SUPERCENE ALTERATION OF URANIUM-BEARING VEINS
IN THE UNITED STATES*

By

George W. Walker

August 1957

Trace Elements Investigations Report 693

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SUPERGENE ALTERATION OF URANIUM-BEARING VEINS IN THE UNITED STATES

By George W. Walker

FOREWORD

This paper, dealing with supergene alteration of uranium-bearing veins, is a chapter of a comprehensive report entitled, "Geology of uranium-bearing vein deposits in the United States," in preparation by George W. Walker, Frank W. Osterwald, and others. The comprehensive report will include detailed information on tectonic and structural setting, kinds of host rocks, wall-rock alteration, mineralogy, physical characteristics, processes of deposition, and concepts of origin of uraniferous veins; but, because it will not be completed until sometime in the future, some chapters of the report are being transmitted as they are finished. The following chapters of the comprehensive report have been transmitted to the Atomic Energy Commission:

Classification and distribution of uranium-bearing veins in the United States (by George W. Walker and Frank W. Osterwald); distributed as U. S. Geological Survey TEI-486.

Host rocks and their alterations as related to uranium-bearing veins in the United States (by George W. Walker); distributed as U. S. Geological Survey TEI-638.

Several of the terms used herein are defined in the chapter on "Classification and distribution of uranium-bearing veins in the United States."
The compilation of data leading to this report and its preparation by the U. S. Geological Survey, was done on behalf of the Division of Raw Materials, U. S. Atomic Energy Commission. The report is based on both published and unpublished information collected principally by personnel of the U. S. Geological Survey, the U. S. Atomic Energy Commission or its predecessor organization, the Manhattan Engineer District, and to a lesser extent by staff members of other federal or state agencies and by geologists in private industry. Information concerning foreign uranium-bearing vein deposits has been extracted almost exclusively from published reports; references to these and other data are included at appropriate places.
INTRODUCTION

Virtually all uranium-bearing vein deposits in the United States show some evidence of supergene alteration, but the degree and products of alteration are very different for different deposits. The hypogene uranium minerals within these deposits, many of the associated non-uraniferous vein minerals, and locally some wall-rock minerals have been altered at or near the ground surface into minerals that tend to be more stable in an oxygenated environment. In some deposits, the transformation of primary minerals into secondary ones has occurred essentially in place, whereas in many other deposits some of the elements have been redistributed resulting in enriched or impoverished zones. Where the altering, meteoric waters were moderately to strongly acid, particularly in some of the deposits characterized by abundant base-metal sulfide minerals, considerable leaching and removal of materials resulted. Thus, three patterns of distribution—or redistribution—for uranium in the oxidized parts of veins have been demonstrated, namely enriched or impoverished zones or zones in which alteration occurred essentially in place; none of these patterns of distribution is directly correlative with the mineralogic class of the veins (Walker and Osterwald 1956).
Several studies of the chemistry of uranium and associated elements, under conditions of supergene alteration have been made by Phair and Levine (1953), Weeks (1956), McKelvey, Everhart, and Garrels (1955), Lovering (1955), Barton (1956), and particularly by Garrels (1953; 1954; 1955), Garrels and Christ (in preparation), and Garrels and Pommer (1956). Most of these studies pertain to uranium deposits other than veins; however, the chemical processes outlined, the physicochemical conditions of alteration, the relation of alteration zones to the water table (or, more correctly, to changes in the redox potential), and the resultant oxidation products are very similar to those that have been noted for uranium-bearing vein deposits in the United States. Few qualitative differences exist between the oxidation of uraniferous veins and other kinds of uranium deposits; some quantitative differences, such as the presence, abundance, or frequency of occurrence of certain minerals, have been noted and are largely attributable to dissimilarities in the original assemblage of hypogene minerals in the deposits, to dissimilarities in the ions that may be available from the wall-rocks, and probably, in part, to differences in permeability. Some uranium-bearing vein deposits are characterized by abundant metallic sulfides; the supergene alteration of these deposits, particularly under wet climatic conditions, commonly results in leached outcrops in which 6-valent uranium minerals are sparse or lacking. Furthermore, there is some evidence to suggest that enrichment of uranium by supergene processes may be more prevalent in veins than in other kinds of uranium deposits.
PROCESSES OF SUPERGENE ALTERATION

