# AUTUNITE FROM MT. SPOKANE, WASHINGTON*

G. W. Leo, *U. S. Geological Survey, Menlo Park, California*

### Abstract

Near Mt. Spokane, Washington, coarsely crystalline autunite is developed in vugs, fractures, and shear zones in granitic rock. With the exception of dispersed submicroscopic uraninite particles, autunite is the only ore mineral in the deposits. A study of associated granitic rocks reveals that apatite, the most abundant accessory constituent, has been preferentially leached and corroded in mineralized zones, suggesting that it may have provided a source of lime and phosphate for the formation of autunite. Leaching may have been effected partly by meteoric water, but more probably was due to the action of ascending connate solutions that may also have carried uranium from unoxidized, as yet undiscovered deposits at depth.

Autunite from the Daybreak mine has been studied optically, chemically, and by $x$-ray diffraction. The autunite is commonly zoned from light-yellow margins to dark-green or black cores, and autunite from the inner zone has a higher specific gravity and higher refractive indices than peripheral light material. $X$-ray powder diffraction patterns of dark and light meta-autunite formed from this autunite show no significant differences in the $d$ spacings; however, diffraction patterns of nine zoned samples each show uraninite to be present in the dark, and absent from the light, phase. $UO_2$ and $UO_3$ determinations range from 0.66–0.70 per cent and 57.9–58.0 per cent, respectively, for light autunite, whereas dark autunite shows a range (in seven determinations) of $UO_2$ from 1.2 to 4.0 per cent, and $UO_3$ from 55.1 to 58.8 per cent. The wide range of $UO_2$ values in dark autunite is tentatively attributed to nonuniform distribution of discrete uraninite particles, which may also account for the dark color and higher density.

Thermogravimetric and differential thermal analyses of autunite suggest discrete water losses at about 90°, 145°, and 220° C. The first water loss probably represents dehydration to meta-autunite II, also recognizable by marked changes in optical properties and the $x$-ray diffraction pattern. The form of the DTA curve above 90° C. resembles that of montmorillonite, suggesting that the dehydrations at about 145° C. and 220° C. may involve interlayer water as in montmorillonites, and the analogy with montmorillonite is further indicated by $x$-ray patterns of meta-autunite II heated just above these temperatures. Autunite heated to red heat shows a diffraction pattern distinct from all others. The cation exchange capacity of autunite, about 2.5 milliequivalents per 100 grams, is substantially lower than that previously reported for artificial material.

## Introduction

Autunite of unusual quality and abundance is developed on the western flanks of Mt. Spokane, about 30 miles northeast of Spokane, Washington (Fig. 1). The autunite deposits occur entirely within granitic rock over an area of about 100 square miles near the eastern limits of the Loon Lake granite.

The present study has a twofold purpose: (1) a consideration of some aspects of the field relations of autunite and the host rocks, in an attempt to shed some light upon the origin of these unusual deposits;

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and (2) a detailed study of the mineralogy of autunite from the Day-
break mine, believed to be unique in its relative abundance and fine
development.

Much helpful information regarding the geology of the area has been
provided by D. C. Alvord and A. E. Weissenborn of the U. S. Geological
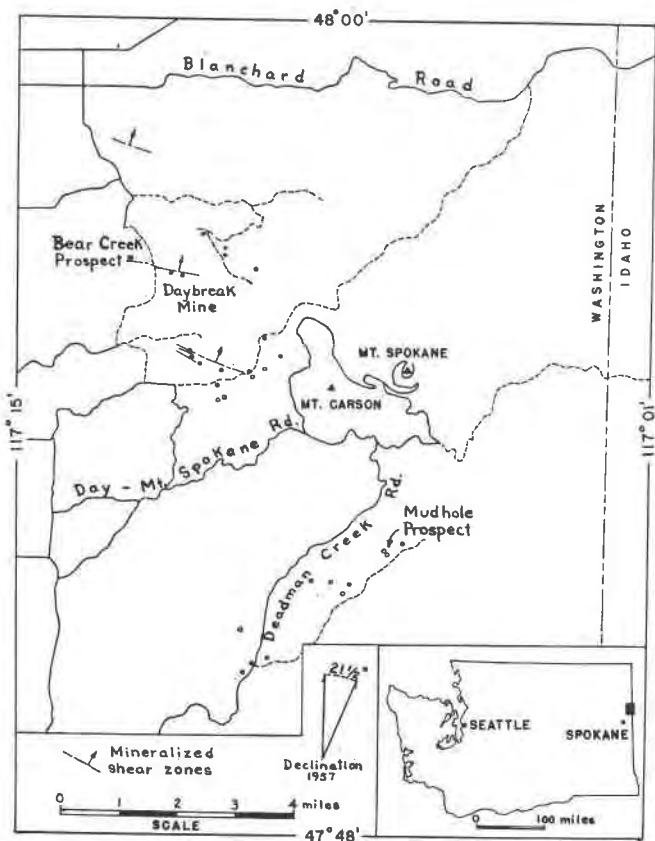


FIG. 1. Location map of the autunite deposits near Mt. Spokane, Washington. Each dot
represents an autunite occurrence. Data from D. C. Alvord and A. E. Weissenborn.

Survey. Other data have been drawn from an article by H. W. Norman
(1957), mining and exploration manager for Daybreak Uranium, Inc.

After work on this manuscript was nearly complete, the writer learned
of a study of meta-autunite from the Daybreak mine by Dr. Alexander
Volborth of the University of Nevada (Volborth, 1959). Conversation
with Dr. Volborth revealed that the two papers did not overlap appre-

ciably, but rather tended to supplement each other, and it was therefore agreed to publish each paper separately. Dr. Volborth was kind enough to present the writer with a copy of his manuscript, and considerable use has been made of his data.

## The autunite deposits

The only uranium mineral in the Mt. Spokane district is the hydrous calcium uranyl phosphate, autunite, which is concentrated along west to
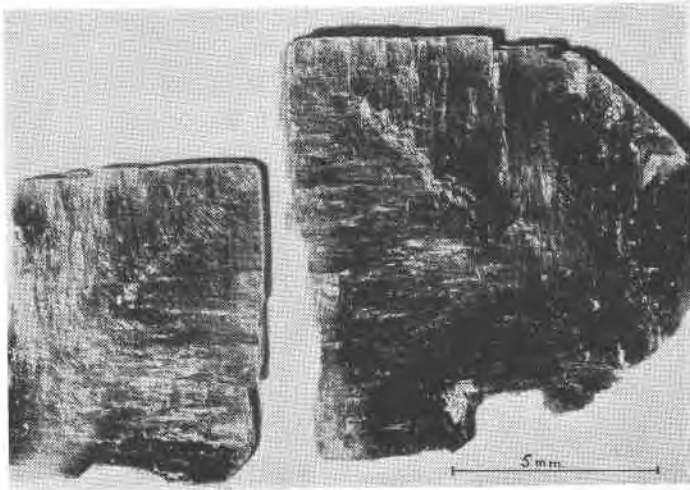


FIG 2. Individual autunite flakes from Daybreak mine, showing characteristic distribution of dark and light phases.

northwest striking shear zones with a low northward dip; especially rich concentrations of autunite occur where shear zones are traversed by fractures. Several such zones have been mapped in the vicinity of Mt. Spokane (Fig. 1); by far the most important is the Daybreak mine, which has produced most of the ore from the district. The geologic relations at the Daybreak mine have been well summarized by Norman (1957).

Autunite occurs in three more or less distinct ways: (1) in veins and fracture fillings, which may locally attain a thickness of twelve to fifteen inches (Fig. 2); (2) in vugs within closely spaced pegmatitic dikes; and (3) disseminated throughout altered granite near fractures and shear zones.

A notable feature of the deposits is their concentration at relatively shallow depth. At the Daybreak mine, production has been almost entirely from a depth of less than 30 feet, and the highest grade ore occurs within 10 feet of the surface; ore of commercial grade, however, has been

reported from a depth of 95 feet (Norman, 1957). Total production from the Daybreak mine through May, 1958, is 13,400 tons, with an average grade of 0.24 per cent $U_3O_8$. This production has been from three distinct pods, now largely mined out, which are generally defined by the intersections of faults with major shear zones. A recently sunk vertical shaft about one-half mile northwest of the Daybreak mine (Bear Creek prospect) has struck autunite at a depth of about 80 feet, apparently on the extension of the Daybreak shear zone (Fig. 1) (A. E. Weissenborn, written communication).

## Use of the term autunite

Because of the readiness with which hydrous calcium uranyl phosphate may change from one hydration state to another, in particular between the fully hydrated and meta-I states, the attempt to denote the material precisely at all times becomes cumbersome and leads to ambiguity. The convention has therefore been adopted throughout this paper of using the term autunite, without qualification, to denote hydrous calcium uranyl phosphate in any hydration state. Wherever the precise hydration state is germane to the discussion, the terms, fully hydrated autunite, meta-autunite I, and meta-autunite II are used (see p. 104).

### PETROGRAPHY

The rocks of the Mt. Spokane area range in composition from granite to quartz diorite, and are markedly rich in biotite except near mineralized zones. A typical, fairly fresh quartz monzonite (DB-20) has the following mode: quartz 42, potassium feldspar 24, plagioclase ($An_{25-35}$) 25, biotite 5, muscovite 2, myrmekite 1, and accessories 1. The rock is medium grained, with a texture ranging from hypidiomorphic to graphic. Highly undulose extinction in quartz, bent twin lamellae in plagioclase, and zones of crushed and shattered grains indicate considerable post-crystallization shearing. The chief varietal mineral is biotite, which forms ragged, partly chloritized plates and shreds associated with anhedral patches of opaque ore; the latter is at least in part a late alteration product. Accessory minerals include apatite, garnet, zircon, monazite, and allanite. The uranium content of this rock and some its constituent minerals are listed in Table 10.

Granite and quartz monzonite alternate irregularly with more mafic rocks corresponding to granodiorite and quartz diorite. Contacts between the different rock types are sharp but irregular; owing to limited exposures, the mutual relations are not clear. Mineral percentages in a typical granodiorite are as follows: quartz 20, plagioclase ($An_{28-45}$) 40, potassium feldspar 10, biotite 13, and deep blue-green hornblende 14.

