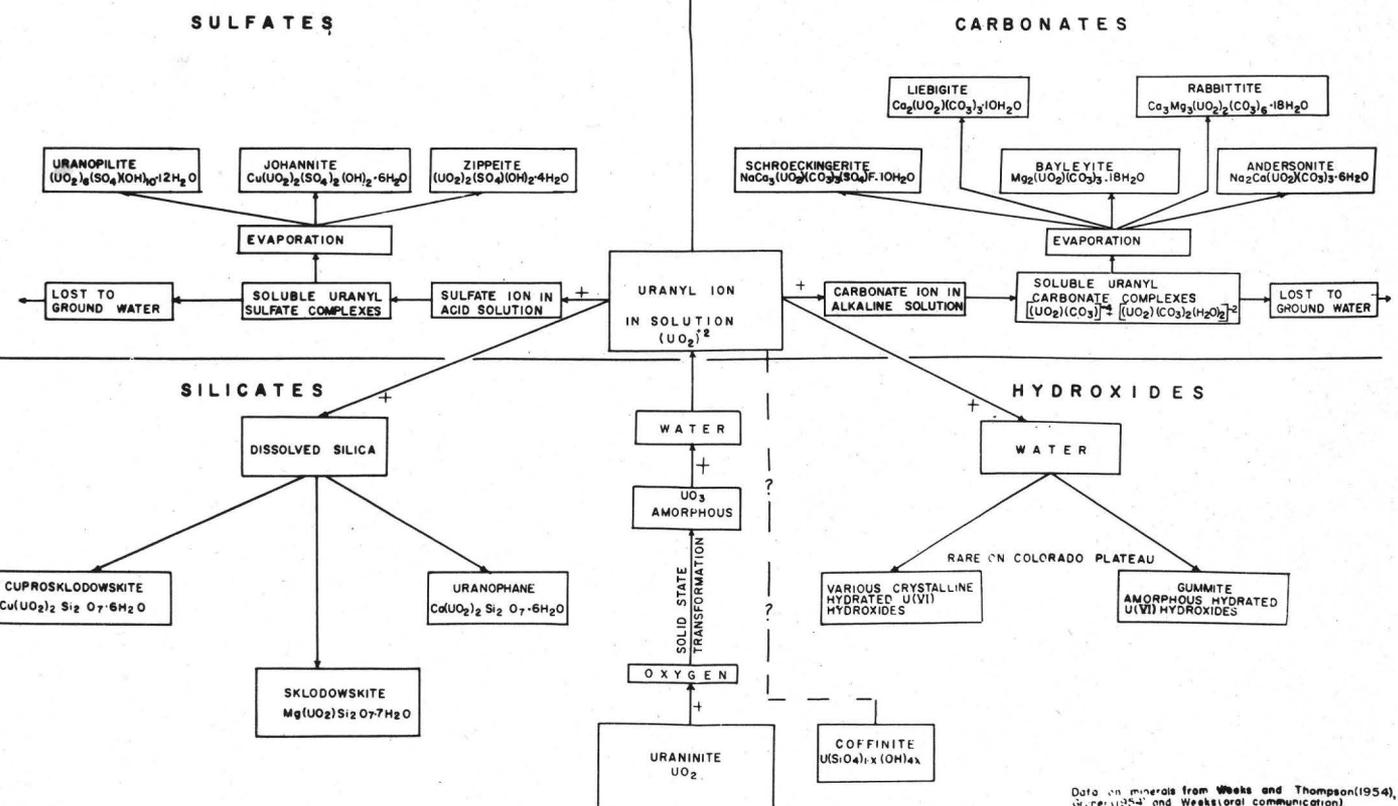
Uraninite from Plateau deposits is fine grained. Analysis of carefully purified materials invariably shows  $UO_2$  and  $UO_3$  in various ratios, with a tendency for the maximum  $UO_2/UO_3$  to occur in massive specimens collected from sites protected from the atmosphere until mining operations took place. Presumably the material originally precipitated was largely  $UO_2$ , and most of the  $UO_3$  reported is a product of the radioactive decay of uranium to lead, plus that from oxidation by the atmosphere (Palache and others, 1944).

