UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON

TEI-108

TEIR 108

A PRELIMINARY REPORT ON METHODS OF DETERMINING THE AGE OF COLORADO PLATEAU CARNOTITE

by

L. R. Stieff, M. N. Girhard, and T. W. Stern

Trace Elements Laboratory Investigations Report 10

U. S GOVERNMENT PRINTING OFFICE 878079

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

A PRELIMINARY REPORT ON METHODS OF DETERMINING THE AGE OF COLORADO PLATEAU CARNOTITE

by

L. R. Stieff, M. N. Girhard, and T. W. Stern

April 1950

Trace Elements Laboratory Investigations Report 10

USGS - TELI Report 10,
April 1950
Consisting of ___ pages
Issued to (see below)

The distribution of this report is as follows:

2 copies	AEC, Washington (J. C. Johnson)
5 copies	AEC, New York (P. L. Merritt)
1 copy	AEC, Denver (C. C. Towle, Jr.)
1 copy	AEC, Spokane, Wash. (E. E. Thurlow)
1 copy	AEC, Grand Junction, Colo. (W. G. Fetzer)
35 copies	U. S. Geological Survey

CONTENTS

ILLUSTRATIONS

TABLES

A PRELIMINARY REPORT ON METHODS OF DETERMINING THE AGE OF COLORADO PLATEAU CARNOTITE

By L. R. Stieff, M. N. Girhard, and T. W. Stern

ABSTRACT

Four methods of dating Colorado Plateau carnotite have been examined and evaluated: mineralogic methods, radioactive-equilibrium methods, lead-uranium-ratio methods, and lead-isotope methods. The data on 12 high-grade samples, from a suite of 50 representative carnotite ores, are presented.

Carnotite has been recognized in both the crystalline and microcrystalline forms. A calcium analogue of carnotite and an unknown yellow uranium-bearing mineral are also thought to be present in some samples. Petrographic study of the thin sections showed that carnotite

was usually the last mineral deposited. Carnotite was found as crystals in vugs and as a filling of fractures in quartz grains. Many of the thin sections show quartz grains with highly irregular boundaries suggesting solution of the quartz prior to or at the same time as the carnotite deposition.

A qualitative alpha-plate study suggests that numerous radiocolloids are usually found with the predominantly crystalline form. The relatively low alpha-particle activity of the crystalline form compared to that of the microcrystalline form indicates that the crystalline form is not in radium-uranium equilibrium.

Two of the 12 high-grade samples are approximately in radium-uranium equilibrium. One sample has a 5-percent excess of radium, and the remaining 9 samples are deficient in radium. The minimum radium-uranium age of the 2 samples in radium-uranium equilibrium is approximately 500,000 years. The maximum radium-uranium ages of 2 essentially lead free samples not in radioactive equilibrium are 15,000 and 40,000 years. Samples which contain lead and which are not in radium-uranium equilibrium cannot be dated by this method. Near-surface occurrences of the predominantly crystalline samples have the greatest radium deficiencies. The only sample of crystalline carnotite found at depth, however, has a 5-percent excess of radium. Radium content of the 7 predominantly microcrystalline samples ranged from an excess of 2 percent to a deficiency of 20 percent.

The 3 high-grade carnotites that are most nearly in radium-uranium equilibrium and that probably have been least disturbed have uncorrected lead-uranium-ratio ages that range from 21 to 77 million years. The age of the 3 predominantly crystalline samples that can be calculated by the lead-uranium-ratio method range from 30 to 35 million years. The calculated ages of the microcrystalline carnotite range from 19 to 169 million years.

The Pb^{206}/U^{238} and Pb^{207}/U^{235} ratio age calculations corrected for common lead but uncorrected for the possible addition of radiogenic lead are essentially in agreement for each sample but range from 27 to 96 million years. The Pb^{207}/Pb^{206} ratio ages are in marked disagreement with the lead-uranium-ratio ages and range from 520 to 600 million years (late pre-Cambrian). Assuming correct analyses the paradox of late pre-Cambrian radiogenic lead in deposits whose maximum age is late Jurassic may be explained by (1) the loss of radon or (2) the introduction of old radiogenic lead. It is believed that the quantitative dating of these ores by the lead-uranium-ratio and lead-isotope methods will be possible when mass-spectrographic analysis has established the source of the lead in the carnotite.

INTRODUCTION

Field evidence demonstrates that most, if not all, of the Colorado Plateau carnotite deposits are epigenetic, and it is generally believed that carnotite was deposited from circulating ground water after the deposition of the enclosing upper Jurassic sediments (Ransome, 1905, p. 17; Hess, 1914, p. 236; Butler, 1920, p. 158; Fischer, 1942, p. 389; 1949, p. 109; and 1950, p. 1; Stokes, 1948, oral communication; Webber, 1947; and others). The postulated times of ore deposition, however, have ranged from about the end of the Jurassic period, 127 million years (Holmes, 1948, p. 45), to relatively recent times. It has been difficult to determine definitely by field methods alone the amount of time that has elapsed between the deposition of the sediments and the formation of the deposits because consistent relations have not been found between the deposits and present or past erosion surfaces or such geologic structures as faults, folds, and igneous intrusions (Fischer, 1949, p. 109). The systematic laboratory investigation of the age of the carnotite deposits is now being undertaken in an effort to resolve this very important and fundamental disagreement about the age of the deposits.

If even an approximate dating of the deposits could be made by laboratory methods, the approach to the problems on the source and the chemical and physical controls of the mineralizing solutions would be simplified. The clarification of these questions on the origin of the deposits would have not only considerable scientific interest but also two immediate practical applications: (1) greater confidence could be placed in the estimates of the ultimate reserves of carnotite ore on the Colorado Plateau and in the selection of new areas for exploratory drilling; (2) more thorough evaluation could be made of the prospecting methods and geologic controls used to guide the drilling.

The problem of determining the age of the Colorado Plateau carnotite deposits by laboratory methods has been divided into three parts. First, some of the limits of the problem have been outlined by studying 50 selected samples of carnotite ore. These samples are representative of different grades of ore and of differing amounts of exposure to chemical weathering. They were collected from different geographic locations and stratigraphic positions. Secondly, the age of individual deposits in contrast to the age of selected samples is to be determined from representative samples of these deposits. Finally, an effort will be made to determine the source and the age of the uranium from which the carnotite was formed.

Primarily, this report discusses in general the qualitative and quantitative laboratory methods of age determination which may be used on samples of carnotite ore. In particular, it presents the data obtained from the study of 12 representative high-grade carnotite samples and the interpretations which can be made of these data. The data on the remaining 38 intermediate- and low-grade samples are incomplete. Samples representative of single deposits and of large amounts of carnotite ore are now being prepared. Therefore, the interpretations of the data in this paper cannot be extended at the present time to include either the intermediate- and low-grade ores or the deposits as a whole.

As the emphasis of the text has been placed on methods of determining the age of the carnotite, this preliminary report has been divided into "Mineralogic Methods", "Radioactive-equilibrium and Lead-uranium-ratio Methods", and "Lead-isotope Methods". The tabulation of the data obtained, the procedures used, and other phases of the investigation not directly concerned with the determination of the time of mineral deposition have been placed in the appendixes.

ACKNOWLEDGMENTS

The following people aided us in the course of the work: G. W. Imirie, Jr., Chemist; W. A. Peavy, Jr., Chemist; R. G. Rice, Chemist; L. L. Stockman, Physicist; Max Swerdlow, General Physical Scientist; J. J. Tregoning, Chemist; all of the National Bureau of Standards. G. P. Schacher, Physicist, Schenectady Laboratory General Electric Company. M. G. Inghram, Physicist, Argonne National Laboratory. J. T. Bracken, W. R. Champion, Evelyn A. Cisney, C. A. Kinser, Irving May, R. G. Milkey, K. J. Murata, Morris Slavin, all of the Geological Survey. The particular phases of the work to which these people contributed are mentioned in the text. We wish also to thank Theodore Botinelly, Arthur P. Butler, E. S. Larsen, Jr., G. Phair, John C. Rabbitt, and Jane Titcomb, all of the Geological Survey, who reviewed the manuscript and made suggestions throughout the work. We wish to acknowledge, also, the aid of the Raw Materials Office, Atomic Energy Commission, in arranging for priority for work done at the National Bureau of Standards and in financially supporting the work.

MINERALOGIC METHODS

The mineralogic studies which have a direct bearing on the relative age of the minerals in the deposits or which may aid in a more quantitative dating of the deposits have been divided into the following sections:

1. Optical studies
2. Synthetic carnotite studies
3. Alpha-plate studies

A brief description of the sample locations is given in appendix 1. A brief description of the separating techniques used is given in appendix 2. Except where noted, only the - 200-mesh fraction of each sample has been used in this work.

In this report "carnotite" is used to describe a naturally occurring, yellow, hydrous uranyl-vanadate even though this material may be a mixture of two or more minerals. Where differences in the samples have been found, the word carnotite will be qualified.

The X-ray and electron-microscope studies which have no direct relation to the age of the deposits have been placed in appendixes 3 and 4. The results of the chemical analyses for potassium, calcium, and sodium are found in appendix 5. Complete chemical analyses of natural carnotite, tyuyamunite, and associated minerals have not been made because pure separates of these minerals have not been obtained. Several of the better analyses of carnotite which have been published are found in appendix 6.

Optical Studies

Purpose

The 12 high-grade carnotite samples were studied optically in an effort to establish relative ages of the carnotite and other minerals in the sandstone and, if possible, to date approximately the deposition of the carnotite. The - 200-mesh fraction of the samples was best adapted to the study of the different forms of carnotite. This disaggregated material can be used to obtain the relative age of the different forms of carnotite if a correlation can be found between these forms and their manner of occurrence. The same size fraction was also studied for evidences of fractured and metamict carnotite caused by disorder in the crystal lattice resulting in part from radioactive disintegration. Thin sections were examined for evidence of relations of the carnotite forms to each other, to associated minerals, and to microstructures in the sandstone. Detailed optical and petrographic data for each sample are in appendixes 7, 8, and 9.

Discussion

Forms of carnotite.--The complete optical properties of the different forms of carnotite found in the - 200-mesh fraction of the high-grade ores are difficult to obtain because the minerals are extremely fine grained, an observation made by Merrill, in a paper by Hillebrand and Ransome (1905, p. 21), by Hillebrand (1924, p. 209), by Fischer (1942, p. 376), and by Melkov (1945, p. 47).

Some optical properties were obtained, however, by use of an oil-immersion objective.

In 1899 the first description of carnotite was published by Friedel and Cumenge (1899, pp. 328-331). Carnotite has been observed in our samples in two forms: crystalline and microcrystalline. The crystalline carnotite (for example, samples 1 and 20) may be further divided into two varieties: pale-yellow rhombic plates (pls. 1B, 6B, 9A) and medium-yellow acicular crystals. Many acicular crystals grow in fan-shaped aggregates (pls. 2, 4, 10). The indices of refraction of the platy carnotite material were estimated to be : nX= 1.90±, nY= 1.93±, nZ= 1.93±. (These indices are estimates as index oils above 1.90 were not available.) The acicular crystals had approximately the same indices. A comparison of these figures with some of the previously published data (Larsen and Berman, 1934, p. 205), indicates that this crystalline carnotite material seems to be the type previously described (appendix 7).

The microcrystalline carnotite (for example, samples 13 and 28) occurs as pale-yellow to nearly colorless masses of very small crystals (pls. 6B, 9B), some of which contain fine splinters. The average index of refraction of this material is about 1.835 which is considerably lower than the average index of previously described carnotites. This may be a new form of carnotite.

Owing to the fine-grained nature of both the crystalline and microcrystalline yellow uranium-bearing material, the first positive identifications were made by combining chemical analyses for uranium, potassium, calcium and sodium with X-ray-diffraction data. See appendixes 3 and 5.

Eight of the high-grade ores, including samples consisting predominantly of either crystalline or microcrystalline material, gave typical carnotite patterns and had approximately the same uranium-potassium ratio as synthetic carnotite. Chemical analyses of sample 12 indicate that this material is the calcium analogue of carnotite and isostructural with the barium analogue as shown by X-ray powder diffraction photographs. Samples 9, 19, and 64 appeared to be a mixture of the calcium analogue and some other unidentified uranium-bearing mineral.

Manner of occurrence.--With the exception of sample 19, samples collected from surface exposures or near-surface deposits contain predominantly crystalline varieties of carnotite or its analogues. The solution of carnotite by near-surface ground water and subsequent recrystallization by repeated evaporation of these waters might account for this variety of carnotite. If after further study it is found that the relation of crystalline material to near-surface deposits can be generalized, the predominance of the crystalline form in this type of occurrence would mean that it is young and probably younger than the microcrystalline form.

Samples collected from a depth of approximately 30 or more feet were predominantly microcrystalline carnotite. This carnotite would be subject to solution and possibly recrystallization by circulating ground water, but recrystallization by evaporation would not be expected. If additional work does not develop many contradictions to the suggestion that the microcrystalline form is found mainly at depth, this form is probably the older. The synthetic and alpha-plate studies also suggest that the microcrystalline carnotite is the older.

Metamict and fractured carnotite.--Metamict minerals are minerals that possess external crystalline form but when studied by X-ray diffraction or optical methods are found to be amorphous. Goldschmidt (1924, pp. 51-58) concludes that the presence of radioactive elements is not primarily responsible for the disruption of the crystal lattice although the change to the metamict state is probably accelerated by radioactivity. When more has been learned about the cause of metamict structures, this information may be used to determine the time which has elapsed since the minerals became metamict. The time for metamict structure to develop in carnotite minerals, however, is not known, but it may be significant that such structure has not been observed in these samples. The carnotite material is definitely not isotropic. The very fine grained material shows evidence of crystal structure. X-ray powder diffraction patterns of natural carnotite from the samples studied and of synthetic carnotite were found to match closely. This may be contrasted with the poor matching of the patterns of natural tyuyamunite from the Fergana type locality and of synthetic tyuyamunite. Also, preliminary Weissenberg studies of tyuyamunite from Fergana indicate possible disorder in the crystal lattice. The Fergana uranium-bearing minerals are associated with Paleozoic sediments, and the possible disorder in the crystal structure may indicate that they are older than the Colorado uranium-bearing minerals. Crook and Blake (1910, p. 275) noted the presence of isotropic patches in carnotite minerals in the pre-Cambrian rocks of the Radium Hill district of South Australia. They suggested dehydration as a possible explanation. The Colorado carnotites occur in different states of hydration, but, as mentioned, they are not isotropic. The carnotite minerals also show no evidence of fracturing such as would be expected in relatively old uranium-bearing materials. The absence of metamict structure in both the carnotites and associated minerals may indicate a relatively recent age for these minerals.

Thin-section study.--The study of thin sections can be used to determine relative ages if the intergranular and microstructural relations can be determined. The typical sandstone containing high-grade carnotite (pl. 5A) is fine- to medium-grained and poorly sorted. Quartz (about 70 percent by volume) and carnotite (about 25 percent by volume) are the major constituents, and sericite, calcite, plagioclase feldspar, zircon, hewettite, rutile, biotite, and opaques (magnetite and/or ilmenite) are the minor constituents. There is no evidence of detrital uranium-bearing minerals.

The two forms of carnotite recognized in the - 200-mesh fraction probably represent different stages in mineralization and may be used to aid in dating this process when a more detailed study has been made. The platy crystalline carnotite occurs as fracture fillings (pl. 3) and as encrustations on grains of quartz and feldspar. The acicular crystals occur in vugs among quartz and sericitic grains and in some places between quartz and secondary quartz. The microcrystalline material is interstitial and also occurs as encrustations on grains. On the basis of the thin-section study alone, microcrystalline carnotite would be considered older as some of the acicular crystals projecting into vugs seem to have grown outward from masses of the microcrystalline material.