Dark fine-grained lamphrophyric dikes and granite pegmatites are widely distributed in the area. The former consist chiefly of quartz, potassium feldspar, biotite, and pale green hornblende, and range up to 15 feet in width. A radioactive but not visibly mineralized rock dike along Deadman Creek Road (Dimitroff claim) has been prospected without known results.

Development of pegmatities is especially conspicuous in mineralized zones, owing perhaps to the better-than-average exposures in these zones along trenches and stripped areas. Pegmatites are commonly sharply bounded and tabular, but may have irregular forms with gradational boundaries into finer-grained rock. Garnet is the predominant accessory constituent.

In general, rock within mineralized zones has a bleached and altered aspect, although examination under the microscope indicates that hydrothermal alteration is not intense. The chief evidence of alteration consists in (1) the relative abundance of muscovite, and almost complete absence of biotite except for local chloritized shreds; (2) cloudiness and moderate sercitization of feldspar, especially plagioclase; and (3) marked leaching of apatite, which is more fully described in the section on origin.

## Mineralogy of Autunite

One of the remarkable features of autunite from Mt. Spokane is its coarseness; individual flakes may attain a diameter of one inch, and bonanza specimens of massive autunite clusters measuring two feet across have been preserved intact from the Daybreak mine. The flakes are generally arranged in books parallel to the prominent {001} cleavage which display a characteristic radiating "bow tie" structure. In large specimens, radiating clusters of crystals standing on edge are tightly intergrown and set against each other at diverging angles. The {001} surfaces, though showing perfect cleavage, are characteristically curved and crenulated in larger flakes. Most crystals are bounded by a prominent prismatic cleavage.

Two types of autunite, dark and light, are almost invariably associated. The light type ranges from pale lemon-yellow to light yellow-green, and the dark type is dark green to black. In a given flake the dark material generally forms the core and the light material the rim; this relationship, however, is variable in that cores may be light in part, and small flakes commonly are entirely light (Fig. 2). The transition between light and dark is usually somewhat gradational, and under the microscope small fragments show a continuous range of color from pale yellow to dark green. Under both short- and long-wave ultraviolet light, light colored autunite fluoresces bright yellow-green, whereas the dark cores

appear dull with little fluorescence; with long-wave light, however, the contrast between light and dark autunite is more pronounced than with short-wave light.

### Hydration states of autunite

Three hydration states are commonly recognized in hydrous calcium uranyl phosphate: fully hydrated autunite, $Ca(UO_2)_2(PO_4)_2 \cdot 10\text{-}12H_2O$; meta-autunite I, $Ca(UO_2)_2(PO_4)_2 \cdot 2\frac{1}{2}\text{-}6\frac{1}{2}H_2O$; and meta-autunite II, $Ca(UO_2)_2(PO_4)_2 \cdot 0\text{-}6H_2O$ (Palache, Berman, and Frondel, 1951, p. 985).

The following observations regarding the nature of successive dehydrations have been previously described (Beintema, 1938, p. 160-163; Palache and others, 1951, p. 985; Donnay and Donnay, 1955, p. 35). Optical changes in autunite with progressive heating were long ago described by Rinne (1901).

Dehydration of fully hydrated autunite to meta-autunite I takes place at room temperature in a dry atmosphere in a few hours; alternately, the dehydration can be brought about much more quickly by moistening fully hydrated autunite with a hygroscopic substance such as acetone and allowing it to dry. Finely divided meta-autunite I may be converted to the fully hydrated form by leaving overnight in an ordinary desiccator with water in the bottom, or, alternately, by boiling briefly in distilled water. Unless a saturated atmosphere is maintained, however, fully hydrated autunite quickly reverts to meta-autunite I, which is clearly the most stable form under ordinary conditions of temperature and humidity.

Irreversible dehydration from meta-autunite I to meta-autunite II takes place at about 80° C.; the dehydration is accompanied by striking changes in optical properties and is, therefore, readily recognizable. Additional dehydrations at higher temperatures are suggested by DTA patterns. When autunite is brought to red heat, a distinct change takes place in the $x$-ray pattern, but the cause for this change was not determined.

It has been suggested that stability of autunite-like minerals in their different hydration states may be controlled by the size of the metal cation (Nuffield and Milne, 1953). The ready transition of autunite between the fully hydrated and meta-I forms is accordingly explained by the size of the $Ca^{+2}$ ion, which is thought to give rise to the approximately equally stable structures in the two hydration states. Minerals with the autunite structure but a smaller metal cation, for example, saléeite (Mg-autunite), are under ordinary conditions stable in the fully hydrated form only, whereas autunite-like minerals with a cation larger than calcium, for example, uranocircite, seem to exist only as the meta-structure.

*Optical character of autunite in the various hydration states*

Autunite has a tabular habit with a perfect basal {001} cleavage. Another cleavage with two mutually perpendicular directions, here called prismatic, is well developed in Daybreak mine material. The three mutually perpendicular cleavage directions control the shape of even the smallest crushed particles of autunite, so that these are always square
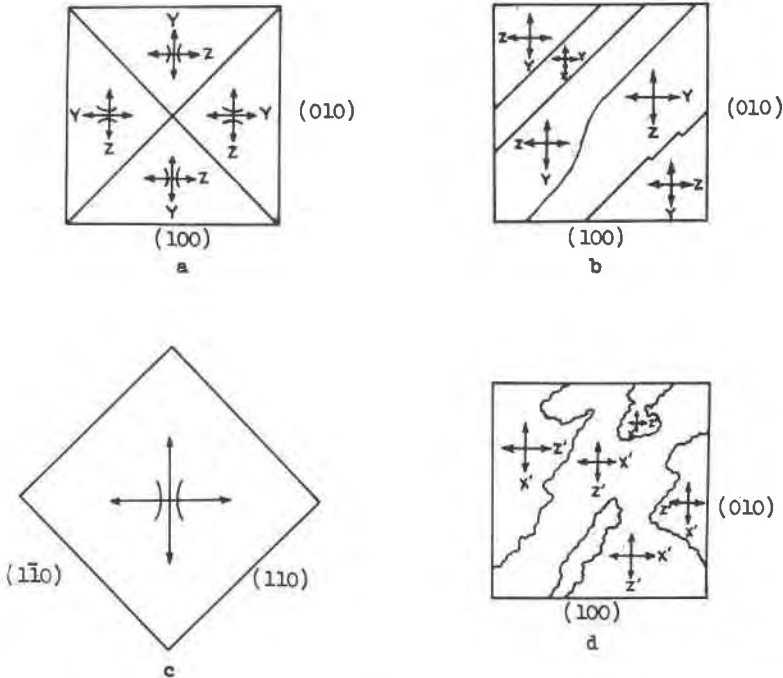


Fig. 3. Optic orientation of autunite in the various hydration states. Idealized cleavage flakes resting on (001).

    a. Fully hydrated autunite with very regular sectoral structure on {110}. Optic axial plane always parallel to neighboring cleavage.

    b. Fully hydrated autunite; example of less regular sectoral structure.

    c. Meta-autunite I; sectoral structure absent. Optic plane diagonal to cleavages.

    d. Meta-autunite II; irregular mottling with opposed though parallel vibration directions, which are parallel to bounding cleavages.

or rectangular in outline. A third cleavage, co-zonal with the prismatic cleavages and at 45° to them, can be observed in some tablets. If the prismatic cleavages are regarded as {110}, the third cleavage is {100} or {010}; however, due to a shift in the optic plane, the designations are different for fully hydrated autunite and meta-autunite I (Fig. 3).

$X$-ray studies by Beintema (1938) and Nuffield and Milne (1953) have shown fully hydrated autunite and meta-autunite I to be structurally tetragonal; an anomalously biaxial character in both phases is attributed to slight distortion in the structure due to variable water content. Meta-autunite II is thought to be orthorhombic (Beintema, 1938, p. 162). Meta-autunite from the Daybreak mine is always biaxial, and fully

TABLE 1. SUMMARY OF OPTICAL DATA ON AUTUNITE FROM DAYBREAK MINE

| State of hydration | Indices of refraction[1] | | Optical character |
|---|---|---|---|
| | Light | Dark | |
| 1. Fully hydrated autunite (boiled in distilled water for 10 minutes.) | $\beta \cong \gamma$[2] $1.578 \pm 0.003$ | $\beta \cong \gamma$ $1.586 \pm 0.005$ | Isotropic or low birefringence, with anomalous blue interference colors, rarely with sectoral arrangement. $2V_x = 0$ to $5°$. Dispersion distinct $r > v$, sometimes crossed (?), optic axial plane parallel to cleavage. |
| 2. Fully hydrated autunite (In desiccator with water vapor for several days.) | $\beta \cong \gamma$ $1.579 \pm 0.003$ | $\beta \cong \gamma$ $1.586 \pm 0.003$ | Isotropic or low birefringence; sectoral arrangement. $2V_x = 0$ to $25°$. Optic axial plane parallel to cleavage. |
| 3. Meta-autunite I | $\beta \cong \gamma$ $1.597 \pm 0.003$ | $\beta \cong \gamma$ $1.609 \pm 0.005$ | Usually low birefringence; sectoral character indistinct. $2V_x = 5$ to $20°$. Optic axial plane diagonal to cleavage. |
| 4. Meta-autunite II (Heated for approximately $\frac{1}{2}$ hr. at $80°$ C.) | $\alpha' = 1.610 \pm 0.003$[3] $\gamma' = 1.624 \pm 0.003$ | $\alpha' = 1.620 \pm 0.005$ $\gamma' = 1.635 \pm 0.005$ | Strongly mottled appearance due to high birefringence and irregular sectoral character. X' and Z' in (001) plane, parallel to cleavages. |
| 5. Heated to red heat in platinum crucible. | $\alpha' = 1.68 \pm 0.01$[4] $\gamma' = 1.71 \pm 0.01$ | $\alpha' = 1.68 \pm 0.01$ $\gamma' = 1.71 \pm 0.01$ | Same as (4). |

[1] Only the indices of refraction corresponding to the two orientations of cleavage plates given in each case, since all flakes, however small, rest on (001).

[2] $\gamma$-$\beta$ does not exceed 0.003 in autunite and meta-autunite I.

[3] $\alpha'$ and $\gamma'$ correspond to X' and Z', and are thought to be equivalent to true $\alpha$ and $\gamma$.