Synthetic preparations of  $UO_2$  give sharp X-ray diffraction powder patterns (Kerr and others, 1954) corresponding to the fluorite structure (fig. 2). Uraninite samples from the Plateau give essentially the same powder patterns, but the definition of the patterns varies widely. The diffuseness

INSOLUBLE OXIDATION PRODUCTS  
VANADATES



SOLUBLE OXIDATION PRODUCTS

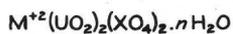
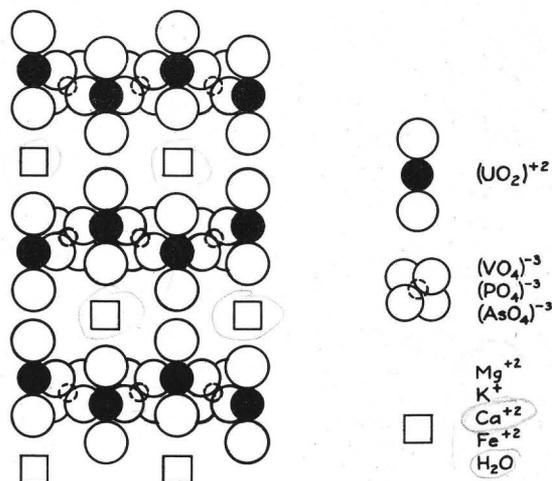


Data on minerals from Weeks and Thompson (1954), Weeks (1954) and Weeks oral communication.

Fig.1 Reactions and products in the weathering of uraninite and coffinite.

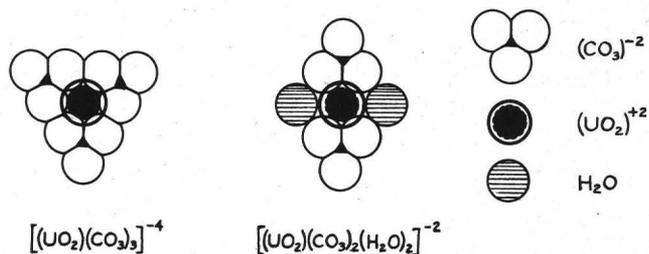
## INSOLUBLE OXIDATION

## PRODUCTS

Vanadates, phosphates,  
arsenates(Illustrated by autunite,  $Ca(UO_2)_2(PO_4)_2 \cdot nH_2O$ ,  
after Beintema, 1938)

Structures unknown

## SULFATES

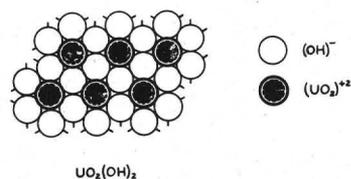


## CARBONATE COMPLEX IONS

 $(UO_2^{++}$  ion normal to plane)

Structures unknown

## SILICATES



## URANYL HYDROXIDES

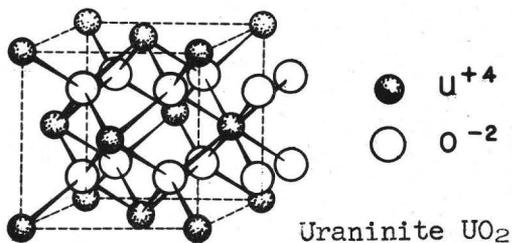
 $(UO_2^{++}$  ion normal to plane)Uraninite  $UO_2$ 

Figure 2.--Some structures involved in oxidation of uraninite.

of the patterns increases with increasing  $\text{UO}_3$ . The reasons for this have been studied by numerous investigators (Brooker and Nuffield, 1952; Kerr and others, 1954). Apparently the loss of definition in the patterns results from a variety of causes including a reduction in crystallite size of the  $\text{UO}_2$  and nonuniform oxidation throughout the sample. No pattern corresponding to a U(VI) compound is found, so presumably the U(VI) exists as  $\text{UO}_3$  in the amorphous state.