In many parts of the thin sections carnotite seems to replace earlier minerals in the sandstone (pls. 1A, 4). In addition, the replacement of hewettite ($CaV_6O_{15}\cdot 9H_2O$) by carnotite is suggested by the gradation from yellow outer edges to indistinct, reddish-brown centers. The relation between carnotite and other vanadium minerals such as roscoelite $[K_2V_4Al_2Si_6O_{20}(OH)_4]$ and corvusite ($V_2O_4\cdot 6V_2O_5\cdot nH_2O$) could not be determined because they were not found in the high-grade ores.

The quartz grains show a similarity throughout the thin sections in having embayed edges which suggest solution or replacement (pl. 5B). There are some quartz grains which show secondary overgrowths (pl. 5A).

Microstylolites are sutured contacts between mineral grains generally caused by solution at points of greatest pressure. They are visible only with a microscope. Compaction seemed to be the cause of the microstylolites in the Cretaceous sandstones of Montana studied by Sloss and Feray (1948, pp. 3-13). If the relation between microstructures in the Salt Wash sandstones and the mineralizing solutions can be determined, it should be possible to restrict the time of mineralization to the period preceding or following compaction. Microstylolites may be present in some of the quartz grains, but their outlines are not distinct in the thin sections of high-grade ore available to us. Fischer (1942, p. 380) has mentioned previously the presence of microstylolites in these Colorado deposits. With future study of oriented thin sections of the intermediate- and low-grade ores, the relation of the microstylolites to the time of deposition of the carnotite may be established.

The time of carnotite mineralization may also be related to the filling of vugs and fractures in the grains. Vugs containing carnotite crystals were found only in the sample subjected to extreme chemical weathering (sample 12, pl. 2). These crystals must have been more recent than the formation of the vugs. Many of the thin sections show carnotite-filled fractures in quartz grains (pl. 3). The fracturing of the quartz grains may have occurred during compaction but probably occurred during regional deformation. Therefore, this carnotite must have been formed later than the deformation which produced the fractures.

Evaluation

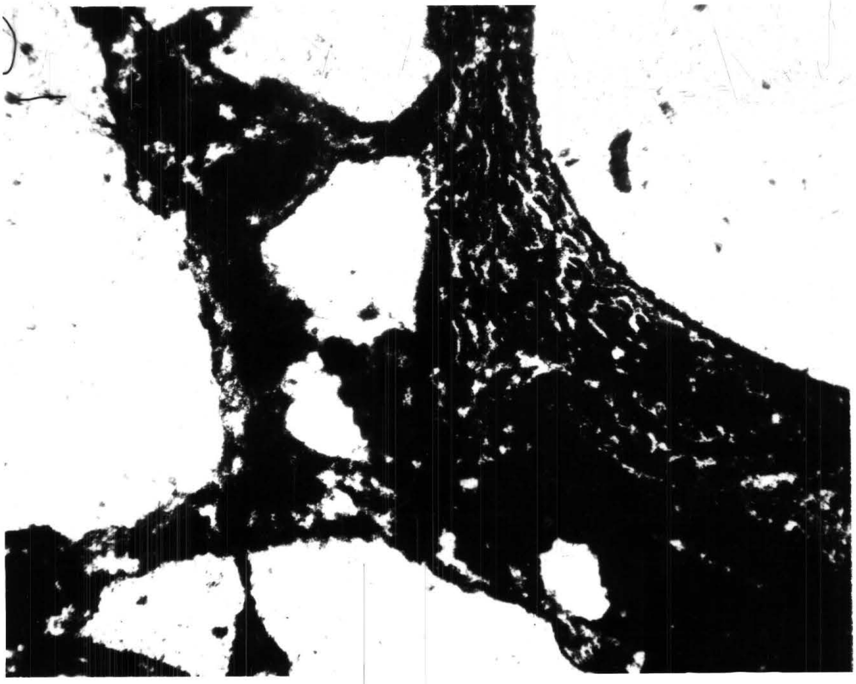
Only the preliminary work has been done in using optical and petrographic data to determine age relationships. Additional work will be done on the relationship of the different forms of carnotite to the type of exposure or weathering to which the samples were subjected. In addition, a petrographic microscope study will be undertaken to establish more conclusively the presence or absence of metamict structure in either the carnotite or associated minerals. When the oriented thin sections of the intermediate- and low-grade ores are studied, the relation of the carnotite to the other vanadium minerals and to microstructures in the sandstone can be stated with more certainty.

PLATE 1

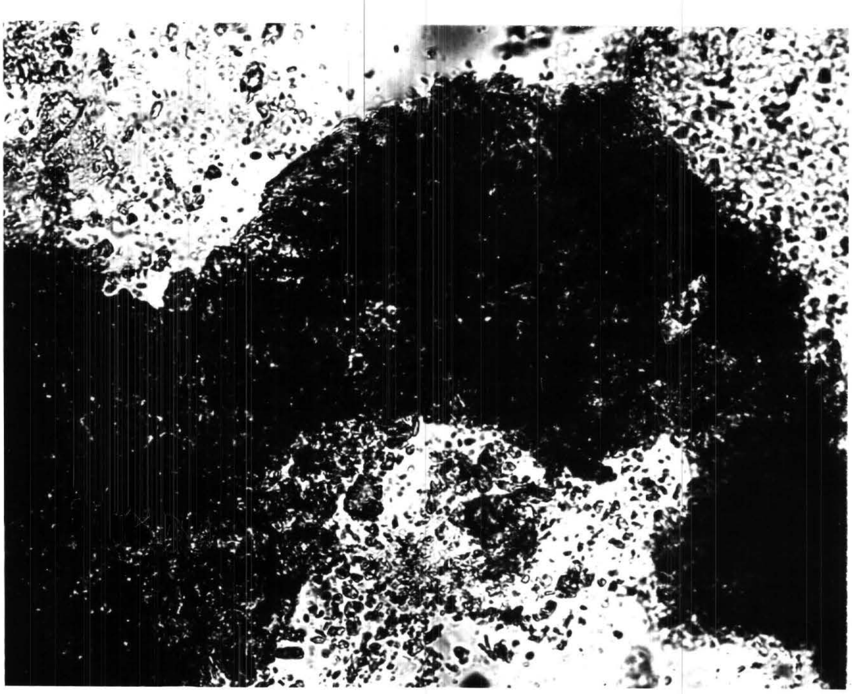
A. Sample 9. Carnotite band in sandstone. Irregular crystal boundaries of quartz suggest replacement. Dark material is carnotite associated with large white quartz grains and small irregular white cavities. Total magnification (optical and photographic) = 102 X, uncrossed nicols.

B. Sample 9. A mass of very small carnotite plates (dark material) in association with quartz (light material). This is a typical example of the clear yellow, interstitial variety of carnotite. Total magnification (optical and photographic) = 450 X, uncrossed nicols.

Plate 1



A



B

PLATE 2

Sample 12. Small carnotite crystals projecting into a vug (white area in center of picture). The acicular crystals on the right side of the vug are the medium-yellow crystals of carnotite described in the text. Note the fan-shaped growth. The very fine grained crystals (gray in the photograph) also seem to be carnotite.

As the openings are probably post-depositional, the crystal growth in the vugs seems to be secondary. Total magnification (optical and photographic) = 970 X (oil immersion), uncrossed nicols.

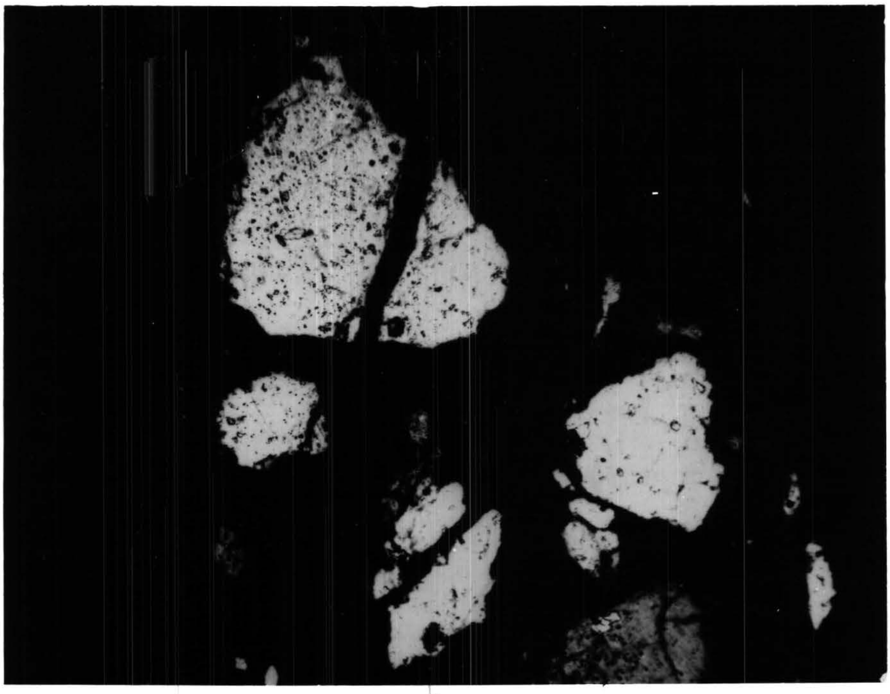
Plate 2

PLATE 3

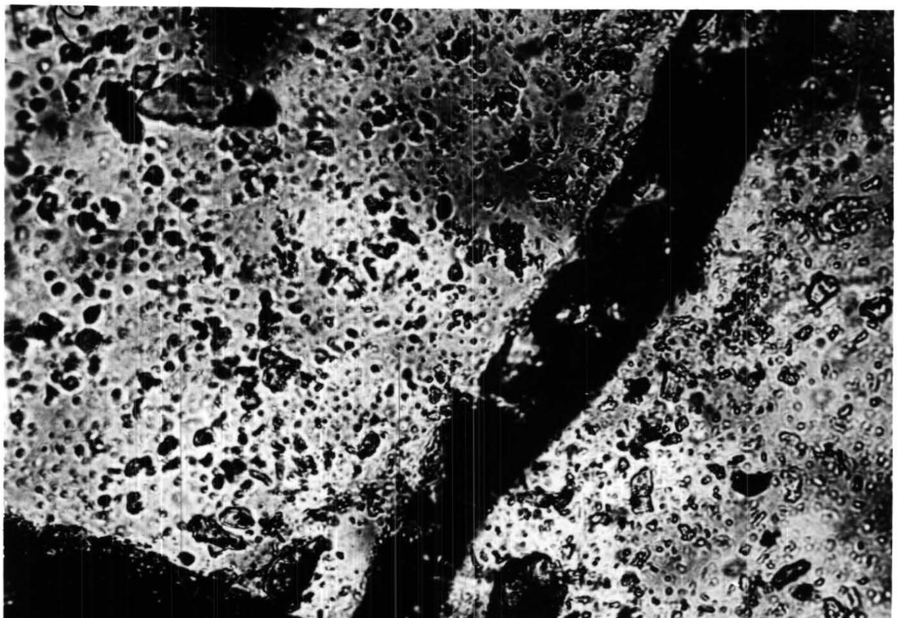
A. Sample 19. A group of quartz grains with carnotite bands cutting through the crystals (white areas are quartz grains; dark bands are carnotite). The fracturing occurred after deposition and may have been associated with regional deformation. Total magnification (optical and photographic) = 102 X, crossed nicols.

B. Sample 19. Detailed view of the lower part of the carnotite vein which cuts through the upper quartz grain in photograph A above. Note contact between quartz and carnotite vein. This carnotite is medium yellow and microcrystalline. Total magnification (optical and photographic) = 450 X, uncrossed nicols.

Plate 3



A



B

PLATE 4

Sample 25. Radial pattern of small acicular carnotite crystals growing inward in spaces having an outline suggestive of euhedral crystals. The acicular crystals are the darker form of the carnotite.

Possibly these are pseudomorphs of carnotite after the original euhedral crystals. The acicular crystals of carnotite seem to be older than the platy interstitial material. Total magnification (optical and photographic) = 450 X, uncrossed nicols.

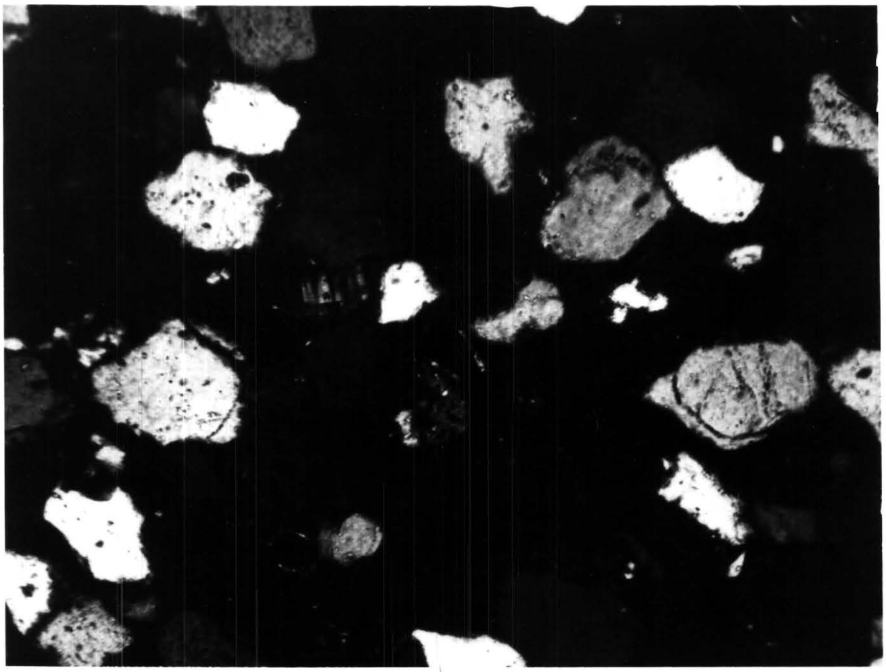
Plate 4

PLATE 5

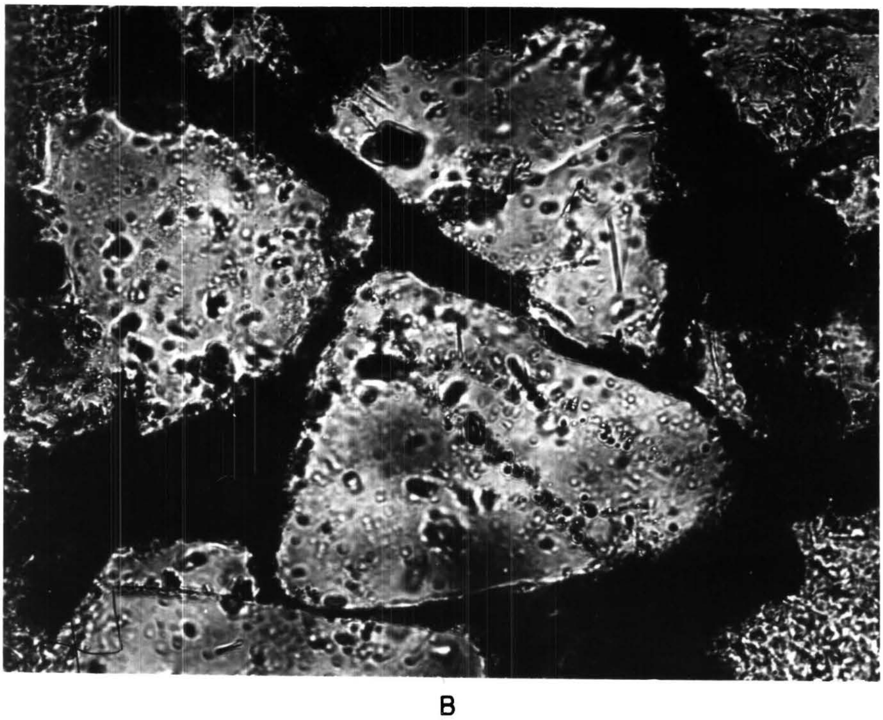
A. Sample 1. General view showing the texture of the sandstone. A quartz grain with a secondary enlargement is visible at right center; twinned plagioclase in center. Total magnification (optical and photographic) = 102 X, crossed nicols.