[4] Values variable and uncertain.

hydrated autunite is biaxial except when hydration is brought about by boiling (Table 1). Whenever 2V is not zero, it is necessary to adopt crystallographic notation appropriate to symmetry lower than tetragonal; specifically, in those cases where the optic plane is parallel to the prismatic cleavages, the latter are designated as pinacoids, {100} and {010}, instead of the second-order tetragonal prism, {010}.

In fully hydrated autunite, $x = c$, and the optic plane is parallel to a prismatic cleavage. The flakes are isotropic or weakly birefringent;

$2V_x = 0 - 25°$, and dispersion $r > v$, distinct. Individual flakes commonly have a sectoral arrangement (see Beintema, 1938, p. 162); that is to say, the flakes are divided into more or less regular sectors or bands joined on {110} (Fig. 3a, b). Adjacent sectors have opposed though parallel vibration directions, so that the optic plane is always parallel to the neighboring prismatic cleavage.

In meta-autunite I there is a distinct change in optic orientation, involving a shift of the optic plane through 45° from its original position, so that it bisects the angle between the prismatic cleavages (Fig. 3c). Most flakes have $2V_x = 5 - 20°$, and possess a slight birefringence. A faint and highly irregular sectoral structure with opposed vibration directions persists in light autunite, but is absent in the dark phase.

Upon hydration of flakes to meta-autunite II, sectoral structure reappears, with irregular isotropic boundaries showing slight control by {110} directions (Fig. 3d). Adjacent areas have mutually perpendicular virbration directions as before, but now show much higher birefringence, with interference colors up to first-order red. The relatively high birefringence and the appearance of a centered "flash figure" in (001) suggest that the vibration directions in this plane, which corresponded to Y and Z in fully hydrated autunite and meta-autunite I, are now X and Z. An attempt to obtain a $Bx_a$ or optic axis figure by means of sections cut normal to (001) was unsuccessful.

Optical characteristics reported by Beintema (1938, p. 160–162) for synthetic hydrated calcium uranyl phosphate are approximately similar to those in Daybreak mine autunite, except that, in the fully hydrated and meta-I states, the position of the optic plane is reversed relative to that in Daybreak mine autunite. Sectoral structure (interpreted by Beintema as twinning on {110}), furthermore, was noted in the meta-I state only, whereas, in Daybreak mine autunite, sectoral structure is restricted to the fully hydrated form. Beintema also noted (p. 160) a gradual change from biaxial to uniaxial character in synthetic fully hydrated autunite exposed for some time to air, and interpreted this as being due to the gradual attainment of truly tetragonal symmetry of loss of excess water. A similar change could not be detected in Daybreak mine autunite; rather, uniaxial crystals were noted only after autunite had been boiled in water and hence most thoroughly hydrated.

All indices of refraction were determined by means of standard immersion oils and sodium light. Because of the strongly preferred orientation of autunite on (001), values for $\beta$ and $\gamma$ only were obtained for fully hydrated autunite and meta-autunite I. In accordance with the nearly uniaxial character of these hydrates, $\beta$ and $\gamma$ are sensibly equal, and their difference does not exceed the limits of variation between different flakes.

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G. W. LEO

In the case of meta-autunite II, two indices of refraction were determined.

Indices of refraction of dark autunite are consistently higher than those of light autunite (Table 1), although the reason for this is not apparent on the basis of chemical and crystallographic considerations. The values are generally in good accord with published data (Palache, Berman, and Frondel, 1951, p. 985; George, 1949, p. 137–138*). For dark meta-autunite I from the Daybreak mine, Volborth (1959) reports $\alpha = 1.584$, $\gamma = 1.607$; the latter value is in good agreement with that determined by the writer.

TABLE 2. ANALYSIS OF FULLY HYDRATED LIGHT AUTUNITE

Analyst: Blanche Ingram, U. S. Geological Survey

| | (1) Weight per cent | (2) Recalculated to 100 | (3) Molecular proportions | (4) Combined molecular proportions SiO2 omitted | (5) Molecular ratios based on (4); $(PO_4^{-3})$ group = 2.00 | (6) $Ca(UO_2)_2(PO_4)_2 \cdot 12H_2O$ |
|---|---|---|---|---|---|---|
| UO₃ | 57.95[1] | 58.38 | 0.204 | 0.204 | 1.96 | 58.00 |
| UO₂ | 0.68[2] | 0.69 | 0.003 ⎫ | | | |
| CaO | 5.3 | 5.34 | 0.095 ⎬ | 0.103 | 0.99 | 5.69 |
| SrO | 0.52 | 0.52 | 0.005 ⎭ | | | |
| P₂O₅ | 14.6 | 14.71 | 0.104 | 2×0.104=0.208 | 2.00 | 14.39 |
| SiO₂ | 0.41 | 0.41 | 0.007 | | | |
| H₂O | 19.8 | 19.95 | 1.107 | 1.107 | 10.64 | 21.92 |
| Total | 99.26 | 100.00 | | | | 100.00 |

Formula based on column (5): $(Ca, Sr, U^{+4})_{0.99}(UO_2)_{1.96}(PO_4)_{2.00} \cdot 10.64 H_2O$.

[1] Average of two determinations: 57.9 per cent and 58.0 per cent.

[2] Average of two determinations: 0.66 per cent and 0.70 per cent.

## Chemical analyses

Chemical analyses of fully hydrated dark and light autunite from the Daybreak mine are recorded in Tables 2 and 3. Preparation of analyzed material required certain precautions. Since intense and prolonged grinding tended to produce irreversible dehydration to meta-autunite II, the necessary reduction in size (to −150 mesh) was accomplished by fine chopping of autunite flakes with a razor blade, followed by gentle grinding under acetone. Separation of the dark from the light phase was then possible, owing to the different densities of the two phases (Table 4). In view of the maximum density of methylene iodide (3.3), autunite in the analyzed samples had to be in the fully hydrated state prior to the

* The range, $\gamma = 1.595–1.613$, listed by George (1949) for "autunite," apparently represents determinations of meta-autunite I.

TABLE 3. ANALYSIS OF FULLY HYDRATED DARK AUTUNITE

Analyst: Blanche Ingram, U. S. Geological Survey

| | (1) Weight per cent | (2) Molecular proportions | (3) Combined molecular proportions 0.7% $UO_2$ added to ($Ca^{+2}$, $Sr^{+2}$)[1] | (4) Molecular ratios based on (3); ($PO_4^{-3}$) = 2.00 | (5) $Ca(UO_2)_2(PO_4)_2 \cdot 12H_2O$ |
|---|---|---|---|---|---|
| $UO_3$ | $55.1–58.8^2$ | 0.193–0.206 | 0.193–0.206 | 1.86–1.98 | 58.00 |
| $UO_2$ | $1.2– 4.0^2$ | 0.004–0.015 | $\begin{cases}0.001–0.012^3\\0.003\end{cases}$ | | 5.69 |
| CaO | 5.3 | 0.095 | $\left.\begin{array}{l}0.095\\0.003\end{array}\right\}0.101$ | 0.97 | |
| SrO | 0.34 | 0.003 | | | |
| $P_2O_5$ | 14.8 | 0.104 | $0.104 \times 2 = 0.208$ | 2.00 | 14.39 |
| $SiO_2$ | n.d. | | | | |
| $H_2O$ | 18.3 | 1.016 | 1.016 | 9.77 | 21.92 |
| Total | 95.0–101.5 | | | | 100.00 |

Formula based on column (4): $(Ca, Sr, U^{+4})_{0.97}(UO_2)_{1.86-1.98}(PO_4)_{2.00} \cdot 9.77H_2O$.

[1] An amount of $UO_2$ equal to that added to ($Ca^{+2}$, $Sr^{+2}$) group for light autunite.

[2] Values represent a range of seven determinations, two of them on 100 mg. samples, the remainder on 50 mg. samples. The determinations were as follows (first figure $UO_3$, and second, $UO_2$, in weight per cent): (1) 58.8, 3.8; (2) 57.5, 3.8; (3) 55.8, 3.2; (4) 55.2, 3.7; (5) 55.1, 4.0; (6) 57.4, 1.8; (7) 58.6, 1.2.

[3] This excess of $UO_2$ represents uraninite not in the structure.

centrifuging, and it was necessary to rehydrate several times during the course of the separation. The final light concentrate had an overall yellow-green appearance, and consisted of flakes ranging from medium gray-green to pale canary yellow. The dark concentrate had a uniformly dark olive-green color, bordering on black in thicker flakes.

The specific gravity of both the fully hydrated phase and the meta-I phase (Table 4) shows a considerable range of variation, but the values are in general agreement with published data (Palache, Berman, and Frondel, 1951, p. 985; Donnay and Donnay, 1955, p. 34; Volborth, 1959). The value of 3.1, given by George (1949, p. 137) for fully hydrated autunite, seems to be too low.

Of particular interest in the chemical analyses is the presence of U(IV), reported as $UO_2$, in both dark and light autunite. The U(IV)

TABLE 4. SPECIFIC GRAVITY OF AUTUNITE

| | Light | Dark |
|---|---|---|
| Fully hydrated autunite[1] | 3.18–3.23 | 3.26–3.28 |
| Meta-autunite I[2] | 3.35–3.40 | 3.45–3.55 |

[1] Determined by means of heavy liquids checked on a Christian Becker Chainomatic density balance.