During radioactive decay, uranium atoms disintegrate through a series of daughter products to lead, leaving an excess of oxygen atoms relative to uranium atoms; hence chemical analysis reports  $\text{UO}_2$ ,  $\text{UO}_3$ , and  $\text{PbO}$ . As an equation (for 50 percent disintegration):



Plateau uraninites are not older than 60 to 70 million years (Stieff and Stern, 1952); the analytical  $\text{UO}_3$  content from development of lead in that time span would be about 2 percent by weight. The least altered uraninite so far analyzed for  $\text{UO}_2$  and  $\text{UO}_3$  has a  $\text{UO}_3$  content of about 30 percent (Stern, T. W., personal communication) showing that no entirely fresh material has been obtained.

The structural pattern of uraninite can still be discerned in X-ray powder photographs of material containing as much as 80 percent  $\text{UO}_3$  (Brooker and Nuffield, 1952, p. 366), and no trace of a  $\text{UO}_3$  pattern can be seen.

The development of  $\text{UO}_3$  by atmospheric oxidation is clearly a pseudomorphic process; the original grain shapes of  $\text{UO}_2$  are retained, and there are no characteristic changes in color or texture. However,  $\text{UO}_3$  percentage of a given specimen does agree with position relative to access to oxygen; cores of massive specimens are lower in  $\text{UO}_3$  content than the rims.

Thus the first stage of supergene oxidation of uraninite is essentially a solid state phenomenon and gives rise to material that analyzes as  $\text{UO}_3$ , but still resembles the parent  $\text{UO}_2$  megascopically. This new material is amorphous to X-rays.

The probable reaction is:



The free energy change probably is somewhat less negative than that calculated here for the crystalline materials because the  $\text{UO}_3$  is amorphous.

Solution of  $\text{UO}_2$  without oxidation is not an important process because of the extremely low solubility of  $\text{UO}_2$  in deaerated water. Instead it oxidizes much more rapidly and effectively in the solid state.

#### COFFINITE

The new mineral, coffinite (Stieff and Stern, 1955), is not well characterized, but is a U(IV) silicate, with more or less hydroxyl substitution for the silicate ion. Presumably its formula ranges between  $\text{U}_2(\text{SiO}_4)_2$  and  $\text{U}_2(\text{OH})_4(\text{SiO}_4)$ . It occurs typically as a replacement of woody material, or in intimate association with carbonaceous material, mostly of woody origin. Very serious problems have arisen in attempting to separate a pure phase from the environment, owing to many causes such as the usual extreme fineness of grain and the intimate intergrowth with other materials. However, X-ray, infrared, and electron diffraction studies show it to be an analogue of zircon and thorite, with the same kind of transition to a hydroxy-substituted species. It is probably a primary mineral, although Weeks and Coleman (personal communication) suspect that it is nearly always late in the paragenetic sequence, and may result from complex reactions among uranium

in solution, woody material, and silica released into solution by the action of the ore fluid on sand grains.

Coffinite's intimate intergrowth with uraninite indicates similar very low solubility relations in a reducing environment, and there is a suggestion that it is somewhat more resistant to oxidation than uraninite. Nevertheless it probably oxidizes much more rapidly than it dissolves, so that, as in the case of uraninite, mineralogic changes involving a quadrivalent uranium ion in solution are an unimportant aspect of its post-depositional history.

The importance of coffinite as an ore mineral is difficult to assess, chiefly because of the short time that has elapsed since its recognition; the number of occurrences already recorded, however, (Gruner and Smith, 1954, p. 8; Stieff and Stern, oral communication) suggests that it comprises a significant proportion of the uranium content of many primary Plateau ores.

In summary, the uranium of coffinite, like that of uraninite, alters rapidly to U(VI) in the presence of air; the mineral structure is destroyed and the greater part of the post-depositional history involves U(VI).

#### REACTION OF URANINITE WITH GROUND WATER WITHOUT OXIDATION

One of the major questions concerning the post-depositional history of the Plateau ores is the possibility of migration of uranium by solution and redeposition as a result of the action of moving ground water. Inasmuch as ground waters below the water table are usually reducing and slightly alkaline, the problem in that environment appears to be related to the direct solubility of uraninite and coffinite in such media rather than to transport by a combined oxidation-transport-reduction process.