The whole process of supergene alteration, including secondary enrichment, encompasses not only the oxidation and reconstitution of the original hypogene assemblage of minerals in uranium-bearing veins but also, in a few places, the subsequent reduction of some of the oxidation products. The process is not unlike that described for copper deposits (Emmons, 1917, 1933; Bateman, 1950; Anderson, 1955) and differs principally in the character and, more largely, quantity of materials involved. Hydration, evaporation, saturation, and chemical interaction between solutions, vein filling, or wall rocks are important aspects of the supergene alteration of uranium-bearing veins. In this report, the discussion of supergene alteration will be restricted largely to the effects upon uranium within vein deposits and only incidentally to the effects on associated elements.
Uranium in vein deposits is found in both the 4-valent and 6-valent state; the 4-valent state is characterized principally by pitchblende or uraninite, and, in a few veins, by coffinite, uranothorite, brannerite, and several other minerals in which uranium is present either as an extrinsic or vicarious constituent (Walker and Adams, in preparation). Partial and complete analyses of pitchblende from several different vein deposits demonstrate that both 4- and 6-valent uranium is invariably present, most commonly with 4-valent uranium predominant (Palache, Berman, and Frondel, 1944, p. 612-613; Brooker and Nuffield, 1952). Uraniferous fluorite, which is common in several vein deposits, presumably contains principally 4-valent uranium. Uranium of valence six is present in vein deposits principally as uranyl phosphates, silicates, vanadates, sulfates, arsenates, or carbonates, and less commonly as uranyl molybdates or hydroxide hydrates; adsorbed uranyl ions are prevalent in the oxidized parts of some vein deposits (Levering, 1955; Barton, 1956), although their abundance in most deposits remains essentially unknown. In most vein deposits, the 6-valent uranium minerals and adsorbed uranyl ions had their origin in the near-surface oxidation of pitchblende, coffinite, or, in a few places, uraniferous fluorite, according to the alteration and oxidation pattern described by Garrels and Christ (in preparation). Many vein deposits, however, contain uranium only in the 6-valent state and lack evidence, other than presence of uranyl compounds, to indicate that 4-valent uranium minerals were ever present. Conceivably, some or all of these deposits resulted from the direct precipitation of uranyl compounds under near-surface oxidizing conditions and are not the result of the
alteration, essentially in place, of 4-valent uranium minerals; such deposits presumably would be like those described as caliche-type by Bell (1956, p. 385).

Inasmuch as Garrels and Christ (in preparation) have described in some detail the behavior of uranium under oxidizing conditions, only a brief summary of their work will be presented here, largely in diagrammatic form (fig. 1). The processes and sequence of oxidation, as described by them, are based on the premise that uraninite and coffinite are the progenitors of all the $^{4+}$ phases for uranium deposits on the Colorado Plateau; a similar premise applies to most uranium-bearing vein deposits, for the only quantitatively important 4-valent uranium minerals reported from veins are pitchblende and, less commonly, coffinite, and uraniferous fluorite.

Figure 1, which is reproduced, with slight modification, from Garrels and Christ's (op. cit.) figure 1, demonstrates the general features of the chemical reactions and the products that result from the oxidation of 4-valent uranium minerals in vein deposits. The sequence and pattern of alteration from hard, massive pitchblende, high in $\text{UO}_2^+$, through amorphous $\text{UO}_3^+$, to uranyl ions in solution and thence to a variety of chemically diversified uranyl compounds or to adsorbed uranyl ions are in all essential characteristics identical with those described by Garrels and Christ (op. cit.) for deposits on the Colorado Plateau. The 4-valent uranium of coffinite and uraniferous fluorite is altered, in an oxidizing environment, to form uranyl ions in solution; these react in the same way as the uranyl ions derived from pitchblende.
FIGURE 1. REACTIONS AND PRODUCTS RELATED TO SUPERGENE ALTERATION OF URANIUM-BEARING VEINS

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The uranyl ions in solution may 1) react with available anions and cations to form soluble or insoluble uranyl compounds, 2) be adsorbed on hydrated iron oxides or other colloidal materials (Rankama and Sahama 1950), or 3) be carried away by migrating ground or surface waters either as uranyl ions or as soluble uranyl carbonate or sulfate complexes.

According to Garrels and Christ (in preparation), "Uranyl ion may form complex carbonate or sulfate ions with resulting soluble compounds, but only in the absence of quinquevalent vanadium, arsenic, or phosphorous."

The uranyl carbonate minerals including schroeckingerite, andersonite, bayleyite, and swartzite, and the uranyl sulfate minerals—johannite, uranopilite, and zippeite—apparently form only by the evaporation of ground water and, consequently, are most abundant in arid to semi-arid regions. In those places where 5-valent vanadium, arsenic, or phosphorous are available, uranyl ions in solution may react to form slightly soluble uranyl vanadates, phosphates, or arsenates; the particular mineral species that forms is dependent, in part, on the presence and abundance of other cations, principally $K^+$, $Ca^{++}$, $Pb^{++}$, and $Mg^{++}$.

In the presence of reactive silica, uranyl ions in solution may react to form hydrous uranyl silicates, including uranophane, kasolite, and sklodowskite; however, according to Garrels and Christ (op. cit.), "Little is known of the environment in which they form, or even concerning their stability after crystallization."