[2] Determined by means of a Berman density balance.

content of dark autunite, determined for seven separate samples, is relatively high and shows a wide range of variation. Since each of the seven samples came from the same fraction of carefully purified dark autunite, the variations in U(IV) cannot be ascribed to admixture of unoxidized uranium minerals susceptible to removal by ordinary separatory methods. A possibility that must be considered is differential reduction of U(VI) during analysis, which is especially likely if ferrous iron is present

TABLE 5. SEMIQUANTITATIVE SPECTROGRAPHIC DATA[1] ON LIGHT AND
DARK AUTUNITE, DAYBREAK MINE

Katherine V. Hazel, analyst, U. S. Geological Survey
L=light autunite, D=dark autunite. Figures represent
number of samples falling in each range

| Weight per cent[2] | Si | | Al | | Fe | | Mg | | Na[3] | | K[3] | | Mn | | Ba | | Be | | Pb | | Sr | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | L | D | L | D | L | D | L | D | L | D | L | D | L | D | L | D | L | D | L | D | L | D |
| 0.3 −1.0 | 5 | 1 | 7 | | 1 | | | | | | | | | | | | | | | | 1 | |
| 0.1 −0.3 | 2 | | | | | | | | | | | | | | | | | | | | 8 | 9 |
| 0.03 −0.1 | 2 | 4 | 1 | 1 | 4 | 1 | | | | | | | | | | | | | | | | |
| 0.01 −0.03 | | 4 | | | 1 | | | | | | | | 1 | | | | | | | | | |
| 0.003 −0.01 | | | 1 | 2 | 2 | 2 | 9 | 9 | 1 | | 1 | 1 | 4 | 6 | 9 | 8 | | | 9 | 9 | | |
| 0.001 −0.003 | | | | 5 | | 3 | | | 1 | | | | 4 | 3 | | 1 | | | | | | |
| 0.0003 −0.001 | | | | | | | | | | | | | | | | | 1 | | | | | |
| 0.0001 −0.0003 | | | | | | | | | | | | | | | | | 4 | | | | | |
| 0.00003−0.0001 | | | | | | | | | | | | | | | | | 4 | 9 | | | | |
| 0 | | | | 1 | 1 | 3 | | | | | | | | | | | | | | | | |

[1] Major elements not listed. Elements looked for but not detected: Ag, As, Au, B, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, La, Li, Lu, Mo, Nb, Ni, Os, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Sn, Sm, Ta, Tb, Te, Th, Ti, Tl, Tm, V, W, Y, Yb, Zn, and Zr.

[2] Comparison of this type of semiquantitative results with the data obtained by quantitative methods, either chemical or spectrographic, show that the assigned group includes the quantitative value about 80 per cent of the time.

[3] Na and K were determined on chemically analyzed samples only.

in the sample (Clarke and Altschuler, 1958). However, in view of the small amount of iron in the autunite, especially the dark variety (Table 5), reducing effects were probably not important. In the event of differential reduction of U(VI), moreover, the U(IV):U(VI) ratios in the different samples should be in approximate inverse proportion, and this is definitely not the case. (See Table 3, footnote 2.)

More probably the variable and relatively high U(IV) content of dark autunite is due to the presence of exceedingly fine, irregularly dispersed uraninite. The presence of uraninite in the dark phase, and its absence in the light phase, is indicated by x-ray powder patterns (see p. 115 and 118), although the mineral could not be detected by optical or separatory means. This dispersed uraninite is thought to account for the deep color

of dark autunite, and its greater density relative to the light-colored phase.

The presence of U(IV) in light autunite, together with the apparent absence of uraninite from this phase, suggests that U(IV) may be present in the autunite structure, probably as $U^{+4}$ substituting for $Ca^{+2}$. This substitution, plausible on theoretical grounds because of the closely similar ionic radii of $U^{+4}$ (0.97) and $Ca^{+2}$ (0.99 Å) (Green, 1953), has been recently demonstrated for apatite (Clarke and Altschuler, 1958; Altschuler, Clarke, and Young, 1958). In calculating formulas from the present analyses, it has been arbitrarily assumed that all U(IV) in light autunite, and an equal amount of U(IV) (approximately 0.7%) in dark autunite, substitute in the structure for calcium. A similar substitution is assumed for strontium, which shows higher values than any previously reported autunite.[1]

$SiO_2$, determined for light autunite only, may be present as $SiO_4^{-4}$ substituting for $PO_4^{-3}$, and thus balance excess positive charges introduced by $U^{+4}$ in $Ca^{+2}$ positions. Substitution of $SiO_4^{-4}$ for $PO_4^{-3}$ has been proposed for apatite (Borneman-Starinkevitch, 1938), and is also assumed by Volborth (1959, p. 709, Table 5) in dark meta-autunite from Mt. Spokane. The analysis of the latter contains 0.39 per cent $SiO_2$ (Volborth, 1959), addition of which to $P_2O_5$ yields molecular proportions close to theoretical values. In the present analysis of light autunite, on the other hand, the molecular proportion for $PO_4^{-3}$ alone (Table 2, column 4) is already somewhat too high, and addition of $SiO_4^{-4}$ to this group would cause further departure of molecular proportions from theoretical values. In view of these considerations, $SiO_2$ has been omitted in calculating the empirical formula of light autunite (Table 2, column 4), but the possibility of some substitution of $SiO_4^{-4}$ for $PO_4^{-3}$ cannot be disregarded.

An alternate explanation for $SiO_2$ is that it represents an impurity. The relatively large amounts of Al in light autunite (Table 5) suggest that the contaminating agent may be clay, although contamination was not apparent in the analyzed sample.

Both analyses have been calculated to empirical formulas on the basis of an arbitrary value of 2.00 for $PO_4^{-3}$. In each case, but especially in dark autunite, the number of water molecules is somewhat low compared to the maximum theoretical value of $12H_2O$ for fully hydrated material. This disparity may probably be ascribed to incipient dehydration to meta-autunite I prior to analysis.

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[1] After this paper went to press, the writer learned of a determination of 1.38% SrO for dark meta-autunite from Mt. Spokane, Washington, by Volborth (1959).

*Spectrographic analyses*

Semiquantitative spectrographic analyses of nine samples each of dark and light autunite from different parts of the Daybreak mine (Table 5) show that trace elements are closely similar, both in kind and amount, throughout the suite of analyzed samples. The lack of consistent differences between light and dark material reinforce the suggestion that the color difference is caused primarily by dispersed uraninite in dark autunite, and not by differential distribution of minor and trace elements. Elements that do show systematic fractionation, notably iron, silicon, and aluminum, are all more abundant in light autunite; as mentioned above, the latter two elements may represent clay contamination.

The suite of minor elements generally corresponds to that reported by Emerson and Wright (1957, p. 226) for meta-autunite from the W. Wilson mine in Montana, although these authors list several additional elements (Cu, Co, Li, Ag, B, Ge, and Mo).

*Differential thermal analyses*

Differential thermal analyses of light and dark autunite are represented in Fig. 4. The curves do not differ greatly from each other, and each is closely similar to the DTA pattern of synthetic autunite (Guillemin and Pierrot, 1956, p. 180).

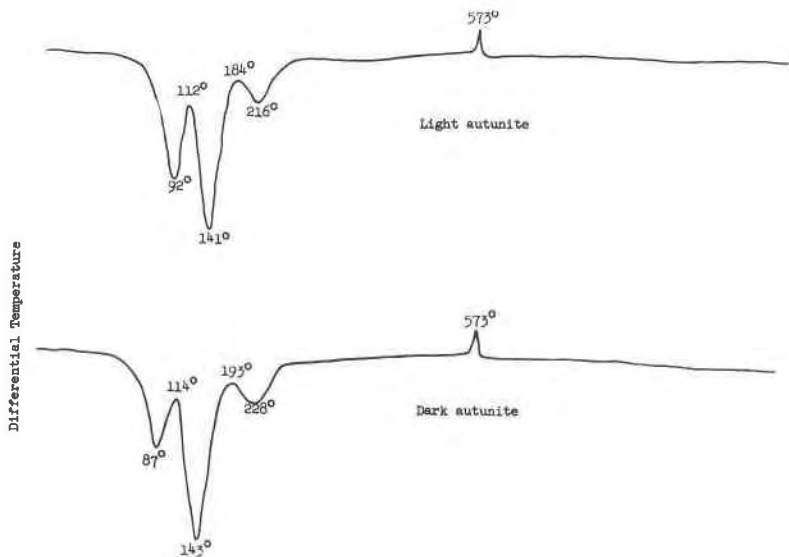Each pattern shows three distinct endothermic troughs. The first



Fig. 4. Differential thermal analyses of light and dark, autunite. Peak at 573° C. is due to quartz standard. Record by George T. Faust.
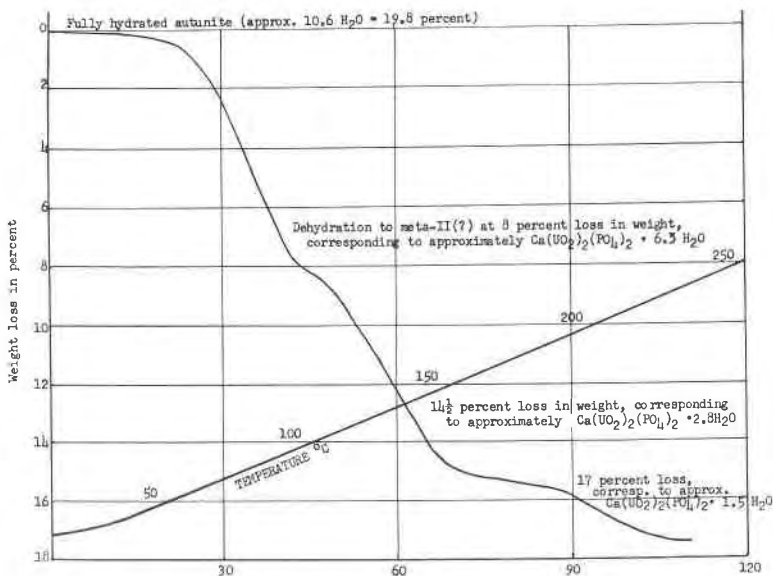
Fig. 5. Thermogravimetric data on light autunite over the range 20°–250° C. Horizontal scale shows time in minutes. Record by Charles A. Kinser.

trough, at 92° C. for light and 87° C. for dark material, probably represents the dehydration of meta-autunite I to meta-autunite II, although the temperatures are slightly higher than that previously determined for this hydration (about 80° C.). On the basis of about ten water molecules per unit formula in fully hydrated autunite (Tables 2 and 3), and a maximum of six water molecules in meta-autunite II, it appears that autunite loses at least four water molecules in the interval between room temperature and about 90° C. (See Brichard and Brasseur, 1958, p. 7.)

The two succeeding endothermic troughs, at 141° and 216° C. for light material, and 143° and 228° C. for dark material, suggest further losses of water. These troughs show a marked similarity to the troughs corresponding to loss of interlayer water in montmorillonites (G. T. Faust, written communication; Grim, 1953, p. 197; Greene-Kelly, 1957, p. 140–164), and may, hence, be analogous. The analogy with montmorillonite is borne out by x-ray powder patterns of meta-autunite II heated above 90° C. (Table 8).