Uraninite is so extremely stable, in terms of giving up U(IV) to water solutions, that it appears doubtful if much movement can take place without oxidation. The same is probably true of coffinite. No good data are available on the solubility of  $UO_2$  in water, although some work has been done on  $U(OH)_4$ , the less stable hydroxide (Leider, 1954). Values reported for the solubility of the hydroxide in water and NaOH solutions range around  $10^{-6}$  mols per liter at average ground water pH values (7-9). There is, however, a strong likelihood that this measured value is that of U(VI), rather than U(IV), inasmuch as oxidation occurs very easily, and the amount of soluble uranium involved is so small.<sup>1/</sup>  $UO_2$  is notably difficult to dissolve even in very strong nonoxidizing acids. According to Phair and Levine (1953, p. 367), "The results of these investigations show that unaltered pitchblende is itself relatively insoluble in even the most concentrated solutions of  $H_2SO_4$  at room temperature. Once, however, it has become partly oxidized by contact with oxygen..."

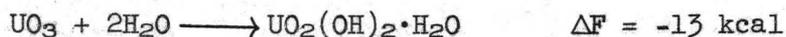
Further indirect evidence on the solubility of  $UO_2$  comes from the tendency of U(IV) in solution to behave as a moderately strong basic cation with little tendency to form stable soluble complexes. In other words, it is quite certain the  $UO_2$  will not dissolve appreciably without oxidation unless very stable complexes exist. We are always in the quandary of not being sure of the composition of ancient ground waters, but at least there is no current reason to expect that they contained any effective U(IV) complexing agents.

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<sup>1/</sup> Also, Leider's results (1954) for the solubility of  $UO_3 \cdot H_2O$  and  $U(OH)_4$  are strikingly similar, both in acid and alkaline solution.

REACTIONS OF  $UO_3$  WITH GROUND WATER $UO_3$  hydrates and related compounds

As shown before, the first stage of alteration of uraninite is to amorphous  $UO_3$ , apparently by an essentially solid state reaction, without the intervention of a solution step.  $UO_3$  is unstable relative to uranyl hydroxide hydrate in water solution (Garrels, 1955), and the reaction



takes place in a pure water solution.

There is a family of uranyl hydroxide hydrates, including  $UO_2(OH)_2 \cdot H_2O$ ,  $UO_2(OH)_2 \cdot 1/2 H_2O$ , and  $UO_2(OH)_2$  (Katz and Rabinowitch, 1951, p. 281-294), but they are not common minerals on the Colorado Plateau. They differ from each other by small increments of free energy, which probably explains their coexistence. It appears that the hydroxide monohydrate [ $UO_2(OH)_2 \cdot H_2O$ ] is in fact the stable species in water at 25° C and atmospheric pressure (Bullwinkel, 1954, p. 8).

The sparsity of uranyl hydroxide hydrates on the Plateau, as opposed to their abundance and striking development in other areas, perhaps is related to the semiarid climate and low water table of the Plateau. Oxidation takes place in thin films of water on the mineral grains after the water table has dropped, and concentration of ions is high in these films, so that compounds other than the oxides develop. The uranyl hydroxide hydrates probably form and persist only in the virtual absence of carbonate species.

Structurally the uranyl hydroxide hydrates are members of the more general class of compounds represented by the formula  $xMeO \cdot yUO_3 \cdot zH_2O$  where Me is Pb or Ba, and perhaps Ca (Christ and Clark, 1955). Among the minerals

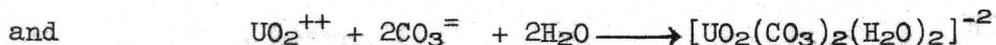
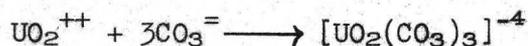
included in this class are becquerelite, schoepite, billietite, masuyite, fourmarierite, and vandendriesscheite. The structure common to all of these minerals is shown in figure 2. It consists of a pseudohexagonal arrangement of linear vertical uranyl ions linked together into infinite horizontal sheets by the hydroxyl ions, with the sheets held together in the crystal in the vertical direction by water molecules or by metal ions and hydroxyl ions. Thus, the formula  $x\text{MeO} \cdot y\text{UO}_3 \cdot z\text{H}_2\text{O}$  should be written as  $x\text{Me}(\text{OH})_2 \cdot y\text{UO}_2(\text{OH})_2 \cdot (z-x-y)\text{H}_2\text{O}$ .