Umohoite, a hydrous uranyl molybdate (Kerr, Brophy, Dahl, and others, 1957, p. 66), has been reported from veins at Marysvale, Utah (Kerr, Hamilton, Brophy, and others, 1953, p. 45-51). Coleman and Appleman (1957)
consider that the uranium or the molybdenum or both in umohoite are in an oxidation state lower than hexavalent as based on studies of a uranium molybdate from the Lucky Mc mine, Wyoming; this umohoite occurs with partly oxidized uranium ore. The processes involved in the formation of umohoite are incompletely understood; it may be a hypogene vein mineral, as postulated by Kerr and others (1953), or it may be either a product of late-stage hydrothermal alteration or supergene alteration as suggested by Walker and Osterwald (1956, p. 127). Umohoite is hydrous and may contain principally 6-valent uranium; consequently, it appears to be more closely allied to the 6-valent uranium minerals that are derived through alteration in an oxidizing environment and its distribution at Marysvale tends to support such a relationship. On the premise that some or all of the umohoite may result from the interaction of uranyl and molybdate ions under conditions of supergene alteration, it has been shown on figure 1.

A few of the minerals containing 6-valent uranium, specifically becquerelite, "gummite," and schoepite, appear to be deposited directly from uranyl ions in solution (Garrels and Christ, op. cit.). In several vein deposits, however, these uranyl hydroxide hydrate minerals, either separately or collectively, occur as pseudomorphous replacements of hypogene pitchblende in which both the external and internal colloform textures of the hypogene pitchblende are largely retained. In these places, it seems likely that the transformation of hard, colloform pitchblende to becquerelite, "gummite," or schoepite by supergene processes occurs essentially in situ and not as a result of precipitation
from uranyl ions in solution; some uranium presumably is given up to
solution as a result of the reaction.

Ianthinite, presumably a UO₂ hydrate, has been reported in association
with pitchblende from the Marshall Pass area, Colorado (Young, E. J., oral
communication, 1956); it is included as a product of supergene alteration
although there is considerable doubt as to its exact mode of formation.
The ianthinite at Marshall Pass occurs as lavender idiomorphic crystals
that coat the walls of cavities or vugs in hard, colloform pitchblende.
The distribution of the ianthinite indicates that it is derived through
alteration of the pitchblende possibly by supergene processes or, as
postulated by Kohl and Haller (1934) for ianthinite at Wolsendorf, by
low-temperature hydrothermal alteration.

Hydration of pitchblende, with only partial oxidation, appears to
be part of the supergene alteration of the uranium-bearing vein deposits
at the North Star mine and the Nigger Shaft deposit, Jefferson County,
Colo. (Adams, Gude, and Beroni, 1953, p. 16). The hydrated pitchblende
in both deposits is closely associated with a supergene suite of copper,
iron, and uranium minerals and texturally is similar to hard, unaltered,
colloform pitchblende that is present at depth. The hydrated pitchblende
is brown or olive green in color, slightly translucent and may be closely
allied to the hydropitchblende (UO₂• kUO₃• nH₂O; k = 2.3-5; n = 3.9-9) of
Getseva (1956). The formation of hydrated pitchblende, containing greater
amounts of UO₃ than UO₂, perhaps can be considered a side and intermediate
product in the transformation of pitchblende rich in UO₂ to amorphous
UO₃ (fig. 1).
In many vein deposits, the mode of occurrence and the physical characteristics of sooty or regenerated pitchblende (Walker and Adams, in preparation), as well as its distribution in regard to hard, massive pitchblende and to the zone of oxidation, suggest that some and perhaps all, of this material is derived through the process of supergene alteration; some may result from alterations related to hydrothermal or solfataric action. According to presently accepted concepts of uranium transport (Phair, 1952; Miller and Kerr, 1954; McKelvey, Everhart, and Garrels, 1955; Gruner, Gardiner, and Smith, 1953; Gruner, 1956), the derivation of "supergene" sooty or regenerated pitchblende perhaps can best be explained by 1) initial oxidation of 4-valent uranium minerals and formation of uranyl ions in solution, 2) migration of these solutions to zones of decreased oxidation potential, and 3) precipitation of uranium in the reduced, 4-valent state. Such a process is comparable to that proposed for the formation of sooty chalcocite (Anderson, 1955).