B. Sample 1. Detailed view of the sandstone showing subangular quartz grains in a matrix of carnotite (dark material). Note irregular grain boundaries and bubble inclusions in the quartz. Total magnification (optical and photographic) = 450 X, uncrossed nicols.

Plate 5



A



B

Synthetic Carnotite Studies

Purpose

The data obtained from the synthesis of carnotite and related minerals can be used only indirectly as a method of dating the carnotite deposits. The effects of pressure, temperature, and chemical environment on the solubility of carnotite can be studied in the laboratory. This information coupled with a knowledge of the changing geological conditions in the Plateau area might exclude, in a general way, the times when the conditions required for the deposition of carnotite did not exist.

In addition, the synthetic carnotite and related minerals have been used as standards for optical, X-ray, and electron-microscope studies. The results of these studies are included in the appropriate sections in the appendixes.

Discussion

Procedure.--Mr. K. J. Murata, Geological Survey, synthesized carnotite and related minerals. A description of the method he used will be found in appendix 10.

The initial precipitate of carnotite was formed at 100°C. in slightly acidic solutions containing concentrated amounts of the essential elements in stoichiometric proportions. This precipitate was gelatinous, and as a result the X-ray powder diffraction pattern was very diffuse. Only after digestion on a steam bath for two to three weeks was the precipitate sufficiently recrystallized to be studied by X-ray and optical methods.

Comparison of natural and synthetic carnotite.--The natural microcrystalline carnotite is similar in appearance to the intermediate stages of the recrystallized synthetic material (pl. 13). If an analogy can be drawn between the laboratory preparation of synthetic carnotite and the conditions which prevailed at the time the natural carnotite was deposited, the natural microcrystalline carnotite was probably precipitated from relatively concentrated solutions of uranium and vanadium. If the time of deposition is restricted to the period during or shortly following sedimentation or to relatively recent times, the temperature of the circulating ground water was probably low. During the intervening time when the now mineralized sediments were buried under thousands of feet of overlying rocks, the temperatures of the rock, connate water, and circulating ground water, if any, were higher.

If the microcrystalline carnotite is late Jurassic in age, it is difficult to understand why it did not recrystallize either during the period when it was deeply buried or before uplift and erosion. This is particularly true in view of the fact that over 100 million years would have been available during which this recrystallization could have taken place. From this type of reasoning, it would seem more acceptable to postulate a relatively recent deposition for the high-grade carnotite studied.

Although gelatinous precipitates of synthetic carnotite may be recrystallized if placed on a steam bath, coarse crystals of any insoluble salt can best be grown from cool, very dilute solutions. The relatively coarse crystalline form of natural calcium and potassium uranyl vanadates may have been recently deposited by the evaporation of cool dilute uranium- and vanadium-bearing near-surface waters.

Base exchange.--In the course of studies of base exchange between synthetic tyuyamunite and synthetic carnotite, Mr. K. J. Murata found that tyuyamunite could readily be converted to carnotite by treatment with solutions containing K^+ ions but that carnotite could be changed to tyuyamunite only with difficulty by treatment with Ca^{++} ions. This is reflected in the relatively coarse size and relative solubility of tyuyamunite as compared with the extreme minute crystal size and relative insolubility of carnotite (pls. 13 and 14). The relative solubilities suggest that the environment through which the mineralizing solutions moved was low in calcium and potassium and that deposition of the ore may have been due to local concentrations of potassium in such minerals as sericite and hydrous micas and in organic matter. This type of inference on the possible chemical controls of mineralization, however, cannot be used readily to date the deposits because the hydrous micas and organic material could have provided an available source of potassium almost from the time of their deposition. The alteration of the feldspars to sericite might have occurred any time after the end of the Jurassic period.

Evaluation

The use of the crystalline and microcrystalline character of carnotite to infer the environment during deposition and the type of mineralizing solution is speculative at the present time. As more specific information is gathered on phase equilibria and the effects of temperature, pressure, pH, and concentration on the solubility and form of carnotite and related minerals, it should be possible to limit more definitely the time of deposition in terms of the environment.

Alpha-plate Studies

Purpose

Emulsions sensitive to heavy ionizing particles may be used to observe the alpha-particle tracks emitted by the uranium and its daughter products in carnotite and to observe local concentrations of radioactive daughter products. The number and length of alpha tracks produced by radioactive grains may be used with certain qualifications as a measure of their departure from radioactive equilibrium and indirectly as a measure of the relative ages of the different forms of carnotite. The presence or absence of local concentrations of daughter products would influence the selection of samples for age determinations by the lead-uranium-ratio method and would aid in the evaluation of the calculated ages.

Appendix 11 gives a description of the type of alpha plate used, preparation of these plates, and method of development and fixation. For each of the high-grade samples studied, a five-day exposure was used. More complete information concerning these techniques has been published by Yagoda (1949, pp. 37-72).

Discussion

Radioactive equilibrium.--Alpha-plate studies may be used in a qualitative way to solve the problem of the relative age of the different forms of carnotite. If these forms have been undisturbed for approximately 500,000 years, they will be nearly in radioactive equilibrium and the alpha-plate method cannot be used. If, however, the carnotite forms are not in equilibrium and have not been disturbed, their departure from this condition may be a relative measure of their age.

Radioactive equilibrium is a state in which the number of atoms of radioactive daughter elements produced in a unit time is equal to the number of atoms of daughter elements which decay in the same interval. The time required for complete equilibrium to be established depends on the half-lives of all the decay products in the series, whereas the amount of daughter product present depends on the half-lives and the atomic weight of the elements. If alpha plates are used, the relative departure of the different forms of carnotite from equilibrium may be roughly estimated by noting the average number of tracks per grain (activity) and by measuring the true alpha-track length (range). Yagoda (1949, p. 182) has mentioned the effect of the lack of equilibrium on the number of emitted alpha particles. A uranium-bearing grain which contains less than equilibrium amounts of the daughter products will emit fewer alpha particles than a similar grain in radioactive equilibrium. Also, shorter average track lengths would indicate a deficiency of more active, shorter half-lived daughter products and consequently a departure from radioactive equilibrium (Yagoda, 1949, p. 101). A strong correlation exists between the maximum energy of the emitted alpha particle and the half-life of the decaying element (Pollard and Davidson, 1946, p. 112). Although the range of the alpha particle does not vary with energy in a simple way (Pollard and Davidson, 1946, p. 10), approximately equal ranges are found for particles of the same energy. A measurement of the range of an alpha particle will give an approximate identification of the decaying element because the maximum energy of the particle emitted by the decay product is unique.

Conditions for age determinations.--The lack of equilibrium can be used as a measure of the relative ages of the different forms of carnotite if the uranium content of the forms is comparable, and if the relative emanating power of the different forms can be established. The uranium content of the microcrystalline form was assumed to be comparable with that of the crystalline carnotite because samples containing large amounts of each form gave the same X-ray powder diffraction pattern (appendix 3).

The emanating power (Hahn, 1936, p. 191) of a radioactive substance has been defined as the ratio of the amount of emanation spontaneously escaping from the substance to the total amount of emanation formed in the substance. This ratio varies with the mineral, surface area, temperature, and the pressure and relative humidity (Hahn, 1936, pp. 205-229). Radon and its isotopes are the daughter products which escape by emanation. A more detailed discussion of emanating power is given in appendix 16.

The effect of emanating power on the estimation of radioactive equilibrium by the alpha-plate method has not been thoroughly studied (Yagoda, 1949, pp. 161, 165, and 167). The greater surface area of the microcrystalline form should increase its loss of radon. The crystalline form, however, seems to be more susceptible to radon loss (appendix 16). This loss seems to be related to the platy structure of the crystals, to their water content (Yagoda, 1949, p. 167), and to changes in relative humidity.

If all the alpha plates are exposed under controlled humidity conditions, the effects of emanating power may be minimized and the lack of equilibrium of the different forms of carnotite may be evaluated with greater confidence.

Relative age.--A qualitative estimate of the range and activity associated with the microcrystalline carnotite (pl. 7) suggests that this form is more nearly in radioactive equilibrium than either the acicular or platy carnotite. The greater relative activity of the acicular form of carnotite (pl. 10) is suggested when it is compared with the platy variety (pls. 6B, 9A). From comparisons of this type, it is thought that the microcrystalline form is probably older than the crystalline material and that the acicular variety is older than the platy variety. The synthetic and optical studies suggest similar interpretations.

Lead-uranium-ratio studies.--Alpha plates may aid in the selection of material to be used for age calculations by the lead-uranium-ratio method (Yagoda, 1949, pp. 165-166, 179). It is desirable to use samples that are approximately in radioactive equilibrium because the effects of recent alterations, if any, of the material are not pronounced. Plate 6 shows a sample that is substantially out of radioactive equilibrium. Activity associated with a sample which contains a slight excess of radium is shown in plate 7A.

Samples selected for age calculations by the lead-uranium-ratio method should also be free from local concentrations of daughter products. These local concentrations have been called radiocolloids (see pls. 8A, 12), and we suggest the term mats for the type of concentrations shown in plate 11.

The inclusion of numerous radiocolloids in the selected samples would modify the lead-isotope-abundance ratios and the ages calculated from them.

Radiocolloids.--Radiocolloids may be formed by the solution and recrystallization of the uranium-bearing minerals which were previously in or approaching radioactive equilibrium. The decay products released in this manner could then be precipitated as discrete, highly radioactive particles. Radiocolloids might also be formed by precipitating the decay products escaping from the surface of the material.

The presence of radiocolloids may be interpreted as an indication of relatively recent alteration of the radioactive equilibrium of the mineral because the radiocolloids are composed of daughter products with very short half-lives. Radiocolloids are, in general, associated with the crystalline form. This association suggests that the crystalline carnotite has been formed from a mineral which was more nearly in radioactive equilibrium.

Evaluation

The use of alpha plates to determine the relative ages of the different carnotite forms is in a preliminary stage. Quantitative studies of alpha plates exposed under carefully controlled conditions will have to be made to replace the qualitative interpretations which have been presented in this section. Such quantitative investigations will materially contribute to a more general understanding of the relative ages of the different forms of carnotite.

The selection of samples for the first lead-isotope studies was guided in part by the information obtained from the alpha-plate studies.

PLATE 6

A. Sample 9. Monument No. 2 mine, Mexican Hat area, San Juan County, Utah. Carnotite of low activity dispersed on an alpha plate.

Total magnification (optical and photographic) = 450 X
Alpha-plate exposure = 5 days
Percent U_3O_8 (chemical) = 44.7
g Ra/g sample (experimental) = 7.62×10^{-8}
g Ra/g sample for equilibrium = 12.6×10^{-8}
Percent Ra deficiency = 40

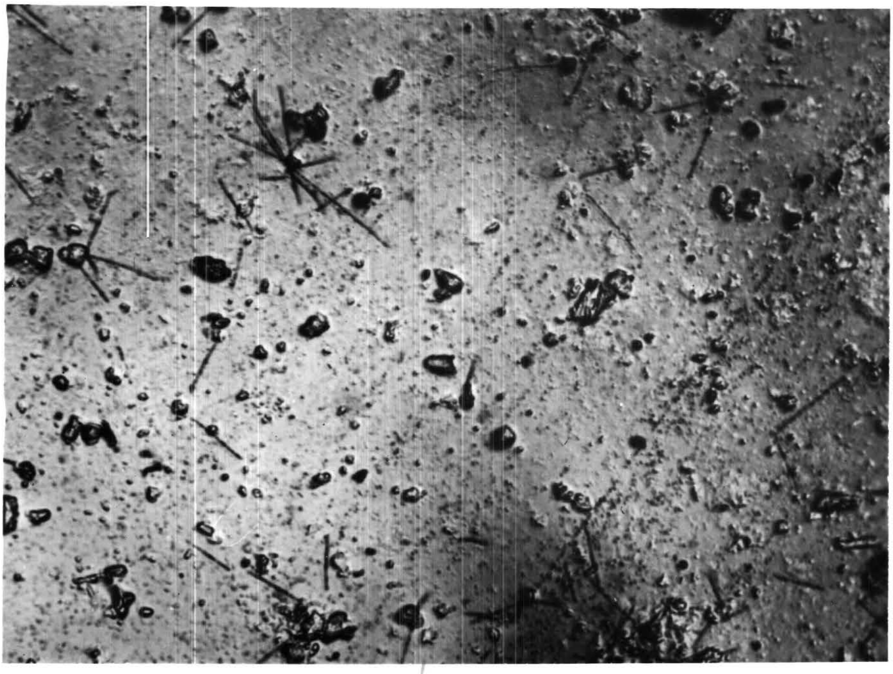
The activity shown on this alpha plate is typical of a sample which is appreciably out of equilibrium. The activity of the opaque and the nonopaque grains is about the same.

B. Sample 12. Jo Dandy mine, Jo Dandy group, Montrose County, Colorado. Carnotite of low activity dispersed on an alpha plate.

Total magnification (optical and photographic) = 450 X
Alpha-plate exposure = 5 days
Percent U_3O_8 (chemical) = 23.6
g Ra/g sample (experimental) = 0.461×10^{-8}
g Ra/g sample for equilibrium = 6.64×10^{-8}
Percent Ra deficiency = 93

The large nonopaque grain slightly below the center of the field is carnotite, but no alpha tracks are recorded. The smaller dark-appearing grains are probably microcrystalline carnotite, and they emit two to seven tracks per grain. This suggests that the large nonopaque grain is not in radioactive equilibrium and is probably a recent secondary mineral.

Plate 6



A

B

PLATE 7

A. Sample 20. Radium No. 6 mine, Radium group, San Miguel County, Colorado. General view of slide showing many carnotite grains of high activity.

Total magnification (optical and photographic) = 450 X

Alpha-plate exposure = 5 days

Percent U_3O_8 (chemical) = 38.5

g Ra/g sample (experimental) = 11.3×10^{-8}

g Ra/g sample for equilibrium = 10.8×10^{-8}

Percent Ra excess = 5

On basis of radium and radiometric determinations, it seems that the alpha-particle activity of this sample is typical of carnotite samples containing an excess of radium.

B. Sample 25. Calamity No. 13 mine, Gateway area, Mesa County, Colorado. General view of alpha plate showing carnotite grains of high activity.