#### UO<sub>3</sub>-carbonate complexes

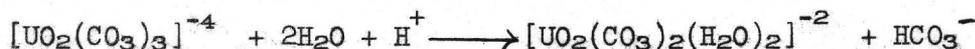
Uranyl ions form soluble complexes with carbonate ions. In many ores calcite is an abundant constituent of the rocks, and during oxidation of accompanying pyrite the calcite is dissolved to give a solution high in  $\text{HCO}_3^-$  ion. Unless there is an excess of pyrite relative to calcite, the resultant solution eventually reaches a pH between 6 and 8, representing ideal conditions for the formation of uranyl carbonate complexes (Bullwinkel, 1954).

The following discussion of the carbonate complexes in water is based largely on the work of Bullwinkel (op. cit.).

Both a di- and a tri-carbonate complex are formed:

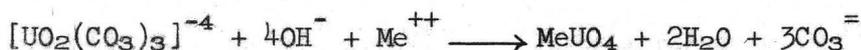


These complexes are most effective in the intermediate pH range because they are destroyed both by  $\text{H}^+$  and  $\text{OH}^-$ . Addition of  $\text{H}^+$  to the tricarbonate complex in solution gives successively the dicarbonate complex and the uranyl ion:



Further acid addition will form  $\text{H}_2\text{CO}_3^-$ .

Addition of  $\text{OH}^-$  to the tricarbonat complex tends to form insoluble metal uranates with available cations:



Thus either acid or alkaline conditions tend to break up the carbonate complexes and reduce the solubility of uranium in solution. Evaporation, on the other hand, tends to precipitate the solid uranyl carbonates. Five of these are known from the Plateau--liebigite, schroeckingerite, bayleyite, andersonite, and rabbittite. Their compositions are shown in figure 1. The particular species formed depends chiefly on the relative abundance of  $\text{Na}^+$ ,  $\text{Ca}^{++}$ , or  $\text{Mg}^{++}$ .

All of these carbonates are hydrated. The crystals contain the complex carbonate ions (fig. 2) as discrete units and accordingly are all easily soluble in water and their geologic behavior reflects this high solubility. The minerals form as efflorescences on mine walls and in the zone of evaporation near the ground surface. Their existence is transitory even by human standards. Changes in the distribution of the carbonates can be observed almost from day to day. With the exception of an occurrence in the Thompsons district, Utah (Weeks, A. D., personal communication) uranyl carbonates are known only from nonvanadiferous ores.

Anhydrous uranyl carbonate  $\text{UO}_2\text{CO}_3$  (rutherfordine) is very rare on the Plateau, although it is relatively abundant in other uraniferous terranes. Some insight into the reason for its rarity can be interpreted from Bullwinkel's observations (p. 35) on the conversion of  $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$  to  $\text{UO}_2\text{CO}_3$  by bubbling of air through a water suspension of the hydrated oxide. The small amount of  $\text{CO}_2$  in air is sufficient to cause the change. On the other hand, if excess carbonate or bicarbonate is added to the solution (as  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$ )

rutherfordine dissolves as uranyl carbonate complexes are formed. Although the experiment has not been performed, it appears likely that evaporation would yield hydrated compounds with a  $UO_2^{++}/CO_3^{--}$  of 1/3, like those observed on the Plateau. Thus rutherfordine probably forms under humid climatic conditions, where relatively pure water is draining through the zone of oxidation; whether it or uranyl hydroxide hydrates forms depends on the partial pressure of  $CO_2$  in the atmosphere. On the Plateau, where the ground waters contain much carbonate and bicarbonate, rutherfordine, if formed, would dissolve, and the only carbonates are those formed by evaporation, which record their genesis from the soluble carbonate complex by the universal  $UO_2^{++}/CO_3^{--}$  of 1/3, as opposed to the 1/1 in rutherfordine. Furthermore the structure of rutherfordine is similar to that of the uranyl hydroxide hydrates, rather than to the hydrated uranyl carbonates (Christ, Clark, and Evans, 1955).