*Thermogravimetric analyses*

As an additional method of determining the nature of progressive dehydration of autunite, thermogravimetric analyses were obtained for dark and light autunite from the Daybreak mine (Figs. 5, 6). The proce-

dure involves a constantly recording balance. The sample is placed in a crucible which is suspended from a balance pan and is enclosed in a furnace which heats the sample either at a uniform rate or in discrete steps, while the resulting loss in weight is continuously recorded on a graph. This technique is similar to that employed in the study of dehydration of clays. (See, for example, Ross and Hendricks, 1945, p. 49–51.)

A slightly modified reproduction of the dehydration curve for light autunite (Fig. 5) represents the course of dehydration at a uniform temperature rise of 2° per minute. The curve shows three more or less
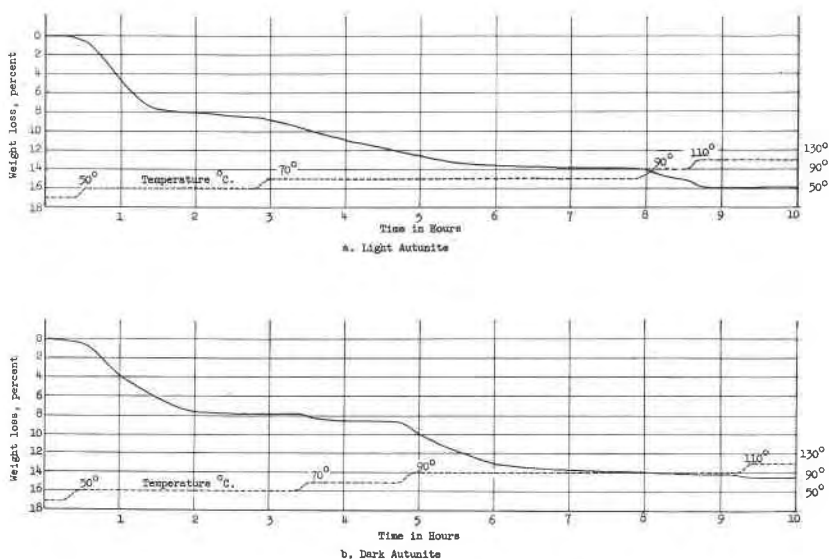


FIG. 6. Thermogravimetric data on light and dark autunite over the range 20°–110° C. Record by Charles A. Kinser.

distinct inflection points, at temperatures fairly similar to those corresponding to endothermic troughs in the DTA patterns (Fig. 4). The first inflection point, at a weight loss of about 8 per cent, corresponds to about 6.3 water molecules per unit formula, which is in satisfactory agreement with the theoretical maximum of six water molecules in meta-autunite II. The temperature at the inflection point, about 97° C., is in good agreement with that of the first endothermic trough in the DTA patterns.

The second and third inflection points, less well defined than the first, occur at approximately 15 and 17 per cent loss in weight; each point appears to mark the beginning of a finite water loss, and they may correspond to the last two endothermic troughs in the DTA patterns. In view

of the previously noted similarity between the dehydration relationships of autunite and those of montmorillonite, these inflection points may be interpreted as representing loss of interlayer water. The above data are in good accord with those of Brichard and Brasseur (1958, p. 7), who depict breaks in the dehydration curve of autunite at about 90° and 215° C.

Dehydration of dark and light autunite over a lower temperature range (20°–110° C.) are represented in Fig. 6. In these runs the temperature was raised in steps of 20°, and was held at each step until constant weight was attained. For reasons that are not apparent, the two curves are markedly different, although both reflect progressive loss of water over the temperature range involved.

*Cation exchange capacity*

Determination of base (cation) exchange capacity of four 0.5 gram samples (−20 mesh) of mixed light and dark autunite (DB-31) by the Bower and Truog colorimetric manganese method (Bower and Truog, 1940) gave values of 2.3–2.7 milliequivalents/100 grams, with an average value of 2.5 milliequivalents/100 grams. The determinations were made by J. C. Hathaway and H. C. Starkey of the U. S. Geological Survey.

Fairchild (1929) showed that artificial autunite may readily undergo base (cation) exchange with Na, K, Ba, Mn, Cu, Ni, Pb, and Mg; in some cases the exchange with original calcium was complete, indicating a cation exchange capacity much greater than that reported for Daybreak mine autunite. The difference may probably be explained by the fact that at least some of Fairchild's experiments were conducted by elevated temperatures over periods of several days, and that the artificial autunite crystals used by him were much finer—on the order of 0.2 mm. across—than the flakes of Daybreak mine autunite on which cation exchange determinations were carried out. The great difference in the experimental procedure in the two cation exchange experiments, thus makes it difficult to evaluate the small measured value of the cation exchange of the natural material.

*X-ray determinations*

X-ray powder films of nine different samples of dark and light meta-autunite I, prepared by Betsy Levin, U. S. Geological Survey, corresponded closely to published data for synthetic autunite (Frondel and others, 1956, p. 120). There was no significant or consistent difference between light and dark meta-autunite I, except that every pattern of dark material showed the strongest uraninite line ($d = 3.13$–$3.14$ Å), whereas that of the light material did not.

Diffraction patterns were also run on a single sample (DB-31) using

the Norelco x-ray diffractometer, taking special precautions to obtain a randomly oriented sample (McCreery, 1949). Some degree of preferred orientation was nevertheless noted, as was the failure of a distinct uraninite line to appear in the pattern of dark autunite, presumably because of the relatively low intensity of the diffracted beam. From the standpoint of number and clarity of reflections, however, the patterns obtained by means of the diffractometer were superior to film data, and are hence reported in preference to the latter. Diffraction patterns were obtained of autunite in the fully hydrated, meta-I and meta-II forms, and also of material heated to higher temperatures, including red heat. The purpose of the latter experiments was an attempt to correlate the pronounced endothermic peaks in the DTA patterns with any possible related changes in the crystal structure. Separate patterns for light and dark material were obtained only for meta-autunite I, and these patterns were so similar that all other x-ray work was done with composite material, that is, the natural mixture of light and dark autunite.

*Fully hydrated autunite*

Some difficulty was experienced in the x-ray diffraction of fully hydrated autunite, because, if wetted excessively, the mineral assumes a highly preferred orientation in the sample holder. If insufficiently moistened, on the other hand, fully hydrated autunite tends to dehydrate to meta-autunite I during the period required for irradiation. A reliable pattern based on repeated runs (Table 6) is in good agreement with data for synthetic autunites (Frondel and others, 1956, p. 98; Brichard and Brasseur, 1958, Table IV), except for the rather strong reflection in the pattern of Daybreak mine autunite at $d = 5.19$, corresponding to (004); the same reflection is designated as weak by Brichard and Brasseur, and is lacking altogether from the pattern of Frondel and others. The strength of this reflection in the pattern of Daybreak mine autunite suggests a degree of preferred orientation. Another fairly strong line in the Daybreak pattern, at $d = 2.08$, is absent from the pattern of Frondel and others, but is listed by Brichard and Brasseur as (028), and also corresponds to (0, 0, 10). Other disparities between the three patterns are minor, and involve weak reflections only.

*Meta-autunite I*

In order to establish the difference in structure, if any, between dark and light autunite, the meta-I hydrates of the two phases were x-rayed separately. Comparison of the $d$-spacings of the two phases (Table 7), however, show that they are virtually identical, with no large or consistent differences. Some of the peaks in the range $2\theta = 60° - 90°$ are

rather indefinite, and lack of close correspondence in this range is not considered significant.

The patterns of both dark and light meta-autunite correspond rather closely to published data (Frondel and others, 1956, p. 120; Brichard and Brasseur, 1958, Tables I and III; Volborth, 1959), except for minor disparities similar to those in fully hydrated autunite.

TABLE 6. X-RAY POWDER DIFFRACTION DATA FOR FULLY HYDRATED AUTUNITE[1]

| $d$ (Å) | I[2] | $hkl$[3] | $d$ (Å) | I[2] | $hkl$[3] |
|---------|------|----------|---------|------|----------|
| 10.4 | 160± | 002 | 2.17 | 9 | 312 |
| 8.72 | 2 | | 2.15 | 12 | 217 |
| 8.24 | 4 | | 2.08 | 24 | 028; 0, 0, 10 |
| 6.67 | 10 | 011 | 2.039 | 9 | 314 |
| 5.19 | 84 | 004 | 1.918 | 7 | 029 |
| 4.96 | 39 | 110 | 1.834 | 2 | |
| 4.48 | 29 | 112 | 1.787 | 4 | 0, 2, 10 |
| 3.58 | 70 | 015 | 1.761 | 4 | 325 |
| 3.51 | 31 | 020 | 1.73 | 8b | |
| 3.33 | 28 | 022 | 1.637 | 12 | |
| 2.91 | 8 | 024 | 1.551 | 6 | |
| 2.86 | 12 | 213 | 1.515 | 6 | |
| 2.73 | 17 | 017 | 1.484 | 4 | |
| 2.60 | 3 | 008 | 1.419 | 7 | |
| 2.50 | 5 | 215 | 1.365 | 8 | |
| 2.48 | 5 | 220 | 1.271 | 3 | |
| 2.41 | 8 | 222 | 1.232 | 4 | |
| 2.30 | 5 | 009 | 1.202 | 3 | |
| 2.22 | 8 | 140 | 1.138 | 3 | |
| 2.19 | 10 | 311 | | | |

[1] Undifferentiated autunite, i.e., the natural mixture of light and dark material, specimen DB-31. CuKα radiation, λ=1.5418 Å; Ni filter; 40 KV, 15 MA; scale factor 8, time constant 4; range 2°–90° 2θ, at 1° 2θ per minute.

[2] Intensities correspond to actual peak heights. Value of I=160 is extrapolated off the chart and hence approximate.

[3] Data after Brichard and Brasseur (1958, Tables II and IV).

b=broad.