The extent and effects of the different chemical reactions that are a part of supergene alteration (fig. 1) differ markedly from deposit to deposit, depending on the original hypogene assemblage of minerals in the veins, the mineralogic and physical characteristics of the enclosing wall rocks, the position of the deposit in regard to the ground surface (or presumably to the water table), and on the chemical and physical character and volume of altering solutions. In arid to semi-arid regions supergene alteration of uranium-bearing vein deposits commonly results in abundant 6-valent uranium minerals at or near the ground surface which is attributable, in part, to the strongly oxidizing character of an arid
environment (Mason, 1949, p. 67) but perhaps more largely to only slight removal by solution of alteration products. In wet regions, the uranium commonly is depleted or removed from near-surface extensions of uranium-bearing veins and 6-valent uranium minerals are sparse or lacking; intensely leached outcrops are particularly prevalent in vein deposits characterized by metallic sulfide minerals.

GEOLOGIC EXPRESSION OF SUPERGENE ALTERATION OF URANIUM-BEARING VEIN DEPOSITS

The geologic expression of supergene alteration of uranium-bearing vein deposits includes not only the presence of oxidized and hydrated uranium minerals or adsorbed uranyl ions but also, in some deposits, 1) a zoned distribution of these minerals and 2) zones of uranium enrichment or depletion in different parts of vein systems according to local environmental conditions.

Some mineralogic aspects of supergene alteration

Supergene alteration and the formation of 6-valent uranium minerals are quantitatively important in three of the seven mineralogic classes of uranium-bearing vein deposits known to occur in the United States (Walker and Osterwald, 1956), namely 1) fluorite-bearing veins, 2) veins in which uranium is subordinate to base-metal sulfide minerals, and 3) veins in which uranium minerals are "dominant." Certain, rather ill-defined assemblages of the more common uranyl minerals, listed below, tend to characterize these three different classes of vein deposits; in part they reflect the metal composition of vein filling and probably the presence of certain ions in the adjoining wall rocks. Many exceptions
can be noted to the general characteristics of these assemblages. The 6-valent uranium minerals within the different assemblages are listed below in the approximate order of decreasing frequency of their reported occurrence, an arrangement that is not necessarily coincident with their relative abundance in any one deposit or district.

**Fluorite-bearing veins**

Autunite and/or meta-autunite, uranophane, torbernite or metatorbernite, carnotite, schroeckingerite, johannite.

**Base-metal sulfide deposits**

Torbernite or metatorbernite, autunite, kasolite, "gummite," zeunerite or meta-zeunerite, johannite, zippeite.

**Uranium minerals dominant**

Autunite and meta-autunite, uranophane, carnotite, tyuyamunite or metatyuyamunite, torbernite or metatorbernite, "gummite," uranocircite or meta-uranocircite.

Several 6-valent uranium minerals, including troegerite?, voglite, dumontite, and kasolite, have been reported only from vein deposits; but of these minerals only kasolite is quantitatively important. Kasolite has been identified from the oxidized parts of a number of vein deposits characterized by abundant hypogene or supergene lead minerals, and in one deposit—the Green Monster mine, Clark County, Nev.—it was the dominant uranium mineral of a few tons of uranium ore.

Data on the occurrence of 6-valent uranium minerals in veins suggest that uranyl phosphates and silicates are more characteristic of vein deposits than are uranyl vanadates and arsenates. Both uranyl phosphates and silicates commonly occur together in the same deposit, but in the vein deposits characterized by uranyl vanadates—such as the deposits near
Cement, Okla., several in the Madison limestone in Carbon County, Mont. and Big Horn County, Wyo., the Ridenour mine, Arizona (Miller, R. D., 1954), and the Miracle mine, California (Bowes, W. A., written communication, 1957) -- phosphates, silicates, and arsenates of uranium commonly are present in only minor amounts.

Many other uranyl minerals have been reported from uranium-bearing vein deposits (Walker and Adams, in preparation); but, because the number of reported occurrences for each mineral species is very few, no valid correlation with mineralogic class of vein is possible. In addition, no clear-cut correlation between sooty or regenerated pitchblende and mineralogic class of deposit can be demonstrated with available data; both have been reported in fluorite-bearing veins, base-metal sulfide veins, and those veins in which uranium minerals are dominant. Sooty pitchblende has been reported most commonly from base-metal sulfide veins; this apparent correlation may have geologic significance in that the metal sulfides may create an environment suitable for the reduction of uranyl ions in solution. On the other hand, this apparent correlation can be easily explained by the fact that uraniferous base-metal sulfide veins have supplied more than their proportionate share of detailed data on the mineralogy of uranium-bearing veins.