#### Uranyl sulfates

When pitchblende or coffinite oxidizes in the presence of iron sulfides or copper-iron sulfides, or both, and in the absence of appreciable amounts of vanadium, phosphorus, or arsenic, small amounts of the sulfates uranopilite, johannite, and zippeite may form. The genesis of the sulfates is similar to that of the carbonates. Oxidation of accompanying sulfides yields sulfate ion in acid solution. Sulfate, like carbonate, forms a complex with the uranyl ion. The sulfate complexes are not nearly so stable as the carbonate but are sufficiently stable to increase the solubility of U(VI) markedly. According to Brown (Brown and others, 1954) the "complex" is undissociated  $UO_2SO_4$ . The dissociation constant of the reaction



is approximately  $7 \times 10^{-4}$  at room temperature, indication that uranyl sulfate dissolved in water would have a few percent of its uranium available as uranyl ion. In the presence of excess sulfate, as would be the case in the oxidation of an ore containing sulfide, the fraction of uranium tied up would be much greater.

Like the carbonates, solid uranyl sulfates apparently form only by evaporation of ground water. The resultant compounds are poorly characterized. They form crystals of appreciable size only with great difficulty; in most occurrences they form colloform precipitates. They are somewhat analogous to the basic copper sulfates, such as brochantite, for the originally precipitated material is essentially a gel of indefinite composition. Upon aging, composition changes progressively with water loss, and continuous recrystallization of a whole series of solid phases takes place. It is likely then that the compositions given in figure 1 are not truly representative of most natural uranyl sulfates inasmuch as they have been determined from the best crystallized minerals available. The natural materials found as crusts and efflorescences are probably more hydrated than the selected materials studied in the laboratory.

Summary of the oxidation-reduction relations in uranium ores  
low in vanadium, phosphorus, or arsenic

As indicated in figure 1 oxidation of primary uranium ores in the absence of vanadium, phosphorus, and arsenic may well result in rapid loss of uranium to ground water. The absence of any "fixing elements", plus complexing of the uranyl ion by sulfate or carbonate ion, provides optimum conditions for retaining uranium in solution. If the primary association is uraninite plus pyrite in a noncarbonate gangue, oxidation produces a strongly

acid sulfate solution in which  $UO_3$  dissolves as fast as it is formed by solid state oxidation of the original  $UO_2$ . Unless evaporation essentially to dryness takes place the dissolved uranium is carried away.

Uranium is even more soluble in the presence of carbonates. The hydrogen ion developed by oxidation of the sulfides is neutralized by reaction with the calcite of the gangue and a neutral or slightly alkaline solution high in sulfate, bicarbonate, and carbonate is formed under these conditions. The complexing action of the carbonate ion is added to that of the sulfate ion producing conditions of maximum uranium solubility.

In the presence of reactive silica, uranium can be fixed into the relatively insoluble silicates. Unfortunately, little is known of the environment in which they can form, or even concerning their stability after crystallization. Locally, however, they are important factors in the fixation of uranium in nonvanadiferous ores.

In nonvanadiferous ores then, there is commonly abundant evidence of the migration of uranium in the zone of oxidation. For example, the outcrop itself may be almost entirely free of uranium and its former presence may be suggested only by traces of oxidized copper minerals. Behind the outcrop, a zone measured usually in a few feet or a few tens of feet may be found in which uranyl sulfates and carbonates are intermixed with iron oxides and oxidized copper minerals. In this zone chemical uranium values may differ markedly and erratically from equivalent uranium, inasmuch as the daughter products of radioactive disintegration are generally less soluble and uranium tends to move differentially. At the margin of oxidation a rather abrupt change to essentially unaltered pitchblende-sulfide ore may take place. The extent and effects of oxidation differ markedly, of course, from place to place, depending upon the details of the geology, but movement, redistri-

bution, and loss of uranium are characteristic. Loss of uranium is retarded by adsorption of uranyl ion on hydrous ferric oxides, and similar colloidal materials, but the efficiency of the process is incompletely understood (Lovering, 1955).