Total magnification (optical and photographic) = 450 X

Alpha-plate exposure = 5 days

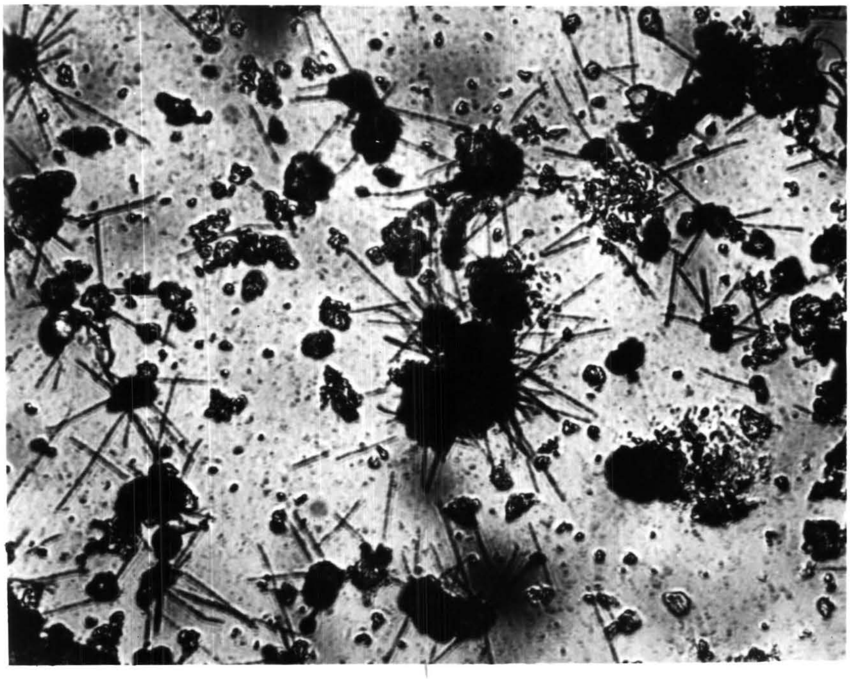
Percent U_3O_8 (chemical) = 38.3

g Ra/g sample (experimental) = 10.6×10^{-8}

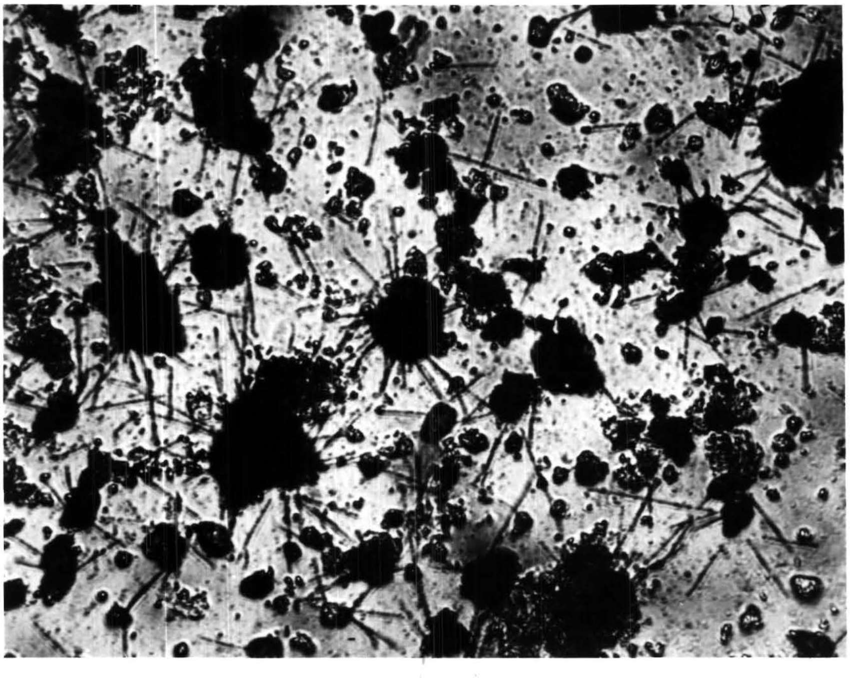
g Ra/g sample for equilibrium = 10.8×10^{-8}

Percent Ra deficiency = 2

Plate 7



A



B

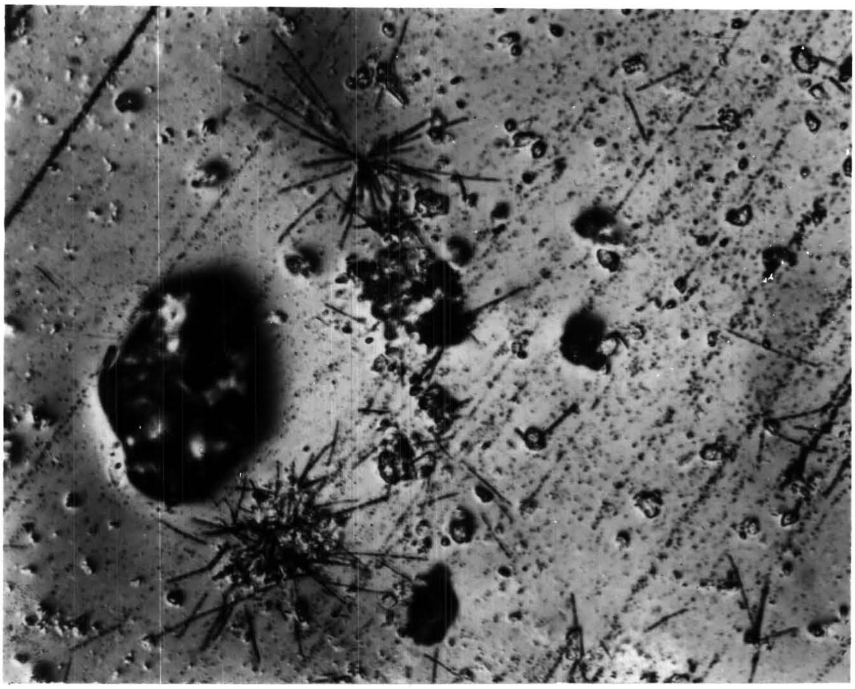
PLATE 8

A. Sample 9. Monument No. 2 mine, Mexican Hat area, San Juan County, Utah. Total magnification (optical and photographic) 450 X. Center left is a large quartz grain with no tracks. Below this is a mat. The radiocolloid in the upper part of the field may be interpreted as a minute grain of radium-bearing material. The diagonal lines crossing the field are scratches on the emulsion.

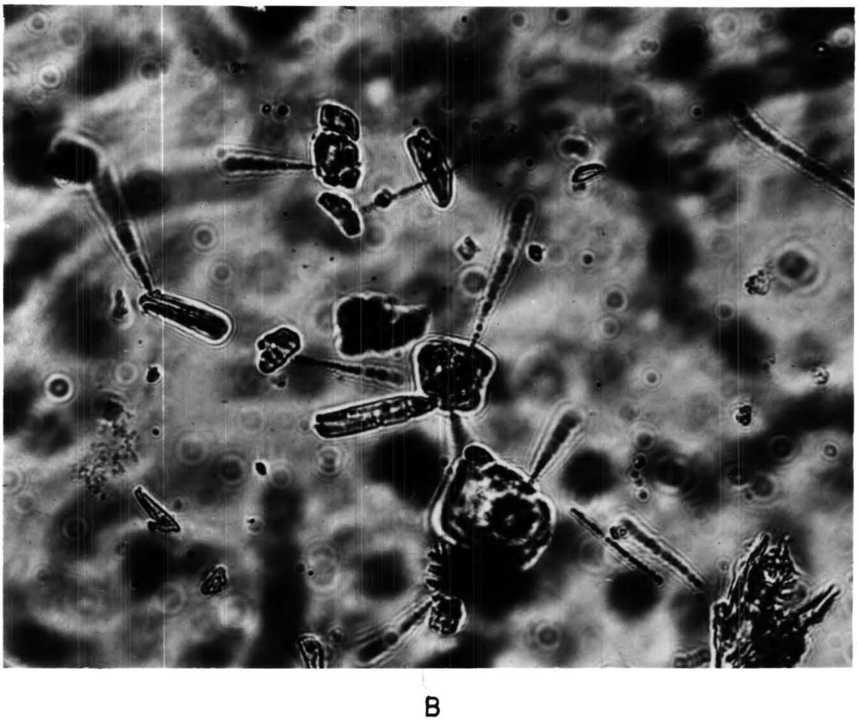
The greater length of the alpha-particle tracks in the radiocolloid suggests that these alpha particles have initially higher energies and probably came from daughter products with extremely short half-lives, and that therefore these radiocolloids are indicative of recent changes in the radioactive equilibrium of the sample. If this interpretation is correct, the radium salt may have resulted from very recent leaching of uranium-bearing minerals.

B. Sample 9. Monument No. 2 mine, Mexican Hat area, San Juan County, Utah. Total magnification (optical and photographic) 970 X, oil immersion. The opaque inclusion in the grain in the center of the field seems to have emitted an alpha particle of high energy. The large grain immediately below also seems to have a radioactive inclusion.

Plate 8



A



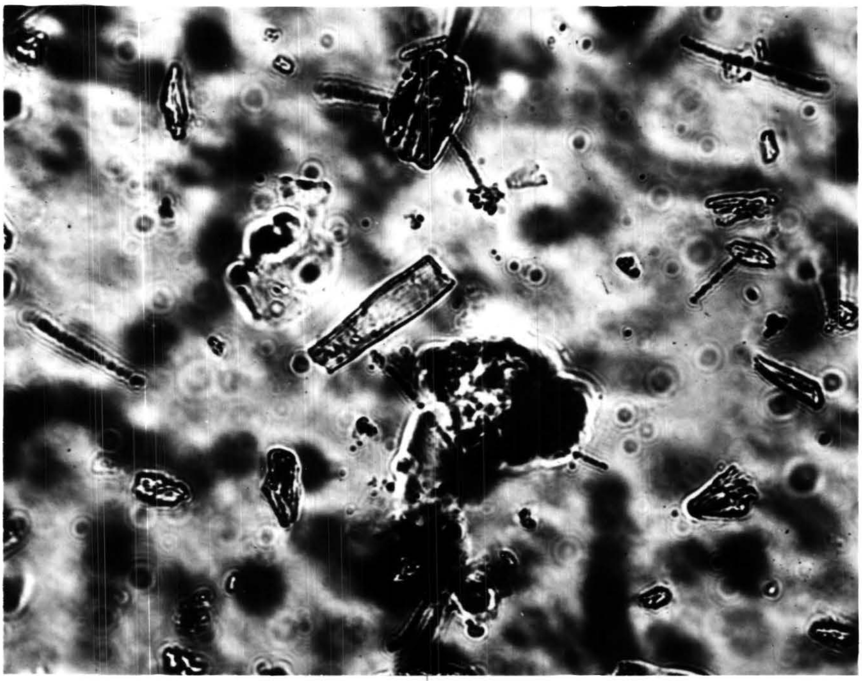
B

PLATE 9

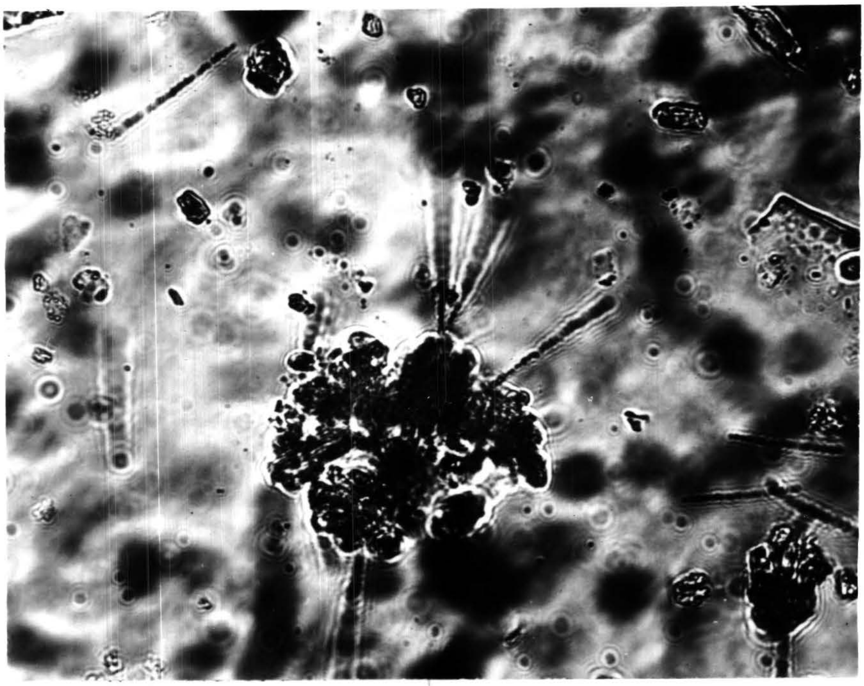
A. Sample 9. Monument No. 2 mine, Mexican Hat area, San Juan County, Utah. Total magnification (optical and photographic) 970 X, oil immersion. A euhedral grain of carnotite. The source of the alpha particle nearest the euhedral grain is in doubt. However, it is not uncommon to find well-developed crystals of carnotite without diverging alpha tracks. This may be due to the recent growth of the crystal and the fact that the radium content is extremely low.

B. Sample 9. Monument No. 2 mine, Mexican Hat area, San Juan County, Utah. Total magnification (optical and photographic) 970 X, oil immersion. A microcrystalline grain of active carnotite. The grain is typical of the finely divided active material in all of the samples. It may be contrasted with the more coarsely crystalline material which does not seem, volume for volume, to have the same order of magnitude of alpha-particle activity. This may be due to the greater surface area exposed to radon adsorption, or it may be due to the greater age of the microcrystalline material.

Plate 9



A

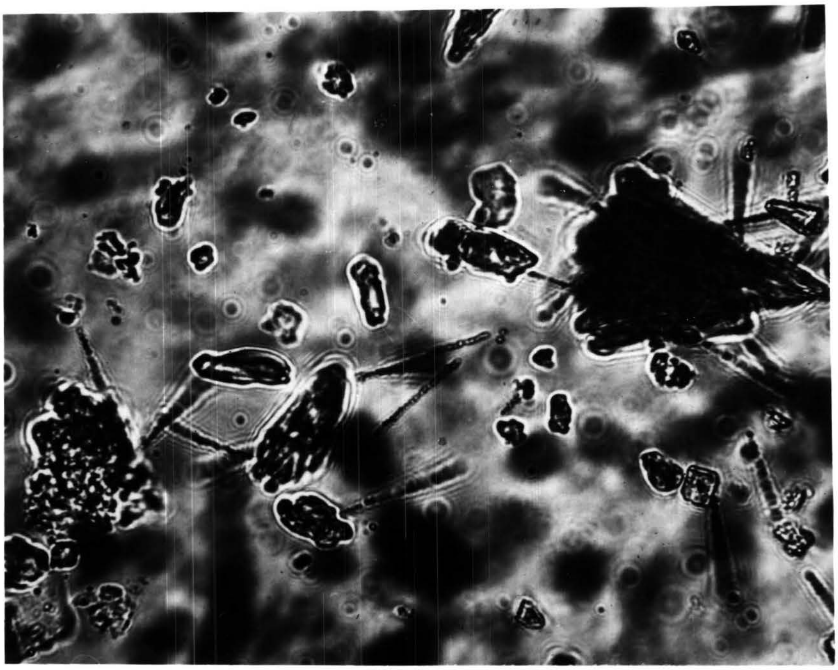


B

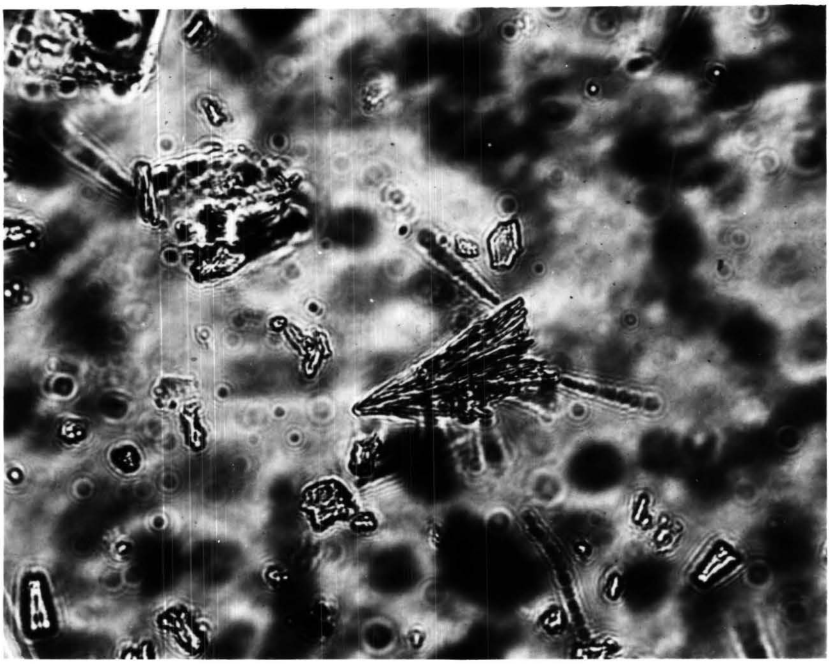
PLATE 10

A and B. Sample 9. Monument No. 2 mine, Mexican Hat area, San Juan County, Utah. Total magnification (optical and photographic) 970 X, oil immersion. The fan-shaped groups of bladed crystals are pale yellow to yellow brown in color. The over-all alpha-particle activity is low to moderate, considering the grain size. This form of carnotite is probably secondary, but when compared to the microcrystalline form, it seems to be more nearly in radioactive equilibrium than the broad-bladed form shown in plate 9A.