The assemblage of uranyl minerals that form in veins (fig. 1 and Walker and Adams, in preparation) as a result of supergene alteration closely resembles the assemblage in deposits in continental, clastic sedimentary rocks (Weeks and Thompson, 1954; Gruner, Gardiner, and Smith, 1954) as exemplified by deposits both on the Colorado Plateau.
and in the northeast part of the Cordilleran Foreland. Some of these minor differences are real and result from differences in the original assemblage of hypogene minerals in the deposits and, consequently, the cations and anions that are available for reaction with $\text{UO}_2^{++}$ ions in solution; other apparent differences probably result only from lack of data regarding the complete assemblage of uranium minerals in one or the other kinds of deposits. Whether geologically significant differences exist in the frequency of occurrence or abundance of secondary iron, copper, lead, or zinc minerals in veins as contrasted with other kinds of uranium deposits is difficult, if not impossible, to establish with available data. Obviously secondary iron, copper, lead, and zinc minerals are common and locally abundant in the oxidized part of uraniferous base-metal sulfide veins, but in other kinds of vein deposits they are no more prevalent than in peneconcordant deposits in sandstone.

Zoned distribution of alteration products

Supergene alteration of 4-valent uranium minerals in vein deposits tends to create a zoned distribution of the uraniferous alteration products according to the stabilities and solubilities of these products. The general pattern of this zoning, considered either in relation to an individual mass of pitchblende or more largely to the ground surface and vein structure that contains masses of pitchblende, is shown diagrammatically in figures 2 and 3, and is described, in part, by Stugard, Wyant, and Gude (1952, p. 19-25, figs. 14 and 17).
As shown in figures 2 and 3, the hydrated oxides and hydroxides of uranium, either separately or together, constitute an innermost zone that forms closest to the unaltered pitchblende; not uncommonly only the pitchblende appears to have been pseudomorphous replaced by "gummite," becquerelite, or schoepite; and rarely are the hydrated oxides or hydroxides found more than a few inches from pitchblende or what was pitchblende prior to supergene alteration.

An intermediate zone of alteration products is characterized by uranyl silicates, phosphates, vanadates, molybdates, or arsenates; the mineral species that form are dependent largely on the availability and abundance of the different anions. In those vein deposits characterized by uranyl vanadates, the intermediate zone commonly contains only carnotite or tyuyamunite, and other uranyl minerals are lacking or are present in only very small amounts. Primary, 4-valent uranium minerals have been reported in only a few of the veins containing uranyl vanadates and, consequently, little information is available as to the spatial disposition of these alteration products in regard to the primary uranium minerals; however, oxidation in situ with little or no migration of the uranium seems to characterize those deposits that contain uranyl vanadates (Garrels and Christ, in preparation). The uranyl molybdate, umohoite, is known to occur only in one group of vein deposits (Marysvale, Utah) in which it is concentrated either deep in or just below the zone of supergene alteration. Its precise spatial relationship to unaltered pitchblende is unknown, although it occurs closely associated with finely divided sandy pitchblende and presumably not far removed from masses of
EXPLANATION

- Non-uraniferous vein filling
- Unaltered pitchblende
- Sooty and regenerated pitchblende and including umahoite at Marysvale
- Uranyl hydroxide hydrates
- Uranyl silicates, vanadates, arietates, and phosphates.
- Increasing oxidation potential

Approximate upper limit of 4-valent uranium minerals

Approximate lower limit of 6-valent uranium minerals

Figure 2. Diagrammatic sketch showing zoned distribution of uraniferous alteration products resulting from supergene processes.

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SILICEOUS FOLIATED ROCKS

SILICEOUS CELLULAR ROCKS

EXPLANATION

PITCHBLende

BEQUERCHELITE ZONE

ORANGE ORE

(Conine, Kasolite, Soddyite, Uranophane)

YELLOW ORE

(Scopellite, Soddyite, Uranophane)

GREEN ORE

(Torbernite and Parsonsite)

FIGURE 3 - VERTICAL SECTION ACROSS A VEIN, SHINKOLOWE

(After a sketch by Stuard, Wyont, and Guide, 1932, Modified from Thorat and du Tres, plate 17, 1933.)

10 Feet

5

0
hard, unaltered pitchblende. Most of the intermediate zones contain both uranyl silicates and phosphates, and in a few deposits minor amounts of uranyl arsenates also are present. The distribution of the uranyl silicates, phosphates, and arsenates within vein deposits indicates that the formation of these compounds can take place essentially in situ without appreciable migration of uranium or, more commonly, that the uranium has migrated short distances from the source material. Most of the uranyl silicates, phosphates, and arsenates occur within the vein structures although locally some concentrations are as far as 10 feet from the veins.