#### THE URANIUM LAYER COMPOUNDS--VANADATES, PHOSPHATES, AND ARSENATES

In the upper part of figure 1 a large number of mineral species are listed under the headings of vanadates, phosphates, and arsenates. There is, however, a single structural theme that unifies them so that their genesis can be discussed almost as if they were but a single mineral. Inspection of their formulas and of their basic structure, as shown in figure 2, shows that they are composed of sheets made up by a combination of uranyl ion with vanadate, phosphate, or arsenate ion and that various metal ions and/or water are rather loosely bound between the sheets. The vanadate, arsenate, and phosphate ions are coordinated around the uranium of the uranyl ion in similar manner. The bonds within a layer are very strong. In addition, as can be seen from figure 2, the planar structure can be extended essentially indefinitely. This possibility of a development of "infinite" sheets explains why the vanadates, phosphates, and arsenates are so slightly soluble, whereas the carbonates and sulfates, which contain finite groups, are so soluble.

The picture emerges that primary uranium minerals oxidize to  $UO_3$ .  $UO_3$  in turn reacts with water to provide a certain amount of uranyl ion. As soon as uranyl ion encounters ~~quintivalent~~ vanadium, phosphorus, or arsenic in solution, there is a tendency to build up the clay-like sheets which are held together loosely by whatever cations happen to be in solution and by water molecules. Neither phosphorus nor arsenic occurs in important amounts in the Plateau deposits except locally. Therefore, the reactions of uranium with vanadium

will be discussed at length and the corresponding phosphates and arsenates will be treated only by implied analogy.

The two major uranium vanadates are carnotite and tyuyamunite (or meta-tyuyamunite, which has a lower degree of hydration). The vanadium in these compounds is 5-valent vanadium. Because the primary oxidizable vanadium mineral apparently is montroseite [V(III) oxide] neither carnotite nor tyuyamunite can form until uranium has achieved a +6 valence and vanadium has gone all the way from +3 to +5. Various studies have shown that pitchblende and coffinite are among the first minerals to oxidize. In most cases uranium reaches +6 valence before all the vanadium has been oxidized to vanadium (IV). Consequently there is a stage during the oxidation of a given uranium-vanadium deposit in which the uranium occurs as uranium (VI) but in which there is no vanadium (V) with which it can combine. Little is known concerning the solid phase in which uranium occurs at this stage. Some specimens have been examined that contain several percent uranium as +6 but in which there is no identifiable uranium mineral. It is conceivable that at this stage the uranium exists as amorphous black  $UO_3$ , although it is difficult to understand why some hydration to give brightly colored  $UO_3$  hydrates has not occurred, but they seem to be absent. Also at this stage the uranium is readily leachable in very dilute acid solution if precautions are taken to prevent any oxidation of vanadium to vanadium (V). Numerous speculations could be made concerning the phases containing uranium at this stage, but so little real evidence is available that these probably should be deferred.

There is another problem related to the transition from unoxidized ores to uranyl vanadates, phosphates, and arsenates. Carnotite and tyuyamunite are orthovanadates, that is, the anion is  $VO_4^{-3}$ . During oxidation the pH ranges from perhaps 1 to 9. From the equilibria among various +5 vanadium

species in solution it must be concluded that the concentration of  $\text{VO}_4^{-3}$  ion in the ground waters is vanishingly small. Some workers go so far as to state that vanadium cannot occur in water solution as a  $\text{VO}_4^{-3}$  ion, and it appears quite certain that pH values of the order of 12 to 14 are the lowest at which  $\text{VO}_4^{-3}$  can possibly exist. Apparently some intermediate solid compound is necessary in the formation of carnotite or tyuyamunite. This compound presumably would be the result of a combination of uranyl ion with metavanadate, pyrovanadate, or even more condensed vanadate ions, rather than with the orthovanadate ion itself. Then a solid state transformation in the structure of the original precipitate, involving release of some of the vanadium to solution, is necessary to form the uranyl orthovanadate sheets. This presumed intermediary compound is shown in figure 1 as rauvite. There is a certain amount of experimental evidence for the presence of such an intermediary. In studies of the system involving  $\text{UO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{K}_2\text{O}$ , and  $\text{H}_2\text{O}$  a uranyl vanadate with a higher vanadium-uranium ratio than carnotite or tyuyamunite has a rather wide field of stability. It is assumed, therefore, that carnotite and tyuyamunite never precipitate directly but are preceded by a solid phase of different composition which reconstitutes by a decomposition reaction. The necessity for such an intermediary may explain the extreme fineness of grain of most natural carnotite and tyuyamunite. If it were possible to react  $\text{UO}_2^{+2}$  and  $\text{VO}_4^{-3}$  directly good crystals might form.