Plate 10



A



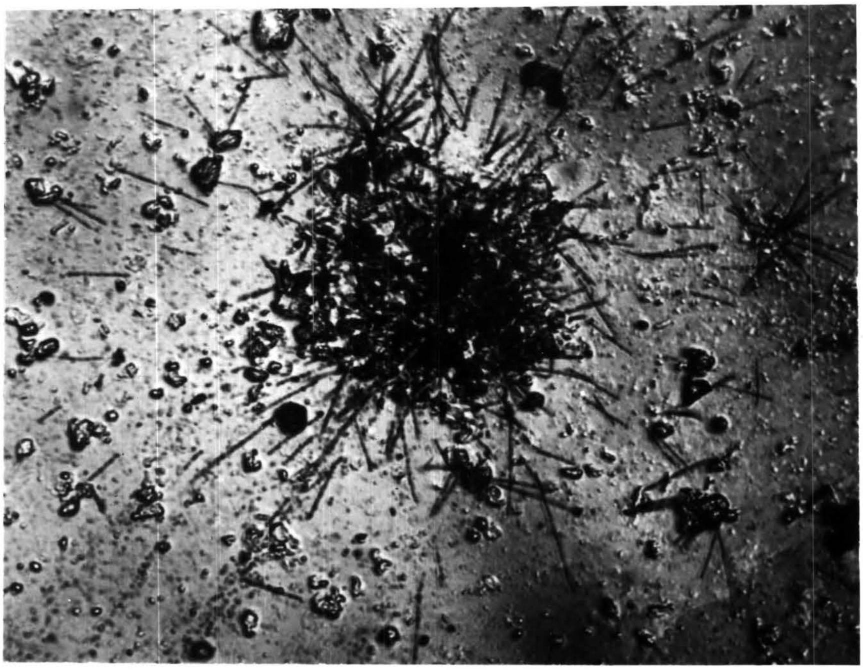
B

PLATE 11

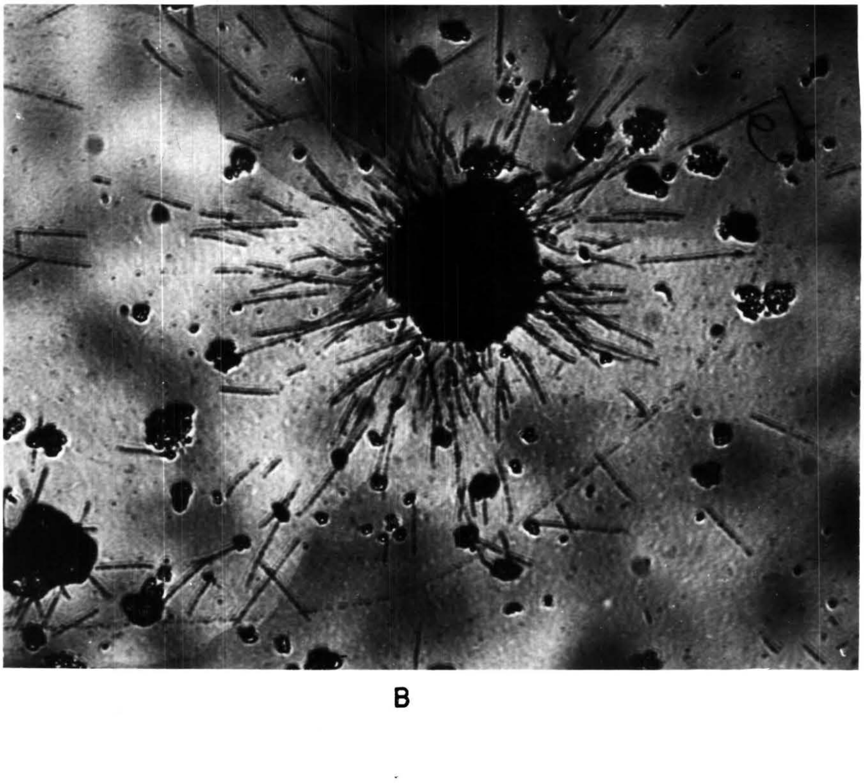
A. Sample 9. Monument No. 2 mine, Mexican Hat area, San Juan County, Utah. Total magnification (optical and photographic) 450 X. An aggregate of grains showing alpha-particle activity. Similar accumulations showing very abundant unoriented alpha-particle tracks have been called mats. The high activity can be accounted for only by a local concentration of short-lived, alpha-emitting materials such as radium and its daughter products. However, it is hard to explain why these materials are localized and why they are not evenly distributed throughout the sample. The appearance of such mats of tracks may be interpreted as evidence of recent migration of the daughter products of uranium and as possible proof of the lack of uniform radioactive equilibrium throughout the sample.

B. Sample 12. Jo Dandy mine, Jo Dandy group, Montrose County, Colorado. Total magnification (optical and photographic) 450 X. A rounded red-brown grain of very active material. This grain is pale yellow under crossed nicols and does not seem to be microcrystalline. The activity is abnormally high, particularly in view of the fact that it occurs in sample 12 (see plate 6, B), which has an appreciable radium deficiency. The particle probably contains a large excess of short-lived daughter products and may represent selective deposition of the products. The occurrence of similar particles is an indication of lack of radioactive equilibrium.

Plate 11



A

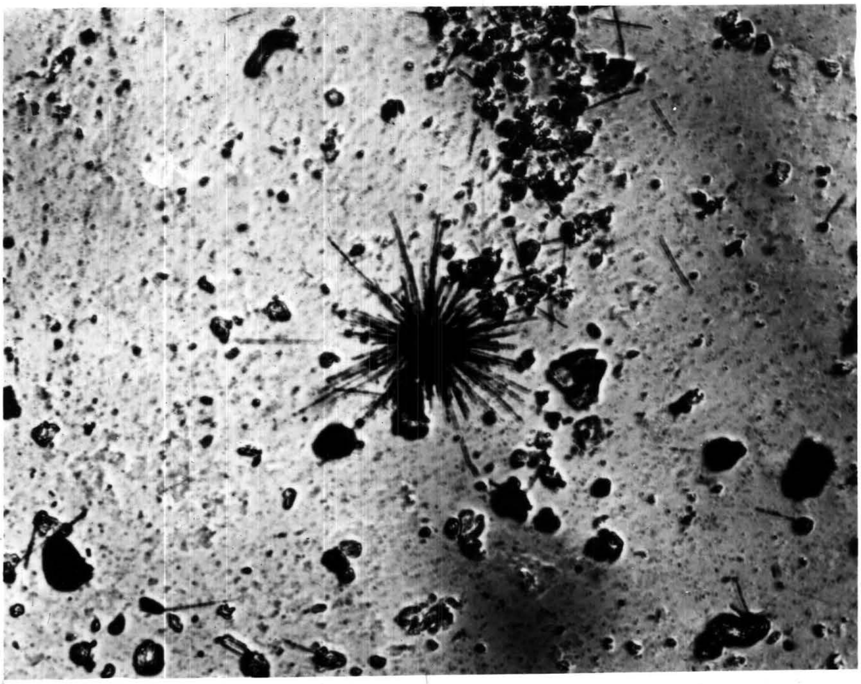


B

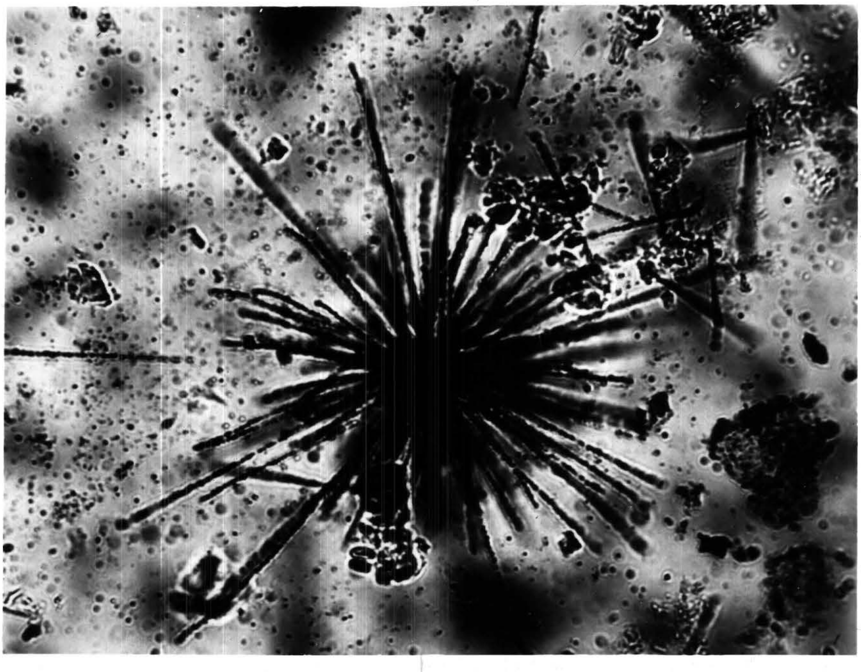
PLATE 12

A. Sample 12. Jo Dandy mine, Jo Dandy group, Montrose County, Colorado. Total magnification (optical and photographic) 450 X. Well-developed radiocolloid. This figure shows the general level of activity surrounding a particularly active radiocolloid. The difference between the length of alpha tracks from the radiocolloid and those from the surrounding material is striking. The intensity of this activity could be accounted for only by the presence of radium or its daughter products, concentrated by leaching, migration, and redeposition.

B. Sample 12. Total magnification (optical and photographic) 970 X, oil immersion, Detail of plate 12 A.



A



B

RADIOACTIVE-EQUILIBRIUM AND LEAD-URANIUM-RATIO METHODS

Radium-uranium equilibrium is established when the rates of radium formation and decay are equal. Ninety-nine percent of radium-uranium equilibrium will be attained in 500,000 years (Kovarik, 1931, p. 110). If the samples do not contain radium in proportion to the equilibrium amount of 3.32×10^{-7} g Ra/g U, this condition may be attributed to either one or both of the following causes:

1. The material may be less than 500,000 years old if the radiogenic lead content has been added or is very low.
2. The material may have been influenced by selective leaching of radium or enrichment of uranium.

Although an understanding of the procedures used in the quantitative determination of uranium, radium, and lead is necessary for an evaluation of the work, these procedures are not directly related to the problem of age of the deposits and consequently have been placed in appendixes 12, 13, and 14, respectively. The samples were studied spectrographically to determine whether any elements were present in sufficient amounts to interfere with the quantitative chemical analysis for lead. These data will be found in appendix 15. The radiometric analyses of the samples are essentially in agreement with the data obtained from the radium analyses. This information has been placed in appendix 16.

Radium-uranium-equilibrium Studies

Purpose

The radium-uranium equilibrium of the 12 high-grade carnotite samples was studied to determine if any of the samples could be dated by their departure from the equilibrium amount of 3.32×10^{-7} g Ra/g U. In addition, minimum ages can be assigned to those samples which are in radioactive equilibrium. Reliable ages cannot be assigned to those samples which are not in equilibrium and which contain lead unless the source of the lead can be determined. It is usually hard to determine what is responsible for the lack of radioactive equilibrium. This condition, however, must be a consequence of relatively recent events.

The information from the equilibrium study should aid in the selection of samples for age determinations by the lead-uranium-ratio method and in the evaluation of the ages calculated. The apparent radium content inferred from the differences between the chemical and equivalent U_3O_8 determinations may be compared to the measured figures (appendix 16). Finally, a knowledge of the radium content is useful in interpreting the results of alpha-plate studies of these ores.

Discussion

Procedure.--The radium determinations were made by the standard radon method at the National Bureau of Standards by Mr. L. L. Stockman. The procedure used has been described by Curtiss and Davis (1943). (See appendix 13.) The National Bureau of Standards has estimated its error in a radium determination to be ± 2 percent, and the errors in the chemical determinations for uranium as used in this work are of the same order of magnitude. Therefore, the results of the calculations for theoretical radium content and percentage excess or deficiency of radium should be interpreted with the experimental limitations in mind.

high-grade carnotite samples

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
Sample No.	Average % U[a]	Theoretical g Ra/g sample[b]	Experimental g Ra/g sample[c]	Difference (Theor. g Ra/g sample)-(Exper. g Ra/g sample)	% Difference
1	27.2	9.03×10^{-8}	2.60×10^{-8}	6.43×10^{-8}	71
9	37.9	12.6×10^{-8}	7.62×10^{-8}	4.98×10^{-8}	40
12	20.0	6.64×10^{-8}	0.461×10^{-8} 0.403×10^{-8}(d)	6.179×10^{-8}	93
13	31.1	10.3×10^{-8}	8.53×10^{-8}	1.77×10^{-8}	17
19	21.7	7.20×10^{-8}	7.36×10^{-8}	0.16×10^{-8} excess	2 excess
20	32.6	10.8×10^{-8}	11.3×10^{-8}	0.5×10^{-8} excess	5 excess
25	32.5	10.8×10^{-8}	10.6×10^{-8}	0.2×10^{-8}	2
28	36.0	12.0×10^{-8}	11.1×10^{-8}	0.9×10^{-8}	8
61	32.2	10.7×10^{-8}	8.64×10^{-8}	2.06×10^{-8}	19
62	14.8	4.91×10^{-8}	1.78×10^{-8}	3.13×10^{-8}	64
63	25.4	8.43×10^{-8}	7.19×10^{-8}	1.24×10^{-8}	15
64	34.6	11.5×10^{-8}	8.45×10^{-8} 7.63×10^{-8}(d)	3.05×10^{-8}	27

a) From table 14 (appendix 12) giving percent U_3O_8 for high-grade samples

b) Computed from g Ra/g U in equilibrium = 3.32×10^{-7} g Ra/g U

c) Prepared for analysis by R. G. Rice and counted under direction of L. L. Stockman, National Bureau of Standards

d) Reconcentration of carnotite from sandstone

Data.--The results of the radium analyses are given in column 4 of table 1. This table also includes the equilibrium amounts of radium to uranium. An example of the calculations used in preparing table 1 is given in appendix 18.

The radium content of sample 62 is much lower proportionately than either sample 61 or 63. As all three samples were collected from the same small stope and were presumably subject to the same type of alteration, the possibility that the determinations for sample 62 are in error should be considered. The radiometric determinations (appendix 16) indicate that each sample has approximately the same radium-uranium ratio.