### Autunite heated at different temperatures

Powder data of meta-autunite II heated at 110°, 170°, and 225° C. are compared in Table 8. These temperatures represent arbitrary points between the pronounced endothermic peaks on the DTA pattern of autunite (Fig. 4), and powder patterns of the different stages were expected to reveal any changes in crystal structure accompanying the endothermic

TABLE 7. X-Ray Powder Diffraction Data for Light and Dark Meta-Autunite I[1]

| Light meta-autunite | | Dark meta-autunite | | $hkl$[3] |
|---|---|---|---|---|
| $d$ (Å) | I[2] | $d$ (Å) | I[2] | |
| 8.59 | 160± | 8.57 | 125± | 001 |
| 5.45 | 38 | 5.44 | 25 | 221 |
| 5.01 | 10 | 4.98 | 12 | 040 |
| 4.26 | 32 | 4.28 | 22 | 002 |
| 3.64 | 73 | 3.64 | 46 | 222 |
| 3.52 | 20 | 3.51 | 29 | 440 |
| 3.25 | 17 | 3.25 | 18 | 042 |
| — | | 3.14* | | |
| 2.95 | 7 | 2.95 | 8 | 621 |
| 2.71 | 3 | 2.71 | 3 | 213 |
| 2.64 | 23 | 2.63 | 13 | 641 |
| 2.53 | 6 | 2.52 | 5 | 323 |
| 2.48 | 5 | 2.47 | 2 | 080 |
| 2.46 | 5 | 2.45 | 3 | 740 |
| 2.38 | 4 | 2.38 | 5 | 423 |
| 2.26 | 3 | 2.25 | 4 | 523 |
| 2.22 | 6 | 2.22 | 8 | 480 |
| 2.15 | 7 | 2.14 | 6 | 613 |
| 2.12 | 26 | 2.12 | 14 | 911 |
| 2.10 | 10 | 2.10 | 9 | 623 |
| 2.045 | 6 | 2.045 | 6 | 633 |
| 2.032 | 6 | 2.027 | 5 | 832 |
| — | | 1.978 | 2 | |
| 1.952 | 9 | 1.948 | 5 | 941 |
| 1.90 | 2b | 1.89 | 2b | 653 |
| 1.815 | 6 | 1.814 | 4 | 942 |
| 1.767 | 5 | 1.762 | 4 | 10, 2, 2 |
| — | | 1.752 | 4 | |
| 1.717 | 2 | 1.715 | 3 | 923, 763 (?) |
| 1.695 | 5 | 1.70 | 2 | |
| 1.604 | 13 | 1.604 | 7 | 10, 2, 3 |
| — | | 1.573 | 2 | |
| — | | 1.566 | 2 | |
| 1.530 | 7 | 1.53 | 5b | 12, 1, 2 |
| 1.413 | 3 | — | | 13, 2, 2 |
| 1.400 | 2 | 1.397 | 2 | |
| 1.384 | 4 | 1.384 | 2 | 10, 4, 4 |
| 1.347 | 5 | 1.346 | 3 | 12, 7, 2 |
| 1.255 | 2b | 1.256 | 2 | |
| 1.234 | 2 | 1.238 | 1b | |
| — | | 1.208 | | |
| 1.191 | 3 | 1.193 | 2 | |
| 1.181 | 2 | — | | |
| 1.151 | 2 | — | | |
| 1.130 | 2b | 1.129 | 3 | |

[1] Specimen DB-31. CuKα radiation; λ=1.5418 Å; Ni filter; 40 KV, 15 MA; scale factor 8, time constant 4; range 2°–90° 2θ, at 1° 2θ per minute.

[2] Intensities correspond to actual peak heights. Values of I greater than 100 are extrapolated off the chart and hence approximate.

[3] Data after Brichard and Brasseur (1958, Tables I and III) and Volborth (1959).

* Strongest uraninite line; on X-ray powder films only.

b=broad.

TABLE 8. X-RAY POWDER DIFFRACTION DATA FOR META-AUTUNITE II HEATED
AT 110°, 170°, 225° C., AND TO RED HEAT[1]

| Meta-autunite II (Heated at 110° C.) | | Heated at 170° C. | | Heated at 225° C. | | Heated to redness | |
|---|---|---|---|---|---|---|---|
| *d* (Å) | I[2] | *d* (Å) | I | *d* (Å) | I | *d* (Å) | I |
| | | | | | | 11.12 | 12 |
| 8.21 | 150± | 8.20 | 165± | 8.20 | 175± | 8.28 | 115± |
| 6.58 | 9 | 6.55 | 7 | 6.57 | 7 | 6.39 | 4 |
| 5.33 | 9 | 5.34 | 6 | 5.34 | 9 | 5.59 | 140± |
| 4.81 | 11 | 4.81 | 11 | 4.80 | 8 | 4.96 | 12 |
| 4.08 | 70 | 4.08 | 100 | 4.07 | 150± | 4.13 | 28 |
| 3.60 | 5 | 3.60 | 5 | 3.60 | 6 | 3.72 | 63 |
| 3.53 | 17 | 3.52 | 15 | 3.52 | 15 | 3.51 | 6b |
| 3.27 | 8 | 3.27 | 8 | 3.27 | 6 | 2.95 | 4 |
| 3.21 | 6 | 3.21 | 5 | 3.22 | 5 | 2.88 | 4 |
| 3.12 | 2b | | | 3.10 | 3 | 2.79 | 18 |
| 2.97 | 10 | 2.97 | 10 | 2.97 | 7 | 2.22 | 24 |
| 2.72 | 16 | 2.72 | 18 | 2.71 | 33 | 1.657 | 3 |
| — | | 2.58 | 2 | 2.58 | 3 | 1.588 | 7 |
| 2.21 | 5 | 2.20 | 4 | 2.18 | 3 | | |
| — | | — | | 2.13 | 2 | | |
| 2.04 | 7 | 2.04 | 7 | 2.04 | 16 | | |
| — | | — | | 1.99 | 3 | | |
| 1.90 | 2 | 1.91 | 3 | 1.90 | 3b | | |
| — | | — | | 1.76 | 3 | | |
| 1.63 | 5 | 1.630 | 4 | 1.63 | 5 | | |
| 1.61 | 3 | 1.613 | 2 | — | | | |
| 1.48 | 3 | — | | — | | | |

[1] Undifferentiated autunite, i.e., the natural mixture of dark and light material. Specimen DB-31. CuK$\alpha$; $\lambda = 1.5418$ Å; Ni filter; 40 KV, 15 MA: scale factor 8, time constant 4; range 2°–90° $2\theta$, at 1° $2\theta$ per minute.

[2] Intensities correspond to actual peak heights. Values of I greater than 100 are extrapolated off the chart and hence approximate.

b = broad.

reactions. The diffraction patterns of heated meta-autunite II in each case were made after the sample had cooled to room temperature in the expectation that any structural changes induced by heating would be maintained upon cooling. This assumption is based only upon the known irreversibility of the dehydration to meta-autunite II.

Comparison of the diffraction patterns corresponding to 110°, 170°, and 225° C. indicates no fundamental differences in structure, and the different peaks and their relative spacings are closely similar in the three patterns. The only progressive variation lies in the increasing relative

intensities of some of the peaks, namely, $d = 4.08$, 2.72, and 2.04, which may be ascribed to progressive loss of water between layers with increasing temperature, in a manner similar to that exhibited by montmorillonite (George T. Faust, written communication).

There is only limited correspondence between the above three patterns and that given by Frondel (1951, p. 677) for the meta-II hydrate of sabugalite, which is said to be "virtually identical with that of the meta-II hydrate of autunite." Marked disparities are found particularly in the lines falling in the range $2\theta = 0° - 25°$, which are especially well defined in the patterns of the Daybreak material.

The pattern of meta-autunite II heated to red heat (Table 8) is markedly different from that of material heated to lower temperatures, indicating that a distinct change in the structure occurs at some temperature above 225° C.

## ORIGIN OF THE DEPOSITS

The Mt. Spokane deposits are strikingly different from other uranium deposits in granitic rocks, for example, within the Boulder batholith (Thurlow and Reyner, 1951; Wright and Emerson, 1957; Emerson and Wright, 1957), or at Marysvale, Utah (Kerr and others, 1952). In the latter cases, autunite is but one of a complex suite of secondary uranium minerals, and is closely related to primary unoxidized ore, notably uraninite; sulfides and oxides of copper, lead and iron are usually also present. The overwhelming preponderance of autunite in the Mt. Spokane area suggests a free supply of lime and phosphate, to the exclusion of other substances that could complex with uranium; the absence of known reserves of unoxidized uranium ore raises a baffling problem concerning a source of uranium to give rise to the large quantities of autunite.

A possible source of lime and phosphate is suggested by a study of the accessory constituents in twenty-seven samples of granitic rock, partly within and partly outside of mineralized zones. Results for representative samples are summarized in Table 9. The most striking observation is that apatite, by far the most abundant accessory constituent in most samples, is notably corroded and leached in specimens from mineralized zones (Fig. 7), whereas, in rocks at some distances from mineralized areas, apatite appears relatively fresh (Fig. 8). The indication is that apatite has been preferentially leached from granite in mineralized zones, releasing lime and phosphate which may have contributed toward the formation of autunite.