The solubility of carnotite in normal ground waters is small, perhaps even in the presence of appreciable carbonate. The solubility of tyuyamunite is considerably greater although no quantitative values are available. This difference can be attributed to the excellent "fit" of potassium ion into the positions between the uranyl vanadate sheets. The calcium ion is smaller than the potassium ion and even though it is doubly charged it does not bind the

sheets together with equal effectiveness. A good parallel can be drawn between the uranyl vanadates, phosphates, and arsenates and ordinary clay minerals. The cations are held in exchange positions. As in the clays potassium and calcium are held very firmly, whereas sodium and magnesium are more easily exchanged.

Therefore, even in the presence of abundant calcium and sodium a small amount of potassium ion in solution is preferentially taken up in the inter-layer positions to form carnotite, so that carnotite is a widespread and extremely important ore mineral even in environments in which calcium ion is more concentrated than potassium in the ground waters. On the other hand, a great deal of yellow powdery material probably has been called carnotite that is in fact tyuyamunite.

The very low solubility of carnotite under most earth surface conditions is shown by the presence of equilibrium between uranium and daughter products in most bulk samples of carnotite-bearing ores. If there were substantial active leaching, relative movement of uranium and daughter products should have disrupted this equilibrium. Furthermore, lead-uranium ages of many carnotite-bearing samples are in good agreement with those containing pitchblende, showing oxidation in situ without migration. On the other hand, near the outcrop, or more generally in the zone in which there is active entrance of water into and evaporation from uranium-vanadium ores, it appears possible that considerable movement of uranium may occur. The thin soils in most of the Plateau area are very high in carbonates, attesting the continuous upward migration of carbonates by a capillary process. Under these optimum conditions for the formation of soluble uranyl carbonate complexes uranium may be leached even from carnotite.

Oxidation of a primary pitchblende--or coffinite-montroseite ore probably follows these steps: First, uranium minerals oxidize to U(VI). The solid species of this stage are unknown. At a slower rate the vanadium oxidizes to vanadium(IV) and then to vanadium(V). As soon as any vanadium(V) is available it unites with uranyl ion to form a uranyl vanadate. The nature of original uranyl vanadate formed is not well defined and perhaps is best described under the general term of rauvite. Then, through decomposition, typical uranyl orthovanadate sheet structure develops and available ions in the solution take up interlayer positions. If there is any appreciable potassium, it is taken up preferentially and binds the sheets together into the very insoluble carnotite. After potassium is essentially used up in forming carnotite, tyuyamunite is formed. Carnotite or tyuyamunite, once formed, tend to be stable under the semiarid conditions of the Colorado Plateau, although local movement and recrystallization along cracks and fractures is observed commonly and it is not unlikely that there is considerable movement at or near the present ground surface. This near-surface movement undoubtedly is promoted chiefly by the presence of carbonates.

No quantitative data are available on the relative solubilities of the uranyl vanadates, arsenates, and phosphates, although from their general geologic behavior the sequence as given probably is in order of increasing solubility.

#### SUMMARY

In summary, primary uranium minerals are essentially insoluble under reducing conditions. As soon as oxygen is added to the system, however, direct oxidation of the solid uranium(IV) phases apparently takes place to give amorphous  $UO_3$ . In the absence of vanadium, phosphorus, or arsenic the

$UO_3$  dissolves easily in ground waters, especially those containing carbonate or sulfate. Deposition of the dissolved uranium takes place only as a result of evaporation of the ground water to form crusts and efflorescences of uranyl carbonates or basic uranyl sulfates, or locally by reaction with dissolved silica to form uranyl silicates. Uranium(VI) is fixed by arsenic and phosphorus and especially by vanadium. It apparently becomes fixed as a uranyl vanadate of transitory existence by reaction with almost any anionic species containing vanadium(V). Decomposition of this intermediate, plus reaction with potassium or calcium produces insoluble carnotite or tyuyamunite. Once precipitated these minerals persist except where exposed at the outcrop.

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