A third and outermost zone, characterized by the extremely soluble uranyl carbonates and sulfates, is based largely on theoretical considerations and is not well demonstrated in vein deposits within the United States. Ideally, for the zoning of uranium-bearing oxidation products to be complete, the most soluble uranyl compounds—dominantly schroekingerite, johannite, zippeite, and uranopilite in vein deposits—should be found farthest from unaltered, 4-valent uranium minerals and consequently should be abundant in surface exposures of uranium-bearing veins. Actually these minerals are extremely rare in the vein outcrop and, among vein deposits, are found almost exclusively as efflorescences on mine walls (Derzay, 1956, p. 140 and oral communication, 1957; Walker and Osterwald, 1956, p. 126-127; Stugard, Wyant, and Gude, 1952, p. 19 and 21); in a few caliche-like vein deposits in semi-arid to arid regions (Bell, 1956, p. 385) these minerals may occur at the surface, but their relation to 4-valent uranium minerals is largely unknown.
For most uranium-bearing vein deposits only fragmentary information is available on the distribution of supergene alteration products as related to the original hypogene uranium minerals and, consequently, the zoning of these alteration products has been well demonstrated in only a very few places. Some of the best examples of the zoned distribution of uraniferous alteration products have been reported in the veins at Shinkolobwe (Thoreau and du Trieu, 1933; Derriks and Vaes, 1956), at Marysvale, Utah (Stugard, Wyant, and Gude, 1952; Taylor, and others, 1951; Gruner, Fetzer, and Rapaport, 1951; Walker and Osterwald, 1956); at the W. Wilson mine (Meschter, D. Y., written communication, 1953; Wright, Bieler, Shulhof, and Emerson, 1954), and at the Moonlight mine, Nevada (Sharp, 1955; Taylor and Powers, 1955).

At Shinkolobwe, according to Thoreau and du Trieu (1933), the uraninite alters in situ principally to becquerelite and curite and locally to ianthinite and schoepite. Farther from the uraninite, a zone composed principally of uranyl silicates gives way outwardly to uranyl phosphates, including torbernite, parsonsite, and dewindtite. Derriks and Vaes (1956, p. 107) have indicated that uraninite also has been altered at depth to a host of uranyl hydroxide hydrates—including billietite, vandendriesscheite, and masuyite—and that dewindtite, dumontite, parsonsite, and sklodowskite have not been observed at depth.

Information on the distribution of uraniferous alteration products at Marysvale, Utah, has been summarized by Walker and Osterwald (1956, p. 126-127) largely from data originally presented by Taylor and others (1951), Gruner, Fetzer, and Rapaport (1951), Stugard, Wyant, and Gude,
(1952), and Kerr and others (1952; 1953, p. 45-51). The alteration products tend to be distributed zonally although it is not the "... typical zonation of uranium minerals ..." as depicted by Stugard, Wyant, and Gude (1952 fig. 14, p. 21). The alteration products that occur closest to unaltered pitchblende at Marysvale are sooty pitchblende and umohoite; presumably some and possibly all of the sooty pitchblende and umohoite result from supergene alteration. Further from unaltered pitchblende and extending to the ground surface is a zone of alteration products composed dominantly of uranyl silicates and phosphates. The uranyl phosphates are rare or lacking in outcrops and are found principally 10 feet or more beneath the ground surface and, locally, as much as 400 feet beneath the surface. The uranyl silicates, on the other hand, are most abundant in surface or near-surface exposures but have been reported to depths of approximately 200 feet. The uranyl sulfates, zippeite, uranopilite, and johannite and the uranyl carbonate, surface schroeckingerite, are virtually lacking in outcrops and have been identified principally as efflorescences on mine walls most commonly from about 10 feet below outcrops to depths of about 100 feet.

The zonation of uraniferous alteration products in the W. Wilson mine, Jefferson County, Mont., involves two different suites of 6-valent uranium minerals that, in general, show uranyl hydroxide hydrates nearest unaltered pitchblende, uranyl silicates in an intermediate position, and uranyl phosphates farthest from the pitchblende. Meschter (written communication, 1953) has described an inner zone of alteration in which
pitchblende appears to have altered directly to gummite and phosphuranylite. The intermediate zone is characterized by uranophane, autunite, and uranocircite, and the outermost zone of alteration is represented by metatorbernite and metazeunerite. In the same deposit, but probably in somewhat deeper workings, Wright, Bieler, Shulhof, and Emerson (1954, p. 5) have established a zonal distribution based on a slightly different assemblage of 6-valent uranium minerals. According to them, "Field study has indicated a zoning of secondary uranium minerals outward from primary ore shoots . . . with gummite, uranophane, beta-uranophane, meta-autunite, and torbernite occurring at successively greater distances from the vein."

Later work on the mineralogy of the W. Wilson mine by Emerson and Wright (1957), has verified the presence of meta-uranocircite, metazeunerite, and phosphuranylite, but their position in the zoned sequence is not given.

At the Moonlight mine, Nevada, autunite, torbernite, "gummite," and uraninite(?) exhibit a zoned distribution with depth. According to Taylor and Powers (1955, p. 12) "Autunite is most abundant near the surface but decreases in concentration down the dip of the vein until it is almost absent at a depth of 96 feet. Torbernite and gummite appear as the autunite disappears. Between 80 and 120 feet on the main inclined shaft, traces of gummite occur as halos and coatings around small black cores presumed to be uraninite. At greater depth the only uranium mineral is probably uraninite."