Fresh apatite may occur in rocks relatively close to mineralized zones (*e.g.*, DB-3, DB-56), whereas apatite from rocks at some distance from known mineralization (*e.g.*, DB-57C, DB-79, DB-83A) may show signs of

TABLE 9. ACCESSORY MINERALS IN SOME ROCKS FROM THE
MT. SPOKANE AREA, WASHINGTON

Percentages based on visual estimates only

| Sample No. | Sample location and description | Accessory minerals | | Condition of apatite | Remarks |
|---|---|---|---|---|---|
| DB-3 | Fairly fresh fine-grained granite three feet above horizontal gouge zone, east of main mineralized zone, Daybreak mine. | Apatite<br>Zircon<br>Opaques | 95<br>2<br>3 | Most grains smooth and euhedral; some etching on larger grains. | Zircon forms tiny fresh euhedral prisms. |
| DB-4 | Altered gouge from ore zone, Daybreak mine. | Apatite<br>Garnet<br>Opaques<br>Monazite and<br>zircon | 64<br>20<br>15<br><br>1 | Generally corroded and embayed, irregular outlines. | Garnet has pitted surfaces, some grains deeply embayed. |
| DB-5 | Altered medium-grained muscovite granite 50 ft. west of main ore zone, Daybreak mine. | Apatite<br>Garnet<br>Opaques | 90<br>5<br>5 | Grains uniformly corroded and dirty, with irregular outlines and occasional embayments. | Garnet partly etched and pitted, partly fresh. |
| DB-12 | Somewhat altered fine-grained granite in mineralized zone, Daybreak mine. | Apatite<br>Opaques | 95<br>5 | Most grains corroded with rough surfaces, sharp irregular edges; rare smooth prisms. | |
| DB-20 | Fairly fresh quartz monzonite above one mile northwest of Daybreak mine. | Apatite<br>Monazite<br>Zircon | 95<br>4<br>1 | Grains mostly clean, unetched, prismatic. | Lead-alpha age on monazite found to be $75 \pm 10$ m.y.[1] |
| DB-36 | Fine-grained autunite-bearing pegmatite, Lehmbecker Claim. | Garnet | 100 | | Garnet forms fresh, light orange-red euhedral grains up to 0.25 mm. in diameter. |
| DB-40 | Medium- to coarse-grained altered muscovite-bearing granite, adjacent to zone of intense shearing; Kessler property. | Apatite<br>Garnet | 95<br>5 | Grains uniformly etched; rough surfaces, irregular jagged outlines, some development of spines. | |
| DB-50 | Sheared and foliated biotite granite along Deadman Creek road near summit of Mt. Spokane. | Apatite<br>Monazite<br>Garnet<br>Zircon and<br>Allanite (?) | 85<br>10<br>3<br><br>2 | Grains mostly clean, unetched, prismatic; slight pitting in some cases. | Monazite in rounded prisms; some grains slightly etched. |
| DB-54 | Altered granite next to autunite stringer in mineralized zone; Mudhole prospect on Deadman Creek. | Apatite<br>Garnet<br>Sphene, Monazite<br>and Zircon | 90<br><br><br>10 | Highly corroded; rough and dirty looking surfaces, extremely irregular outlines; spines and deep embayments on many grains (See. Fig. 8.) | Garnet, sphene, and monazite slightly etched; zircon completely fresh. |

[1] Analyst, T. W. Stern, U. S. Geological Survey.

TABLE 9 (*continued*)

| Sample No. | Sample location an description | Accessory minerals | | Condition of apatite | Remarks |
|---|---|---|---|---|---|
| DB-56 | Fine-grained biotite granite from end of trench, approximately 10 yards from autunite mineralization; Mudhole prospect. | Apatite Zircon and Allanite (?) | 95 5 | Nearly all grains clean, fresh, euhedral; slight etching on larger grains only. (See Fig. 9.) | One of the freshest concentrates examined. |
| DB-57C | Fresh biotite granite 7 miles north of Daybreak mine. | Apatite Opaques (mostly pyrite) Sphene, monazite and zircon | 80 15 5 | Most grains fresh and euhedral, but some etching and pitting, especially on larger grains. | |
| DB-64 | Altered medium-grained muscovite granite cut by pegmatites. From trench, Dahl property. No visible autunite. | Apatite Garnet Monazite Pyrite and misc. | 65 15 10 10 | Most grains corroded, with jagged outlines, spines, and embayments. | Monazite partly etched though less than apatite; garnet fairly fresh. |
| DB-73A | Fairly fresh biotite granite, Deadman Creek road, 0.1 mile west of Mudhole prospect. | Apatite Allanite Zircon Misc. | 90 7 2 1 | Fresh clean euhedral or slightly rounded prisms, no sign of etching. | Allanite forms irregular grains and subhedral prisms, partly etched. Zircon forms sharply euhedral prisms. |
| DB-79 | Slightly altered biotite granite, Deadman Creek road at junction of north and south forks of Deadman Creek. | Apatite Monazite and misc. | 98 2 | Most grains slightly etched and pitted; generally euhedral but some with embayments and irregular outline. | |
| DB-83A | Slightly altered medium-grained muscovite-bearing granite along Blanchard Creek road 1½ miles northwest of Daybreak mine. | Apatite Monazite | 98 2 | Most grains etched and pitted, though less strongly than apatite from mineralized zones. Shapes of grains often irregular. | Monazite shows slight etching. |
| DB-83B | Fine-grained aplite dike in granite DB-83A | Garnet Apatite | 90 10 | Most grains prismatic, slightly etched. | Garnet in euhedral or slightly rounded grains 0.1–0.2 mm. in diameter. |

corrosion. The first observation suggests that intense leaching of apatite is a rather localized process, evidently restricted to immediate shear zones, and thus closely related in space to development of autunite. Corrosion of apatite in relatively unaltered rocks, on the other hand, may perhaps be attributed to normal weathering, unrelated to the active leaching that apparently prevailed in shear zones. The number of specimens studied is insufficient to warrant generalization on these points; the above observations, however, must be considered in any discussion regarding the origin of these deposits.
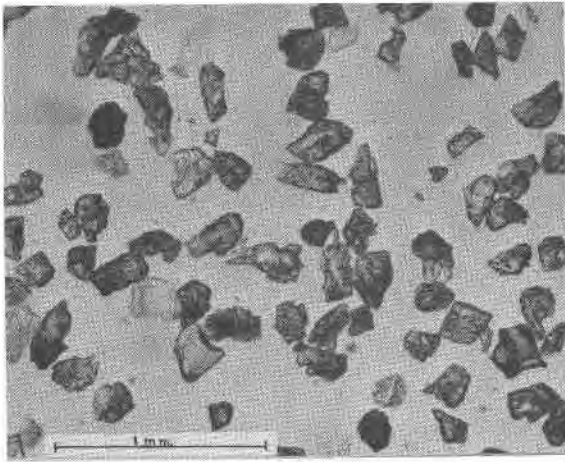
FIG. 7. Apatite from specimen DB-54, altered granite from mineralized zone at
Mudhole prospect, Mt. Spokane area.

Leaching of apatite with subsequent crystallization of autunite has
been proposed as a weathering process by Frondel (1951b, p. 685). In
the western part of the Wind River district, Wyoming (R. G. Coleman,
U. S. Geological Survey, written communication), incrustations of autun-
ite have formed on nodules and stringers of apatite, apparently as the
result of reaction of apatite with weakly acid groundwater. Apatite in
water solution dissolves appreciably below pH 8 (Kazakov, 1950), and
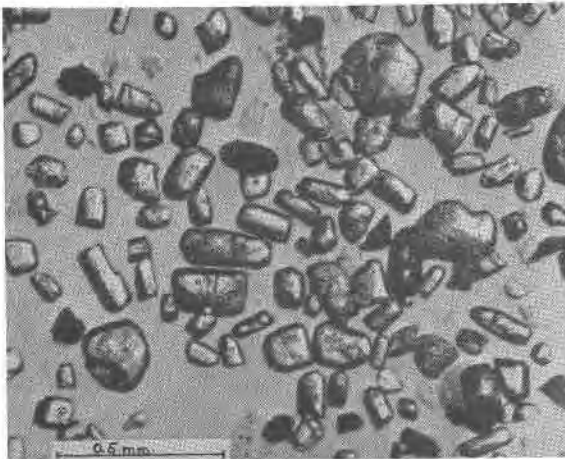


FIG. 8. Apatite from specimen DB-56, fairly fresh biotite granite about 30 feet
distant from most intense autunite mineralization, Mudhole prospect.

its solubility increases markedly below pH 4 (Stelly and Pierre, 1942, p. 140). Leaching of apatite in the Mt. Spokane area may have been effected by near-surface meteoric waters, but for reasons considered below, it appears more probable that ascending juvenile waters were more important. A possible indication of a generally acid environment in this area is the absence of uranophane and phosphuranylite, which are thought to form by reaction of autunite with silica-bearing solutions above pH 7 (Shcherbina and Ignatova, 1956). Noticeable decomposition of autunite at room temperature in solutions of HCl with pH 5 or lower, on the other hand, indicates an effective lower limit of pH during and after mineralization.

TABLE 10. URANIUM CONTENT OF QUARTZ MONZONITE AND SOME
CONSTITUENT MINERALS FROM MT. SPOKANE, WASHINGTON
In parts per million[1]

| | |
|---|---|
| Quartz monzonite (DB-20)[2] | 2.1 |
| Apatite[3] | 23 |
| Biotite[3] | 10 |

[1] Each figure represents the average of two determinations.

[2] Analyst, Wendell P. Tucker, U. S. Geological Survey.

[3] Analyst, Joseph Budinsky, U. S. Geological Survey.

Whereas lime and phosphate for autunite formation appears to be potentially abundant, an adequate source of uranium is much less apparent. Some uranium, like calcium and phosphorus, may have been derived from the granitic rocks by leaching. Relatively unaltered quartz monzonite about one mile north of the Daybreak mine (DB-20) contains about 2 ppm. uranium (Table 10), about one-half of which might be leached from the rock (Larsen and others, 1955, p. 68). Even on the assumption, however, that this figure represents an average for the granitic rocks of the area, the amount of uranium derived by leaching would be scarcely adequate to account for the known autunite deposits.* It is therefore necessary to look for additional sources of uranium. One possibility is that the deposits represent originally unoxidized veins almost entirely converted to autunite; alternately, uranium may have been transported from depth by oxidizing solutions.

* A phosphate determination for specimen DB-20 indicated a $P_2O_5$ content of 0.14 per cent. Assuming all $P_2O_5$ to be in apatite, and apatite to be 20 per cent leached, it is estimated that available lime and phosphate from a ton of rock could yield about 1,500 grams of autunite, whereas available uranium (assuming 50 per cent leaching) would yield less than two grams of autunite.