Previous work.--In the study of the variation of the radium-uranium ratio in minerals other than pitchblende Boltwood (1904, pp. 97-103; 1908, pp. 269-298) and McCoy (1904, pp. 2641-2656; 1905, p. 391) found that carnotite did not show any abnormalities. Mlle. Gleditsch (1911, pp. 256-273), and Marckwald and Russell (1911a, p. 771; 1911b, p. 457) found, however, that small samples of carnotite were appreciably deficient in radium.

Lind and Whittemore (1915, pp. 1-28) have published the only detailed study of the radium-uranium ratio in carnotite. They found that in samples of a few hundred pounds to several tons the ratio was in agreement with that of pitchblende, whereas small samples of a few pounds or less exhibited abnormal ratios. In one sample the ratio was 25 percent deficient and in another 39 percent in excess of the normal ratio for pitchblende. The facts that abnormal radium-uranium ratios, both high and low, occurred in samples representative of small quantities of ore, and that all samples from bulk specimens of ore showed normal radium-uranium ratios, were interpreted as an indication of transportation of radium within the ore body rather than removal of the radium by leaching. Should this conclusion be correct, the determination of equivalent U_3O_8 by radiometric analyses of small samples of carnotite ore would be of doubtful significance. (See appendix 16.)

If extensive transportation of radium within the ore body has occurred, the carnotite deposits of the Colorado Plateau might be expected to exhibit the uranium-free radium-bearing barites, $(Ba,Ra)SO_4$, and radium-bearing carbonates, $RaCO_3$, found in relatively high concentrations in both upper and lower horizons of the Tyuya Muyun deposits in the Fergana Valley of Russia (Shimkin, 1949, p. 58). The existence of radiocolloids, noted in the alpha-plate studies, is the only direct evidence for the transportation and possible formation of radium-bearing barites or carbonates in the high-grade Plateau ores.

It should be mentioned that we have found only one additional reference on the radium-uranium ratio in carnotite since that published by Lind and Whittemore in 1915. This reference (Hess and Foshag, 1927, pp. 1-6) cites the result of one analysis which is 32 percent deficient in radium.

On the basis of this analysis of crystalline carnotite from the Bridger Jack flat, Cane Springs Pass, Utah, Holmes (1931, p. 351), using the currently accepted time required to reach radium-uranium equilibrium (500,000 years), estimated that the carnotite was approximately 170,000 years old. This age agrees more closely with the geologic evidence than the age determined from the same sample by Hess and Foshag (1927, pp. 4-6) who used 10,000,000 years as the time required to reach radium-uranium equilibrium.

Present work.--Of the 12 samples analyzed, 9 were deficient when compared with the equilibrium amount of radium that the samples should have contained, 2 samples were within 2 percent of radioactive equilibrium (1 deficient and 1 in excess), and 1 sample showed a 5-percent excess of radium (table 1). These results are consistent with those reported for small samples by Lind and Whittemore (1915, pp. 1-28) and those reported by Gleditsch (1911, pp. 256-273).

The near-surface occurrences of the predominantly crystalline samples have the greatest radium deficiencies. The single sample of crystalline carnotite which was found at depth, however, has a 5-percent excess of radium. The radium content of the 7 predominantly microcrystalline samples ranged from an excess of 2 percent to a deficiency of 19 percent. As the predominantly microcrystalline samples most exposed to chemical weathering contain a slight excess of radium and the less exposed samples are deficient in radium, there does not appear to be a consistent relationship between the departure from radium-uranium equilibrium and the weathering to which the microcrystalline form has been exposed.

If the slight excesses of radium are not a result of cumulative experimental errors, these excesses might be accounted for by the selective loss of small amounts of uranium. At the present time, the loss of uranium is considered to be the most common source of error in uranium-ratio age determinations.

Samples for which maximum ages can be obtained.--Samples 1 and 12 which have the greatest radium deficiencies, 71 and 93 percent respectively, are the only samples containing less than 0.001 g Pb/g sample. The crystalline carnotite in these samples seems to be fresh and unaltered, therefore, the loss of large amounts of radium by selective leaching does not seem probable. For these reasons it has been assumed that these samples may be dated approximately by the radium-uranium-equilibrium method.

The material in sample 1 occurred as a thick, predominantly crystalline carnotite coating on near-surface joints and fractures and clearly could not be older than the joints and fractures themselves. The material in sample 12 occurred as predominantly crystalline coatings on sand grains and as interstitial fillings in an outcrop of very friable sandstone (appendix 1). The platy form of carnotite probably was derived from the microcrystalline carnotite. The number of alpha tracks associated with this platy form is small, confirming a lack of radium-uranium equilibrium.

The absence of abundant radiocolloids in sample 1 suggests that radium has not been added. If this interpretation is correct, the age of the material in sample 1 on the basis of the departure from radium-uranium equilibrium is approximately 40,000 years. The maximum age of the material in sample 12 is approximately 15,000 years. These two ages are computed using the table given for the time required to reach radium-uranium equilibrium (Kovarik, 1931, p. 110). Sample 12, however, contains many radiocolloids, which suggests that the age based on the radium content is too great. The radium may have been derived from the leaching of the platy carnotite, but more probably the radium was freed by the relatively recent alteration of an older uranium-bearing mineral.

Samples for which ages cannot be determined.--The presence of lead in the remaining samples which are appreciably deficient in radium may be interpreted in two ways:

1. The radium-uranium-equilibrium condition has been altered by selectively removing radium or adding uranium without completely removing lead.
2. The radium-uranium equilibrium condition is representative and the lead has been added; that is, the lead has not been derived by radioactive decay of the carnotite in the sample.

Detailed mass-spectrographic studies of the lead obtained from the high-, intermediate-, and low-grade samples will have to be made before it will be possible to determine whether or not this lead has been introduced. Until this has been done, the departure of these samples from radioactive equilibrium cannot be used as a method of dating.

Samples for which minimum ages can be obtained.--Obviously, the three samples (19, 20, and 25) which are essentially in radioactive equilibrium or have a slight excess of radium cannot be dated by their radium-uranium ratios. The fact that these samples are in radioactive equilibrium, however, indicates that they have been undisturbed for a minimum of 500,000 years and that they should give the most reliable lead-uranium ratio age determinations.

Evaluation

Radium-uranium-equilibrium determinations can be used with reasonable confidence to date those samples which do not contain lead. In samples containing lead this method cannot be used until the source of the lead has been determined. Assuming that the lead has been derived from the carnotite, the samples which are in radium-uranium equilibrium and which seem to be undisturbed by recent leaching would be expected to give the most reliable lead-uranium-ratio ages.

Lead-uranium-ratio Studies

Discussion

Procedure.--Mr. R. G. Milkey of the Geological Survey chemically analyzed the samples for lead. A detailed account of the procedure used is found in appendix 14. The quantitative lead determinations given in column 3 of table 2 are tentative, pending the completion of experiments now in progress on the percentage of lead recovered by the procedure used in the analysis. The reproducibility of the method (table 15, appendix 14), however, enables one to place reasonable confidence in the third place (0.00X) and some confidence in the fourth place (0.000X). Because of the small amount of sample 9 available, only one analysis was made. A sample of the calculations used to prepare table 2 is found in appendix 18.

Lead-uranium-ratio ages.--The postulated times of carnotite deposition may be compared with the uncorrected ages of the carnotite computed from the lead-uranium ratios. As has been mentioned, the majority of the samples are not in radioactive equilibrium, and corrections for the addition of common or radiogenic lead have not been made. It is not surprising, therefore,

Table 2.--Departure from radium equilibrium and age of high-grade carnotite calculated by the lead-uranium-ratio method

Column 1 Sample No.	Column 2 Departure from radium equilibrium in percent	Column 3 g Pb/ g sample	Column 4 g U/ g sample	Column 5 Age in millions of years
1	71	0.0000[a]	0.272	< 2.8
9	40	0.0015	0.379	30.1
12	93	0.0000[a]	0.200	<3.8
13	17	0.0008	0.311	19.5
19	2 (excess)	0.0006	0.217	21.0
20	5 (excess)	0.0015	0.326	34.9
25	2	0.0033	0.325	77.2
28	8	0.0038	0.360	80.2
61	19	0.0032	0.322	75.5
62	64	0.0033	0.148	169.0
63	15	0.0031	0.254	92.7
64	27	0.0014	0.346	30.7

[a] Figure of 0.000099 g Pb/g sample used to compute age

that the calculated ages range from 2.8 million years to 169 million years. (See table 2.) In a single stope the computed age of the carnotite ranged from 75 to 169 million years. This difference in age emphasizes the necessity of collecting samples from within a small deposit to study the variations of the lead-uranium ratio and to determine the mobility of uranium, its radioactive daughter products, and the isotopes of lead. If the transportation of radium is confined to the deposits, as suggested by Lind and Whittemore (1915, p. 26), it is reasonable to suppose that the migration of lead derived from the carnotite would also be similarly confined. Therefore, the average lead and average uranium content should be expected to give a very close approximation of the true age of the deposit. The most reliable ages calculated for single samples by this method are for samples 19, 20, and 25 which are in radioactive equilibrium. These ages are approximately 21, 35, and 77 million years, respectively. The ages calculated for samples 1 and 12 are the maximum possible ages for them, assuming no leaching and correct lead analyses.

Hess (1925, p. 78) calculated the age of Montrose County, Colorado, carnotite by the lead-uranium-ratio method. His results, when recalculated using modern constants, are 27.4 million years for an average and 40.3 million years as a maximum. He concluded that 27.4 million years is probably much too small, that 40.3 million years seems to be more nearly correct, and that the lead-uranium ratios are no more irregular than would be expected from a mineral as "mobile" as carnotite. In referring to Colorado Plateau carnotite Holmes (1931, p. 349) writes:

> Beyond showing that the individual samples are of Tertiary--and probably late Tertiary age, the results are, however,

of little value for our purpose, for atomic weight of the lead clearly reveals the presence of a high proportion of ordinary lead.

Evaluation

It is difficult to obtain reliable lead-uranium-ratio ages of the carnotite not only because the effect of selective leaching of lead would give too low an age but also because the undetected presence of common or unrelated radiogenic lead would give too great an age. Assuming that lead has not been added, the best estimate of the age of the carnotite material in radioactive equilibrium indicates an age between 40 and 80 million years. If it is possible to determine the origin of the lead in the samples by isotopic studies, a more reliable and probably younger age will be found. Additional intermediate- and low-grade ores will have to be analyzed for lead, radium, and uranium before more definite information can be obtained on the mobility of these elements.

LEAD-ISOTOPE METHODS

Purpose

Quantitative determinations of the lead isotopes from 4 selected, high-grade carnotite samples were made for the purpose of computing the amount of common lead present in the samples and to compare the ages calculated from the Pb^{206}/U^{238}, Pb^{207}/U^{235}, and the Pb^{207}/Pb^{206} ratios. By means of such comparisons it may be possible to estimate both the extent and the type of alteration that the carnotite has undergone and thereby to arrive at the most reliable age for the samples studied.

Discussion

Procedure.--Mr. Irving May of the Geological Survey extracted the lead from the 4 high-grade samples and converted it to the iodide form. An account of the preparation of the lead iodide is given in appendix 17. The isotopic analyses were done by Mr. G. P. Schacher, General Electric Company, Schenectady, New York. A check on the analysis of sample 63 was made by Mr. M. G. Inghram, Argonne National Laboratory, Chicago, Illinois. A brief description of this work is given in appendix 17.

Data.--The results of Mr. Schacher's isotopic analyses are given in table 3. He estimated that the instrumental error of the General Electric Company's mass spectrometer is ± 1 mole percent. The isotopic composition of the lead from 3 of the carnotite samples, corrected for the amount of common lead present (approximately 7 percent) are given in table 4. The ages computed from the Pb^{206}/U^{238}, Pb^{207}/U^{235}, and Pb^{207}/Pb^{206} ratios are tabulated in table 5. An example of the calculations used in preparing tables 4 and 5 are given in appendix 18.

In preparing table 4 (Corrected isotopic abundances of lead from high-grade carnotite samples) it was found that sample 28 had only one-half of the amount of Pb^{208} necessary to satisfy the accepted Pb^{204}/Pb^{208} abundance ratio of common lead (Nier, 1938, pp. 1571-1576). The inability to correct this sample for Pb^{208} suggests that the corresponding common lead deductions for Pb^{206} and Pb^{207} are also incorrect. The age calculations for both the Pb^{207}/U^{235} and Pb^{207}/Pb^{206} ratios are markedly changed by only slight variations in the corrected value of Pb^{207}. Therefore, the age determinations for sample 28 have not been included in table 5.

Table 3.--Isotopic abundances of lead from high-grade carnotite samples [a]

Sample	Isotopic abundances in percent			
	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}
Common lead	1.5	23.59	22.64	52.29
20	0.1	87.3	6.5	6.0
28	0.1	92.7	6.0	1.28
63	0.1	88.6	6.7	4.6
64	0.1	89.4	6.7	3.8

[a] Analyst, G. P. Schacher, Schenectady Laboratory, General Electric Company, Schenectady, New York

Table 4.--Corrected isotopic abundances of lead from high-grade carnotite samples

Sample	Isotopic abundances in percent corrected for common lead			
	Pb^{206}	Pb^{207}	Pb^{208}	Grams of radiogenic Pb
20	92.0	5.3	2.7	0.0014
63	93.2	5.6	1.2	0.0029
64	94.1	5.6	0.3	0.0013

Age calculations.--As has been mentioned, reliable age calculations can be made only when the uranium-bearing mineral has been undisturbed since its deposition and when corrections have been made for the deposition of lead, common or radiogenic, with the uranium mineral. Most of the high-grade carnotite samples are deficient in radium, either because they have been disturbed by leaching or are too young to have reached equilibrium, and there is evidence that common lead and possibly radiogenic lead have been added. It would be expected, therefore, that the calculated ages would disagree.

The computed ages given in table 5 show the three following types of variations:

1. The largest variations occur between the ages calculated from the Pb/U ratios and those calculated from the Pb^{207}/Pb^{206} ratio.
2. Moderate variations in calculated lead-uranium-ratio ages occur among different samples.
3. The smallest variations within a single sample occur between the ages computed from the Pb^{206}/U^{238} and the Pb^{207}/U^{235} ratios.

1. An unexpected result of the isotopic analyses was the fact that the minimum difference between the two lead-uranium ratios and the Pb^{207}/Pb^{206} ratio age calculations was 490 million years (sample 20). This discrepancy is almost 4 times the minimum possible syngenetic age of the sample and it is 18 times greater than the Pb/U ratio age. The result is particularly interesting when it is realized that the age

calculated by the Pb^{207}/Pb^{206} ratio is, in general, the most reliable of of the three (Nier, 1939, pp. 161-163; Holmes, 1947). This ratio is not only independent of the recent leaching of lead or uranium but also it is independent of the recent deposition of uranium or common lead.

The apparent excess of Pb^{207} or the deficiency of Pb^{206} might be due to (A) incorrect isotopic analyses, (B) an unusual increase in the abundance of U^{235}, (C) a continuous loss of radon, and (D) the introduction of old radiogenic lead.

(A) As has been mentioned, the lead-isotope composition of sample 63 was checked by Mr. M. G. Inghram of the Argonne National Laboratory. His results (1949, personal communication) agree with those made by Schacher to within approximately a tenth of one mole percent. Mr. Inghram's more precise determination of Pb^{204}, however, has resulted in a smaller corrected Pb^{207}/Pb^{206} ratio. This ratio gives a slightly younger age than the Pb^{207}/Pb^{206} ages given in table 5. When more precise determinations of the Pb^{204} isotope have been made on the remaining samples, however, changes in the lead-uranium and lead-lead ages should be expected.