Most other uranium-bearing vein deposits in the United States either do not exhibit zoning of the 6-valent uranium minerals or the zoning is poorly defined commonly because the deposits contain only two or three different species of uranium minerals.
Leaching and enrichment

Supergene alteration of the 4-valent uranium minerals is accompanied in nearly all vein deposits within the United States by redistribution of uranium most commonly with substantial loss of uranium to migrating ground waters. In many of these deposits the processes of supergene alteration have created zones from which uranium has been leached and, in a few deposits, zones of uranium enrichment; in several deposits leaching of uranium at or near the ground surface is accompanied by redeposition and enrichment of uranium at depth in zones of decreased oxidation potential. In only a few vein deposits do alteration and solution of 4-valent uranium minerals and redeposition of 6-valent ones occur essentially in place.

Leaching of uranium in veins as a result of near-surface oxidation is particularly prevalent in those deposits characterized by common or abundant metallic sulfide minerals, and is largely attributable to the chemical processes described by Phair and Levine (1953). Their work has shown that altered and oxidized pitchblende "... is readily susceptible to solution by the $\text{H}_2\text{SO}_4$ invariably present in and around sulfide mines ..." (Phair and Levine, 1953, p. 367) and that the amount of uranium leached is relatable principally to the $\text{UO}_2/\text{UO}_3$ ratio in the altered pitchblende and to the amount of $\text{H}_2\text{SO}_4$ in solution; the pitchblendes high in $\text{UO}_3$ are more readily attacked by the sulfuric acid solutions. Commonly, where the solutions were moderately acid, virtually all the uranium was removed and, in such places, 6-valent uranium minerals are rare, as for example in many of the pyritic deposits of the Colorado Front Range (Sims and Tooker, 1956; Drake, 1957; Sims, Phair, and Moench,
in preparation), apparently in the St. Kevin district, Colorado (Pierson and Singewald, 1954), possibly in the Cebolla district, Colorado (Burbank and Pierson, 1953), and elsewhere. Less stringent leaching of uranium in veins, commonly with associated formation of 6-valent uranium minerals, tends to be characteristic of those deposits containing only small amounts of base-metal sulfide minerals, particularly pyrite, and those deposits that have been altered and oxidized in an environment in which there is little migrating ground water, as for example in the oxidized parts of several uraniferous base-metal sulfide veins in the Goodsprings district, Nevada (Albritton and others, 1954; Barton, 1956).

Sims and Tooker (1956, p. 109) in summarizing data on supergene alteration of vein deposits in the Central City district and adjoining areas, Colorado, make the following general comments:

"In the oxidized parts of the veins, pitchblende was leached and altered where the meteoric waters were acid, and green secondary uranium minerals were deposited where the solutions were nearly neutral. For the most part, the oxidized portions of the veins were impoverished; but locally, particularly in the lower part of the oxidized zone, the veins were enriched in uranium.

The meteoric waters were relatively acid along veins of the pyritic and composite types; the pitchblende was leached and dissociated, and uranium was not reprecipitated as secondary minerals. The solutions were only slightly acid along veins of the galena-sphalerite type . . . [as for example the Carroll mine (Sims, Osterwald, and Tooker, 1955, p. 20-22)] . . . , because these sulfides provide less acid than pyrite on weathering. By reaction with the wall rocks . . . [as well as calcite gangue] . . . the solutions were locally neutralized, and uranium was reprecipitated at places as secondary minerals."

Bird and Stafford (1955, p. 62), in reviewing the geology of several uranium-bearing vein deposits in the Colorado Front Range with special emphasis on deposits near Ralston Creek, suggested that uranium was leached for the first 10 or 20 feet below the surface and at depths of
about 100 feet the deposits probably were enriched with "secondary" pitchblende. The suggested leaching and enrichment of uranium is based on 1) an increase in the chemical uranium: equivalent uranium ratio with depth and 2) a transition with depth from leached outcrops to completely oxidized uranium minerals, to a zone containing mixed 6-valent uranium minerals and sooty pitchblende, and thence to a zone characterized by both sooty pitchblende and massive, unaltered pitchblende.

Studies of the uranium-bearing vein deposits in the Boulder batholith, Montana, including principally the W. Wilson, Free Enterprise, and Gray Eagle mines, have indicated that although alteration of 4-valent uranium minerals to form 6-valent uranium minerals locally occurs essentially in place (Roberts and Gude, 1953a, p. 79; 1953b, p. 153) redistribution and depletion of uranium is characteristic (Roberts and Gude, 1953a, 1953b; Wright, Bieler, Shulhof, and Emerson, 1954). Considerable migration of uranium in some parts of these deposits has been suggested by Thurlov and Reyner (1952, p. 27), but they (1950, p. 1) indicate that there is little, if any, enrichment of uranium at depth.