As evidence for the first origin may be cited the presence of finely dispersed uraninite throughout cores of autunite clusters, which might be interpreted as remnants of incompletely converted uraninite veins. However, there are important differences, already alluded to, between the deposits of Mt. Spokane and many other oxidized vein deposits in granitic rocks. At the W. Wilson mine south of Helena, Montana (Wright and Emerson, 1957), a complex suite of secondary uranium minerals, mainly meta-autunite, meta-uranocircite, uranophane, and phosphuranylite, is developed above the water table within a few feet of uraninite-bearing veins. Meta-autunite is disseminated in the wall rock up to four and one-half feet from veins; direct replacement of uraninite by autunite or other secondary minerals, although noted, is very rare. In the Marysvale district (Kerr and others, 1952), autunite, torbernite, and schroeckeringite are disseminated in the oxidized zone, above unoxidized veins containing sooty uraninite, pyrite, and fluorite. These and other pitchblende-bearing vein deposits in felsic intrusive rocks (Everhart and Wright, 1953) are furthermore characterized by a variety of other ore minerals, predominantly base-metal sulfides, and commonly show hematite alteration. Since the above features are essentially lacking in the Mt. Spokane district, the latter can certainly not be regarded as typical of uraninite-bearing vein deposits.

An alternate explanation for accumulation of uranium is that the latter may have been leached from unoxidized deposits at depth by oxidizing, slightly acid juvenile waters. The uranyl-bearing solutions, ascending along structurally controlled channels, may have leached apatite and subsequently deposited autunite along shear zones and fractures.

As pointed out earlier, the chief difficulty with the above hypothesis is the apparent absence of significant amounts of unoxidized ore, at least within a depth of about 100 feet. Much deeper drilling at mineralized sites may be required to locate primary sources of uranium that gave rise to the autunite deposits.

*Origin of uraninite*

No obvious explanation is apparent for the occurrence of uraninite in submicroscopic particles throughout the inner portions of autunite flakes. One possibility, that the uraninite represents unoxidized remnants of original uraniferous veins, seems improbable because of the complete absence of larger remnants of unoxidized ore in the process of replacement. Alternately, it is suggested that uraninite may have been precipitated within autunite during and following crystallization of the latter. The solutions depositing autunite were probably mildly oxidiz-

ing, with a pH of about 5 to 7. According to the diagrams of Garrels (1955, Fig. 5), under the above conditions a very small quantity of $U^{+4}$ ions would be in equilibrium with uranyl-bearing solutions, and the amount of $U^{+4}$ would increase greatly with a moderate drop in Eh. If, after initial crystallization of autunite, the environment for a period became more reducing, uraninite might have been precipitated.* In the event of fluctuation of Eh across the boundary of stability of U(IV) relative to U(VI), alternate crystallization of autunite and uraninite might have taken place.

Because of limited evidence for such a mechanism, especially with regard to the likelihood of a fluctuating oxidation-reduction environment in the Mt. Spokane area, the above idea is put forward only speculatively. However, such a mechanism, if tenable on theoretical grounds, would be in better accord with the observed occurrence of uraninite than to suppose the latter to represent remnants of unoxidized veins.

## REFERENCES

ALTSCHULER, Z. S., CLARKE, R. S., JR., AND YOUNG, E. J. (1958), The geochemistry of uranium in apatite and phosphorite: *U. S. Geol. Survey Prof. Paper* **314-D**, 45–90.
BEINTEMA, J. (1938) On the composition and the crystallography of autunite and the meta-autunites: *Rec. travaux Chim. Pays-Bas* **57**, 155–175.

* The possibility of precipitating sooty uraninite at low temperatures and pressures by means of a reducing agent such as $H_2S$ has been demonstrated by Gruner (1952) and Miller and Kerr (1954). McKelvey and others (1955, p. 490) state that "Precipitation of primary uranium minerals may be caused solely by a decrease in temperature and/or pressure, or may be the result of chemical interaction with the host rock."

Borneman-Starinkevitch, I. D. (1938), On some isomorphic substitutions in apatite: *Acad. Sci. U.R.S.S., Comptes rendus (Doklady)* 19, no. 4, 253–255.

Bower, C. A., and Truog, E. (1940), Base exchange capacity determination of soils and other materials using colorimetric manganese method: *Indus. and Eng. Chemistry, Anal. Ed.* 12, 411–413.

Brichard, H., and Brasseur, H. (1958), Sur les autunites naturelles et synthétiques: *Soc. française minéralogie et crystallographie Bull.* 81, 4–10.

Clarke, R. S., Jr., and Altschuler, Z. S. (1958), Determination of the oxidation state of uranium in apatite and phosphorite deposits: *Geochim. et Cosmochim. Acta* 13, 127–142.

Donnay, G., and Donnay, J. D. H. (1955), Contribution to the crystallography of uranium minerals: *U. S. Geol. Survey* TEI-507, 42 p., issued by U. S. Atomic Energy Comm. Tech. Inf. Service Extension, Oak Ridge, Tenn.

Emerson, D. O., and Wright, H. D. (1957), Secondary uranium minerals at the W. Wilson mine in the Boulder batholith, Montana: *Am. Mineral.* 42, 222–239.

Everhart, D. L., and Wright, R. J. (1953), The geologic character of typical pitchblende veins: *Econ. Geology* 48, 77–96.

Fairchild, J. G. (1929), Base exchange in artificial autunites: *Am. Mineral.* 14, 265–275.

Frondel, C. (1951a), Studies of uranium minerals (VIII): Sabugalite, an aluminum-autunite: *Am. Mineral.* 36, 671–679.

———— (1951b), Studies of uranium minerals (IX): Saléeite and novacekite: *Am. Mineral.* 36, 680–686.

Frondel, C., Riska, D., and Frondel, J. W. (1956), *X*-ray powder data for uranium and thorium minerals: *U. S. Geol. Survey Bull.* 1036-G, 91–153.

Garrels, R. M. (1955), Some thermodynamic relations among the uranium oxides and their relation to the oxidation states of the uranium ores of the Colorado Plateaus: *Am. Mineral.* 40, 1004–1021.

George, D'Arcy (1949), Mineralogy of uranium and thorium bearing minerals: *U. S. Atomic Energy Comm.* RMO-563, 198 p., issued by U. S. Atomic Energy Comm. Tech. Inf. Service Extension, Oak Ridge, Tenn.

Green, Jack (1953), Geochemical table of the elements for 1953: *Geol. Soc. Am. Bull.* 64, 1001–1012.

Greene-Kelly, R. (1957), The montmorillonite minerals (smectites), *in* Mackenzie, R. C., ed., The differential thermal investigation of clays: Miner. Soc. (Clay Miner. Group) London, 140–164.

Grim, R. E. (1953), Clay mineralogy: New York, McGraw-Hill Book Co., Inc., 384 p.

Gruner, J. W. (1952), New data for syntheses of uranium minerals, *in* Annual report for July 1, 1951, to June 30, 1952, pt. 1: *U. S. Atomic Energy Comm.* RMO-983, 26 p., issued by U. S. Atomic Energy Comm. Tech. Inf. Service Extension, Oak Ridge, Tenn.

Guillemin, C., and Pierrot, R. (1956), La sabugalite du gite de Margnac II. Haute-Vienne: *Soc. française minéral. et cryst. Bull* 79, 179–182.

Kazakov, A. V. (1950), The fluorapatite system of equilibria in the conditions of formation of sedimentary rocks: *Akad. Nauk SSSR, Inst. Geol. Nauk* 114, Geol. ser. no. 40, 1–21. (Unpublished translation, 1951, by V. L. Skitsky.)

Kerr, P. F., Brophy, G., Dahl, H. M., Green, J., and Woolard, L. E. (1952), A geologic guide to the Marysvale area, Annual report for July 1, 1951, to June 30, 1952, pt. 1: *U. S. Atomic Energy Comm.* RMO-924, 57 p., issued by U. S. Atomic Energy Comm. Tech. Inf. Service Extension, Oak Ridge, Tenn.

Larsen, E. S., Jr., Phair, G., Gottfried, D., and Smith, W. L. (1955), Uranium in magmatic differentiation, *in U. S. Geol. Survey Prof. Paper* 300, 65–74.

McCreery, G. L. (1949), Improved mount for powdered specimens used on the Geiger counter x-ray spectrometer: *Am. Ceramic Soc. Jour.* **32**, 141–146.

McKelvey, V. E., Everhart, D. L., and Garrels, R. M. (1955), Origin of uranium deposits: *Econ. Geology*, **50**th **Anniversary Volume**, pt. 1, 464–533.

Miller, L. J., and Kerr, P. F. (1954), Progress report on the chemical environment of pitchblende, *in* Annual Report for June 30, 1953, to April 1. 1954, pt. 2: *U. S. Atomic Energy Comm.* **RMO-3096,** p. 72–99, issued by U. S. Atomic Energy Comm. Tech. Inf. Service Extension, Oak Ridge, Tenn.

Norman, H. W. (1957), Uranium deposits of northeastern Washington: *Mining Eng.* **9,** 662–666.

Nuffield, E. W., and Milne, I. H. (1953), Studies of radioactive compounds: VI. Meta-uranocircite: *Am. Mineral.* **38**, 476–488.

Palache, Charles, Berman, Harry, and Frondel, Clifford (1951), Dana's system of mineralogy, 7th ed., **2**: New York, John Wiley and Sons, Inc., 1124 p.

Rinne, F. (1901), Kalkuranit und seine Entwaesserrungsprodukte (Metakalkuranite): *Centralbl. Mineral. Geol. und Palaeontl.*, 709–713.

Ross, C. S., and Hendricks, S. B. (1945), Minerals of the montmorillonite group, their origin and relation to soils and clays: *U. S. Geol. Survey Prof. Paper* **205-B**, 23–77.

Shcherbina, V. V., and Ignatova, L. I. (1956), Formation and dissolution of autunite: *Geokhimiya*, no. 2, 56–61.

Stelly, M., and Pierre, W. H. (1942), Forms of inorganic phosphorus in the C horizons of some Iowa soils: *Soil Sci. Soc. Am. Proc.* **7**, 139–147.

Thurlow, E. E., and Reyner, M. L. (1951), Preliminary report on uranium-bearing deposits of the northern Boulder batholith region, Jefferson County, Montana: *U. S. Atomic Energy Comm.* **RMO-800,** 62 p., issued by U. S. Atomic Energy Comm. Tech. Inf. Service Extension, Oak Ridge, Tenn.

Volborth, A. (1959), Strontian meta-autunite from the Daybreak mine, Mt. Spokane, Washington: *Am. Mineral.* **44,** 702–711.

Wright, H. D., and Emerson, D. O., 1957, Distribution of secondary uranium minerals in the W. Wilson deposit, Boulder batholith, Montana: *Econ. Geology* **52**, 36–59.