(B) The abundance of the uranium isotopes in the 4 high-grade carnotite samples has not been determined. Dunning (1949, p. 511) states that the U^{238}/U^{235} ratio measured to five significant figures is the same for different uranium-bearing ores including low-grade Colorado carnotite. The work of Nier (1939a, p. 151) also indicates that the uranium-isotope ratios do not seem to depend on the source of the uranium. Uranium extracted from Swedish Kolm by Nier (1939a, p. 151) showed a normal U^{238}/U^{235} ratio. The isotopic analysis of lead from this sample (Nier, 1939b, p. 159) gave a Pb^{206}/U^{238} ratio age of 338 million years and a

Table 5.--Age of high-grade carnotite samples on the basis of Pb^{206}/U^{238}, Pb^{207}/U^{235}, and Pb^{207}/Pb^{206} ratios

Sample	Age in millions of years from		
	Pb^{206}/U^{238}	Pb^{207}/U^{235}	Pb^{207}/Pb^{206}
20	30.0	34.0	520
63	82.0	96.0	600
64	27.0	32.0	600

Pb^{207}/Pb^{206} ratio age of 770 million years (the largest percentage difference in computed ages for a single sample, other than carnotite, known to us). In this case, the discrepancy could not be attributed to an abnormal U^{238}/U^{235} ratio. Therefore, the explanation that the high Pb^{207}/Pb^{206} ratio is a result of an unusual increase in the abundance of the uranium isotope U^{235} does not seem very likely. When a mass spectrograph is available, however, the abundances of the uranium isotopes in samples 20, 28, 63, and 64 will be checked.

(C) The explanation of the excessively large Pb^{207}/Pb^{206} ratio of the Swedish kolm by the selective loss of large amounts of radon (that is, emanation of radon) has recently been proposed by Wickman (1942, pp. 465-476). This argument is based on the fact that radon, the heavy, inert, gaseous daughter product of U^{238}, has a half-life of 3.8 days whereas actinon, the isotope of radon and a daughter product of U^{235}, has a half-life of 3.9 seconds. Presumably radon, because of its greater half-life would diffuse but actinon would not. If this occurred, the sample would contain less Pb^{206} than if no radon had been lost, and the Pb^{207}/Pb^{206} ratio would be proportionally larger. Wickman (1942, p. 468) has shown that the emanating power of a lens of uranium-bearing material is a function of the thickness of the lens, the diffusion constant for the material, the disintegration constant of radon, and the radon content of the surrounding material in relation to the radon content of the uranium-bearing material. As might be expected, the Pb^{207}/Pb^{206} ratio age of a sample which has lost radon is much greater than the calculated Pb^{206}/U^{238} ratio age of the same sample. The Pb^{207}/U^{235} ratio age is independent of the loss of radon, and, therefore, Wickman (1942, p. 466) defined this ratio age to be equal to the radon "diffusion age" and suggested that for the Swedish kolm the age given by the Pb^{207}/U^{235} ratio was the most nearly correct.

Experimentally, it should be possible by mass-spectrographic study of many carnotite samples to establish clearly if the loss of radon is a dominant process in the carnotite ores. Isotopic analysis of lead extracted from the intermediate- and low-grade carnotite ores adjacent to the high-grade ores should show abnormally low Pb^{207}/Pb^{206} ratios if there has been diffusion of radon from the high-grade material. If the Pb^{207}/Pb^{206} ratios for all types of carnotite ores are essentially the same, radon diffusion could not have occurred.

If the loss of radon is demonstrated, the ages calculated from the isotopes of lead extracted from the high-grade carnotite ores could not be used without appreciable modification, but samples taken from the centers of large disseminated intermediate- or low-grade deposits might be expected to give ages unaffected by radon loss. This conclusion follows from Wickman's theory (1942, p. 468) concerning the relation between the thickness of the uranium-bearing lens and the emanating power. He found that the loss of radon by emanation would approach zero as the thickness of the lens increased. Therefore, a reliable quantitative determination of the age of the carnotite deposits would seem to be attainable at the present time if a comprehensive mass-spectrographic program on the carnotite leads could be undertaken.

(D) The possibility that lead has been introduced into the carnotite has been suggested by Holmes (1931, p. 349). On the basis of the chemical determination of the atomic weight of two carnotite leads (Richards and Lembert, 1914, p. 1329; Richards and Wadsworth, 1916, p. 2613) it was thought that most of the lead in the samples was common lead. The isotopic study of the 3 high-grade carnotite leads indicates that the amount of common lead present is not in excess of 7 percent (appendix 18). The disagreement between the chemical and mass-spectrographic determinations of the amount of common lead present may be due to the use of reagents containing trace amounts of lead in the processing of the carnotite ore from which Richards' lead sample was obtained.

The isotopic analysis of carnotite lead by Rose and Stranathan (1936, pp. 792-796) using the hyperfine structure of the line λ 5372 in the lead spectra is the only published isotopic analysis known to us. The sample used was obtained as a lead chloride residue from the U. S. Radium Corporation. The chemical atomic weight computed from the isotopic abundances is 206.75. Because no more than a trace of thorium was found in the ores, the presence of 32.2 percent of Pb^{208} indicates that the sample contains approximately 60 percent of common lead. The Pb^{207}/Pb^{206} ratio corrected for common lead is 0.0475 and, using the same method employed to compute the Pb^{207}/Pb^{206} ratio age in table 5, an approximate age of 68 million years is obtained. (See appendix 18.) As the method of analysis used by Rose and Stranathan required 2 to 4 grams of metallic lead, it is obvious that the lead must have been obtained from a very large sample of ore. Although the lead may have been representative of the ore, the large quantities of reagents used in the refining process may have introduced some of the common lead found in the sample. The absence of geologic information on the occurrence of the ore and the difficulties encountered in the evaluation of the method of isotopic analysis used qualify the value of the interpretations of these data.

Nier (1938, p. 1574) has suggested that some of the unusual isotopic compositions of the so-called common lead might be a result of the addition of radiogenic lead to a primeval lead of relatively uniform composition prior to the deposition of the lead-bearing mineral studied. The fact that the addition of old radiogenic lead to uranium-bearing minerals has not been recognized may be due to the fact that relatively few radiogenic lead isotope analyses have been made. Also, this contamination by old radiogenic lead would be undetected unless the amount of radiogenic lead added was large or unless the discrepancy between the age based on the geological evidence and the age based on the Pb^{207}/Pb^{206} ratio is large. Perhaps, the explanation of the apparently abnormal Pb^{207}/Pb^{206} ratios from the Swedish kolm might be accounted for in this way. Thus, the possibility of the introduction of both common and radiogenic lead in the carnotite cannot be discounted.

If most of the radiogenic lead found in the high-grade ores has been added recently, a mass-spectrographic study of the adjacent intermediate- and low-grade ores should show approximately the same Pb^{207}/Pb^{206} ratio as was found in the high-grade ores. Such evidence would exclude the possibility that the abnormal ratio in the high-grade ore was a result of radon loss. Before a final interpretation of the lead in the carnotite deposits can be made, however, it is essential that the isotopic composition of the lead from the barren sandstone be determined.

An example of the type variation in the Pb^{207}/Pb^{206} ratio which might be expected even if most of the radiogenic lead was added can be found in sample 20. This sample has the lowest Pb^{207}/Pb^{206} ratio, it has a lead deficiency of 75 percent assuming an age of 130 million years for the deposits, and a slight excess of radium. The lower Pb^{207}/Pb^{206} ratio may have resulted from the introduction of lead younger than that found in the other samples or from the incomplete removal of carnotite lead before the addition of the old lead. Another possibility is that if the deposit is young but contains a slight excess of radium, enough lead may have accumulated since the deposition of the carnotite and old lead to alter the 600-million-year lead to 520-million-year lead.

From the discrepancy between the lead-uranium- and lead-lead-ratio ages, it may be said that the age calculated from the Pb^{207}/Pb^{206} ratio does not have any relation to the true age of the samples studied, in spite of the fact that the lead-lead ratio usually gives the most reliable age determinations. The apparent deficiency of Pb^{206} may be due to the loss of radon or it may be due to the addition of old radiogenic lead. A comprehensive study with a mass spectrograph of the isotopic composition of carnotite leads should establish the cause of the measured lead-isotope abundances.

2. The present inability to explain conclusively the abnormal Pb^{207}/Pb^{206} ratios makes a detailed discussion of the relatively moderate variations in the lead-uranium-ratio ages from sample to sample inadvisable. If the greatest changes in the carnotite since its deposition have been due to the selective loss of radon, the Pb^{207}/U^{235}

ratio age would be the most reliable. In particular, the difference between the Pb^{207}/U^{235} age of samples 20, 63, and 64 would probably be real and be due to different periods of carnotite deposition. If the observed Pb^{207}/Pb^{206} ratio is a result of the introduction of old radiogenic lead, both of the lead-uranium ratios would have little relation to the true age of the carnotite and these two ratios would simply indicate the amount of radiogenic lead added. In this case, the true age of the carnotite would be much younger.

3. A detailed discussion of the variations between the Pb^{206}/U^{238} and Pb^{207}/U^{235} ratio ages for a single sample must also wait for a satisfactory explanation of the observed Pb^{207}/Pb^{206} ratios of the high-grade carnotites. It should be mentioned, however, that either a loss of radon or the introduction of old radiogenic lead followed by alteration would result in a sequence of ages in which the Pb^{206}/U^{238} ratio age was the youngest and the Pb^{207}/Pb^{206} ratio age was the oldest.

Evaluation

Although, at the present time, insufficient data are available to date the carnotite deposits of the Colorado Plateau, the 3 isotopic analyses of the high-grade carnotite leads indicate the direction in which the future isotopic study of the carnotite leads should proceed. The most important problem is presented by the abnormal Pb^{207}/Pb^{206} ratios. Explanation of these abnormal ratios by loss of radon or introduction of old radiogenic lead can be evaluated by a comprehensive mass-spectrographic study of the intermediate- and low-grade carnotite ores both adjacent to the high-grade ores and from the large disseminated ore bodies. If radon loss is the cause of the excess of Pb^{207}, the selection of samples from thick, disseminated ore bodies would be expected to give age determinations least affected by this phenomenon. The Pb^{207}/U^{235} ratio ages of the high-grade samples indicate that the time of carnotite deposition might be expected to be between the end of the Cretaceous and the middle of the Tertiary. If the addition of old radiogenic lead, possibly derived from primary uranium minerals which were the source of the uranium now found in the carnotite and probably deposited from the same solutions that carried the uranium and vanadium, is found to be the explanation of the observed Pb^{207}/Pb^{206} ratios, the lead-uranium- and lead-lead-ratio ages would be of little value but at the same time it would establish the fact that the carnotite was probably formed in the Tertiary period. An approximate dating of the deposits would permit a rapid and direct approach to the problems of chemical and physical controls of carnotite deposition. This information could then be applied to the numerous problems encountered in the exploration for and the development of the carnotite deposits.

SUMMARY

Limitations

This preliminary study of the methods of age determination cannot be used at the present time to establish the age of the Colorado Plateau carnotite deposits because:

1. Only extremely high-grade material was studied. The intermediate- and low-grade ores may have entirely different characteristics
2. The number of samples is statistically insufficient to make broad generalizations
3. Most of the work is in a preliminary stage
4. Only the - 200-mesh fraction and one thin section for each sample were studied
5. Some of the analyses are still being verified

Although no general statement can be made about the age of the carnotite deposits until the study of the intermediate- and low-grade ores has been completed, it is thought that the 12 samples of high-grade ore which were studied are representative of their type and that some of the data obtained may be generalized.

Mineralogic Methods

Carnotite has been recognized in both the crystalline and micro-crystalline forms. With one exception the crystalline form is found in near-surface deposits or outcrops of the ore. As a result of chemical analyses, a calcium analogue of carnotite is believed to be present in some of the crystalline samples, but additional optical work is necessary for positive identification. The relation to the surface suggests that the crystalline form may have been deposited by the evaporation of cool, dilute surface waters containing uranium and vanadium and that the deposition has been recent. The microcrystalline form of carnotite is found, with one exception, in deposits which are more than 30 feet below the surface. A comparison of the microcrystalline form with synthetic carnotite suggests that the natural microcrystalline carnotite was deposited from relatively concentrated solutions and that this form is usually older than the crystalline carnotite.

The relatively low alpha-particle activity of the crystalline form compared to that of the microcrystalline form indicates that the crystalline carnotite is not in radium-uranium equilibrium. This lack of equilibrium may be due to the youth or alteration of the sample, or perhaps both. Many radiocolloids have been found only in the samples containing predominantly crystalline material. These radiocolloids were probably formed by the recent solution of a pre-existing uranium-bearing mineral nearly in radium-uranium equilibrium.

Satisfactory X-ray powder diffraction photographs were obtained from most of the high-grade samples studied, suggesting that there was little or no disorder in the crystal structure. Metamict structures and radioactive fracturing of the crystalline carnotite were not recognized. These indications of undisturbed crystal structure may be contrasted with the indications of disturbed crystal structure in the possibly older carnotite from Radium Hill, Australia, and the tyuyamunite from Fergana Valley, U.S.S.R.

Petrographic study of the thin sections showed that carnotite was usually the last mineral deposited. It seems reasonable that vugs in the sandstone are relatively young and that the carnotite crystals projecting into the vugs are not older than the openings themselves. Many of the quartz grains have fractures that are filled with carnotite. The exact dating of the fracturing is uncertain at this time. Many of the thin sections show quartz grains with highly irregular boundaries suggesting solution of the quartz prior to or at the same time as the carnotite deposition.

Radioactive-equilibrium and Lead-uranium-ratio Methods

Two of the 12 high-grade carnotite samples studied are approximately in radium-uranium equilibrium; 1 sample has a slight excess of radium; and the remaining 9 samples are deficient in radium. The minimum radium-uranium age of the 2 samples which are essentially in radium-uranium equilibrium is approximately 500,000 years. The maximum radium-uranium ages of the 2 essentially lead free carnotite samples that are not in radium-uranium equilibrium are 15,000 and 40,000 years. The other samples which contain lead and which are not in radium-uranium equilibrium cannot be dated by this method.

The near-surface occurrences of the predominantly crystalline samples have the greatest radium deficiencies. The sample of crystalline carnotite which was found at depth, however, has a 5-percent excess of radium. The radium content of the 7 predominantly microcrystalline samples ranged from an excess of 2 percent to a deficiency of 20 percent. As the predominantly microcrystalline samples most exposed to chemical weathering contain a slight excess of radium and the less exposed samples are deficient in radium, there does not seem to be a consistent relationship between the departure from radium-uranium equilibrium and the weathering to which the microcrystalline form has been exposed.

The most reliable lead-uranium-ratio age calculations not corrected for the addition of common or radiogenic lead can be obtained from uranium-bearing minerals which have been undisturbed since their deposition. The 3 high-grade carnotite ores that are most nearly in radium-uranium equilibrium and that probably have been least disturbed have ages that range from 21 to 77 million years. The ages of the 3 predominantly crystalline samples that can be calculated by the lead-uranium-ratio method range from 30 to 35 million years. The calculated ages of the microcrystalline samples not in radioactive equilibrium range from 19 to 169 million years. This variation in age may indicate a real difference in the age of the carnotite deposits. These variations, however, may also be explained by the loss of uranium or by the addition or loss of lead. If lead is added or uranium lost, the calculated ages will be greater than the actual age of the sample. If lead is lost (a possible but less probable explanation), the calculated ages would be too small.