Secondary (supergene) enrichment of uranium as well as alteration in place has been postulated by Wilmarth and Johnson (1954) for uraniferous vein deposits at the Silver Cliff mine near Lusk, Wyo. They suggest that . . . "During supergene alteration, the primary copper minerals were converted to cuprite, and the pitchblende was altered to guaninite, uranophane, and metatorbernite. The deposits of uraniferous sandstone probably are the result of alteration of the primary minerals in place, whereas those in the light buff sandstone result from solution and
redemption of the uranium by descending ground waters to form a commercial secondary uranium deposit."

Supergene enrichment of uranium immediately below the outcrop of an oxidized lead-zinc ore shoot has been noted at the Green Monster mine, Clark County, Nev. (Albritton and others, 1954). Kasolite and dumonite, intermixed with hydrozincite, calamine, hydrated iron oxide, cerussite, and anglesite (Albritton and others, 1954), were sufficiently abundant below the outcrop to constitute uranium ore and small patches of oxidized material contained slightly over 9.0 percent uranium; presumably some of the uranium is present as uranyl ions adsorbed on several different colloidal materials (Behre and Barton, 1954; Barton, 1956). The amount of uranium diminishes rapidly with depth. One might speculate that the 6-valent uranium minerals represent a dispersed halo around what was a small high-grade mass of pitchblende or other 4-valent uranium mineral contained in the lead-zinc ore body. On the other hand, minute amounts of 4-valent uranium originally may have been dispersed in the unaltered lead-zinc ore body and concentrated in the 6-valent state, as the ore shoot was oxidized and degraded. A similar type of surface or near-surface enrichment of uranium also has been proposed by Staatz and Osterwald (in preparation) for most of the uraniferous fluorite deposits of the Thomas Range, Juab County, Utah. According to them "The increase of uranium content near the surface is believed to have been caused by slow leaching of the upper part of the ore body, in part from material being actively eroded. The uranium is carried downward and redeposited
... as carnotite or some other 6-valent uranium mineral... at some level between a few inches and approximately 30 feet below the surface."

Secondary (supergene) enrichment of uranium in a base-metal sulfide deposit apparently has taken place in the Madonna mine, Chaffee County, Colo. (Dings and Schafer, 1953). Although the deposit contains only small amounts of uranium, it appears to be concentrated in porous oxidized material that borders an ore body of primary base-metal sulfide minerals.

In a few places, uranium in vein deposits appears to be neither enriched nor greatly depleted as a result of near-surface supergene alteration. In most vein deposits, solution, redistribution, and subsequent loss of uranium to migrating ground waters is characteristic, but, in a few veins, largely in arid to semi-arid regions, alteration and oxidation occur essentially in place.

At Marysvale, for example, hydrothermal pitchblende- and fluorite-bearing veins grade upward into a complex assemblage of 6-valent uranium minerals (Walker and Osterwald, 1956), including principally autunite, torbernite, metatorbernite, and uranophane; some sooty pitchblende and umohoite also are present and apparently are most abundant just below the oxidized zone. In general, the pitchblende- and fluorite-bearing veins show no marked tendency to be richer in uranium than their overlying secondary counterparts, and both the oxidized and unoxidized vein segments have yielded ore of about the same grade. Presumably in these veins as
well as elsewhere, the solution of hypogene uranium minerals and redposition of supergene ones occurred essentially in place.

CONCLUSIONS

In general, the causal chemical processes and the resultant geologic expression of supergene alteration of uranium-bearing veins are similar to those described for copper or other base-metal sulfide deposits.

The products of supergene alteration of uraniferous veins are many and include not only hydrated 4-valent uranium minerals but, locally, uranyl ions adsorbed on several different alteration products and, in some places where reduction has occurred, several supergene 4-valent uranium minerals. Commonly, in those vein deposits characterized by several different uranyl compounds, a zoning of the uranium-bearing alteration products has been demonstrated, in which hydrated oxides and hydroxides occur closest to unaltered pitchblende, whereas uranyl silicates, phosphates, vanadates, molybdates, and arsenates occur in an intermediate position, and uranyl carbonates and sulfates are found farthest from unaltered pitchblende.

Solution, redistribution, and subsequent loss of uranium to migrating ground waters are characteristic of most uranium-bearing vein deposits subjected to supergene processes and are most common at or near the ground surface. In a few vein deposits supergene alteration occurs essentially in place and shows no marked tendency toward uranium enrichment or depletion in the more oxidized parts of the veins. In still other vein
deposits, supergene enrichment of uranium in zones of decreased oxidation potential has been established; commonly, the enriched zones are characterized by sooty or regenerated pitchblende.
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