Lead-isotope Methods

The Pb^{206}/U^{238} and Pb^{207}/U^{235} ratio age calculations of 3 high-grade samples corrected for the addition of common lead but not corrected for the possible addition of radiogenic lead or the selective loss of radon are in reasonable agreement for each sample but range from 27 to 96 million years. The Pb^{207}/Pb^{206} ratio age is in marked disagreement with the lead-uranium-ratio ages and ranges from 520 to 600 million years (late pre-Cambrian). Assuming correct analyses, the paradox of late pre-Cambrian radiogenic lead in deposits whose maximum age is late Jurassic may be explained by (1) an unusual U^{235}/U^{238} isotope ratio, (2) the loss of radon, or (3) the introduction of old radiogenic lead.

The difference in the U^{235}/U^{238} ratio necessary to account for the observed Pb^{207}/Pb^{206} ratio is large. Although such large variations have not been reported in the literature, the isotope composition of the uranium in the carnotite will be determined in order to test the first explanation. If the loss of radon has occurred, the Pb^{207}/U^{235} ratio age of the high-grade carnotite would be the most reliable. If old radiogenic lead has been added to the carnotite, both the lead-uranium- and lead-lead-ratio ages would be too great, and the actual age of this carnotite would be relatively young.

Evaluation

The most significant result of this preliminary study of the age of the carnotites is that the previously unrecognized problem of the origin of the radiogenic lead in the carnotite has been clearly delineated. The lead-uranium-, lead-lead-, and radium-uranium-ratio age calculations depend on an unequivocal solution of this problem. A systematic mass-spectrographic study of the lead extracted from all grades of carnotite ore should show whether the apparent excess of Pb^{207} is a result of the loss of radon or the introduction of old radiogenic lead. A loss of radon would result in appreciable changes in the Pb^{207}/Pb^{206} ratio in different parts of the deposit, whereas the same Pb^{207}/Pb^{206} ratio would be expected throughout the deposit if the radiogenic lead were added.

By carefully selecting the sample the effect of radon loss, if any, on the Pb^{206}/U^{238} and the Pb^{207}/Pb^{206} ratio ages can be minimized and the Pb^{207}/U^{235} ratio age would be expected to approximate closely the true age of the carnotite ore. A quantitative dating of the deposits might not be possible if a relatively large amount of old radiogenic lead has been added to the carnotite. If this is true, however, the important fact that the deposits are relatively young would be established. Even an approximate dating of the deposits would simplify the problems concerning the source and chemical and physical controls of the mineralizing solutions. The clarification of these questions on the origin of the deposits would, in turn, have immediate practical applications: (1) the estimates of ultimate reserves of carnotite ore on the Colorado Plateau and the selection of new areas for exploratory drilling could be made with greater confidence and (2) the prospecting methods and geologic controls used to guide the drilling could be more thoroughly evaluated.

APPENDIX 1

Sample Descriptions

Between August 25 and October 9, 1948, about 100 samples were collected. Of the 50 samples now being studied, 12 are high-grade carnotite; the remaining 38 samples are intermediate- and low-grade carnotite ores. The other 50 samples were collected for special studies which have not yet been undertaken. This group includes samples of barren sandstone collected for comparison with mineralized rock; a few samples collected for a study of banding and weak mineralized zones; samples of the "galena band" from the Rifle deposit, and other material from the Rico area for additional lead-isotope studies; and samples of most of the common vanadium minerals. Almost all of the work so far has been confined to the 12 high-grade carnotite samples. These samples were selected for the first part of this investigation because it was desirable to work with material of high uranium content in order that experimental errors would be proportionately small.

Sample 1, Parco mine, Yellow Cat group, Thompson area, Grand County, Utah.--The Parco mine is in the lower part of the Salt Wash sandstone member of the Morrison formation. However, in the Thompson area there is some mineralized rock in almost every sandstone unit of the member. The sample was collected from coatings of carnotite found on the surface of joint blocks at the entrance to the mine and from blocks of sandstone found on the mine dump. Both the float and the rock found in place should have been subjected to a high degree of chemical and mechanical weathering. The mineralizing solutions in this deposit were controlled by the joint system which probably developed during the regional deformation. The sample was collected because the maximum age of the carnotite was established by the age of the joints and because the effects of chemical and mechanical weathering on the radioactive equilibrium could be studied.

Sample 9, Monument No. 2 mine, Mexican Hat area in Monument Valley, San Juan County, Utah.--This deposit is in the Shinarump conglomerate. Uranium and vanadium ores have been reported in the underlying and overlying sandstones. The sample was collected from a freshly blasted face of the open cut. The carnotite is found as coatings on the joints and fractures, as disseminated material in the sandstone and conglomerate, in thin veins of very pure material, and as carnotite replacements of clay pebbles.

The sample was covered by a minimum of 6 to 10 feet of sandstone and should have been protected from extreme weathering. This material was collected because the enclosing rocks are Triassic; most of the other samples were collected from the Salt Wash sandstone member of the Morrison formation (late Jurassic). If the deposit is late Triassic in age and if it has not been leached by ground waters, the ages calculated from the lead-uranium and lead-lead ratios should be greater than in any other carnotite samples studied.

Samples 12 and 13, Jo Dandy mine, Paradox Valley, Montrose County, Colorado.--This deposit is found in the upper part of the Salt Wash sandstone member of the Morrison formation. Its exact position is in doubt because of faulting and slumping in the area. The vertical distribution of the mineralized zone is between 30 and 40 feet.

Sample 12, taken from a completely unprotected outcrop of very friable mineralized sandstone in an open cut leading to the main haulage adit of the mine, was subjected to chemical weathering. Sample 13, taken from a small pocket of very high-grade carnotite with corvusite approximately 140 feet inside the portal of the haulage adit, was very well protected and probably represents the conditions of radioactive equilibrium that would be expected in an undisturbed sample. The appearance of sample 13 strongly suggests that the mineralizing solutions were controlled by a small joint. If it is assumed that the material in both samples was deposited at approximately the same time, any differences in the degree of radioactive equilibrium or the lead content should be attributed to the effects of weathering.

Samples 19 and 20, Radium No. 6 mine, Radium group, San Miguel County, Colorado.--This deposit is in the upper part of the Salt Wash sandstone member of the Morrison formation. The sandstone unit in this area is 15 to 40 feet thick and is overlain by another sandstone unit of the member. The mineralized zone extends vertically for approximately 40 feet. Sample 19 was collected from a pillar at the mine portal and should be representative of the effects of moderate weathering. The carnotite occurs as a clayey seam as much as 1 inch thick and also as disseminated material. The material in sample 20 was taken from a pillar approximately 100 feet inside the portal where the carnotite occurs both in small pockets and as disseminated material. This sample was overlain by approximately 30 feet of sandstone. If the material of both samples was deposited simultaneously, the differences in radioactive equilibrium and lead content would be due to weathering and the action of ground water.

Samples 25 and 28, Calamity No. 13 mine, Calamity Mesa, Mesa County, Colorado.--This deposit is found in the upper part of the Salt Wash sandstone member of the Morrison formation. In this area the sandstone unit is approximately 30 feet thick. The mineralizing solutions were restricted to the lower part of the unit.

The deposit is reached by an incline. Sample 25 was collected from a clayey seam of almost pure carnotite in the back of a small drift approximately 25 feet from the foot of the incline. Sample 28 was taken from another clayey seam in the back of a stope approximately 160 feet from sample 25. The samples could have been altered only by circulating ground water as they were covered by a minimum thickness of 25 feet of sandstone. Any variations in lead content or the radioactive equilibrium should therefore be directly attributed to the action of circulating ground water.

Samples 61, 62, and 63, Club mine, Uravan area, Montrose County, Colorado.--This deposit is in the upper part of the Salt Wash sandstone member of the Morrison formation. Mineralized rock has been reported from many positions in this ore-bearing part of the member.

All three samples were collected from a small stope approximately 200 feet from the entrance to the upper workings of the mine. Samples 61 and 63 were collected from clayey seams near the back and on opposite sides of the stope. Sample 61 was collected slightly lower in the formation than sample 63. Sample 62 was collected from the back near the middle of the stope. This sample seemed to be a carnotite replacement of a crushed log. Because of the continuity of the deposit, it is reasonable to suppose that the samples collected within 30 feet of each other are essentially the same age. In addition, they have been subjected to approximately the same amount of leaching by ground water. Therefore, any variation in radioactive-equilibrium conditions and lead content should be due to the slight differences in the relative positions of the samples with respect to each other.

Sample 64, Bob Tail mine, Monogram group, Paradox Valley, Montrose County, Colorado.--This deposit is in the upper part of the Salt Wash sandstone member of the Morrison formation. The precise position is in doubt because this area has been cut by faults parallel to the rim of Paradox Valley.

The deposit has been developed by an incline. The sample was obtained from the first drift to the left down the incline. Close to the sample location the deposit was overlain by about 10 to 15 feet of sandstone. The sample was taken from a rich pocket of clayey carnotite and corvusite. The carnotite is disseminated or occurs in thin clayey seams. A possible interpretation of the field relations in this area is that the mineralizing solutions were controlled in part by a fault which cuts the deposit. In any event, the fault should provide a good channel for migrating ground water.

APPENDIX 2

Sample Preparation

The same methods of separation have been used on all of the samples studied. As the uranium-bearing minerals were very fine grained, they were concentrated in the - 200-mesh fraction. This size fraction was used in the study.

Depending on the amount of carnotite present, hand-picked material weighing approximately 150 to 200 grams was gently crushed and placed in a set of ASTM sieves. The 50-, 100-, and 200-mesh sizes were used.

The set of sieves was shaken for ten minutes in a Ro-Tap. The material retained on the 50-, 100-, and 200-mesh sieves was gently crushed and then replaced in the sieves. The sample was again agitated for ten minutes in a Ro-Tap. The fractions retained on the different sieves and the - 200-mesh fraction were then weighed and bottled. Approximately 30 grams of the - 200-mesh fraction of each sample was obtained in this way.

After each sample separation, the sieves were cleaned by knocking, then thoroughly washed in a rapid stream of warm water. The sieves were dried with warm compressed air.

Another method of separating the radioactive material from the sandstone in which it is usually found is by means of a small separator which has been deisgned in this laboratory. The separator consists of three units:

1. A bottle-shaped glass container in which the crushed sample may be scrubbed by air from jets mounted symmetrically around the base of the container
2. A vertical glass column of variable length which connects the scrubbing chamber with the precipitating unit
3. A Cottrell precipitator unit which is connected to the upper end of the glass column and which removes the very fine particles from the vertically rising air current

The operation of the separator depends on the abrading action of the sand grains on each other as they are accelerated by the air from the jets. The fine particles adhering to the sand grains are rubbed off and are separated from the sand by the slowly rising current of air which moves up the vertical column. The fine particles are charged in the Cottrell precipitator and are driven to the walls of the unit where they adhere.

By changing the pressure of the air in the jets, the column length, and the voltage applied to the Cottrell precipitator, a great variety of particle sizes may be obtained. By varying these conditions, a separation may also be obtained on a compositional basis. This method of separation might be applied to beneficiation of the carnotite ores.

Specimen mounts for use in the electron microscope may be placed inside the precipitator unit. Mounts prepared in this way show almost complete dispersal of the material. The largest particle observed on the mounts prepared in this way had a maximum diameter of 15 microns.

APPENDIX 3

X-ray Analysis

X-ray powder diffraction pictures of material from the high-grade carnotite samples were taken by Mrs. E. A. Cisney of the Geological Survey. Comparisons were made with patterns obtained from synthetic carnotite and tyuyamunite and with the standard patterns of natural carnotite and tyuyamunite.

All patterns were obtained with nickel-filtered copper radiation in Debye-Scherrer powder cameras of 114.59 mm diameter. Cellulose was used as a binder in the spindles to prevent dehydration of the minerals.

Tables 6 and 7 are comparisons of the d-spacings of synthetic and natural carnotite (sample 61) and of synthetic tyuyamunite and natural tyuyamunite from the Fergana Valley, Russia, the type locality.

The pattern of sample 12 (table 8) is very close to that obtained from synthetic barium uranyl vanadate. However, spectrographic analysis showed calcium but no barium or strontium. This similarity in pattern may be a fortuitous occurrence and seems to be related to the hydration state of the mineral.

Table 9 gives the identifications obtained from the X-ray powder diffraction studies of the 12 high-grade samples, using the - 200-mesh fraction in each case. The identifications are tentative as only one X-ray diffraction photograph has been made of each sample. Additional X-ray powder patterns will have to be made to determine whether all the forms of carnotite present in the sample have been identified.

Table 6.--Comparison of d-spacings of synthetic carnotite and sample 61

Synthetic carnotite prep. 15 film 57		Sample 61 film 45	
d in A	Estimated intensities	d in A	Estimated intensities
6.4	10	6.4	10
5.0	2	5.0	2
4.19	4	4.19	4
3.48	5	3.49	5
3.21	3	3.21	3
3.10	7	3.10	7
2.69	2	2.69	2
2.58	1	2.55(diffuse)	3
2.53	3		
2.45	1	2.45	1
2.14	4	2.14	3
2.01	2	2.01	1
1.979	2	1.981	1
1.926	3	1.929	3
1.895	2	1.895	1
1.817	1	1.817	1
1.765	1	1.765	1
1.734	1	1.734	1
1.667	2	1.667	2
1.645	1	1.647	1
1.598	1	1.598	1
1.570	1	diffuse	-
1.523	1	diffuse	-
1.495	2	1.497	2
1.445	1	1.445	1

Table 7.--Comparison of d-spacings of synthetic and natural tyuyamunite

Synthetic tyuyamunite prep. 6 film 19		Tyuyamunite from Fergana, U.S.N.M. R-5697 film 14172	
d in A	Estimated intensities	d in A	Estimated intensities
9.9	10	9.8	10
--		8.5	5
6.7	0.5	--	
6.3	0.5	6.4	1
4.96	8	4.98	5
4.23	0.5	4.27	1
4.08	1	4.02	1
3.77	2	--	
3.63	0.5	--	
3.29	4	3.36	2
3.18	3	3.24	3
2.99	1	--	
2.90	1	2.89	1
2.61	0.5	--	
2.56	1	--	
2.51	0.5	--	
2.47	1	2.45	2
2.23	0.5	--	
2.19	0.5	--	
2.12	3	2.13	2
2.02	2	2.04	2
1.981	1	--	
--		1.97	2
1.899	2		
1.841	1		
1.807	0.5		
1.784	2		
1.746	2		
1.707	0.5		
1.667	0.5		
1.634	0.5		
1.605	0.5		
1.585	0.5		
1.535	2		
1.499	0.5		
1.463	1		
1.429	0.5		
1.414	0.5		
1.380	2		
1.341	2		
1.285	1		
1.265	0.5		
1.242	0.5		
1.188	0.5		
1.102	0.5		
1.065	0.5		

Table 8.--Comparison of d-spacings of synthetic barium uranyl vanadate and sample 12

Synthetic barium uranyl vanadate prep. 8 film 21		Sample 12 film 60	
d in A	Estimated intensities	d in A	Estimated intensities
8.4	6	8.4	10
5.1	2	--	
4.19	8	4.19	8
3.75	2	3.72	2
3.28}	3	3.23	6
3.20}	3		
3.04	2	3.03	7
2.98	10	2.96	1
2.57	3	2.56	4
2.11	7	2.11	5
--		2.04	1
--		1.985	2
1.953	4	--	
--		1.937	2
1.852	2	--	
--		1.888	1
1.817	1	1.817	1
1.759	2	1.759	2
1.725	3	1.722	1
1.675	1	1.678	1
1.639	1		
1.605	1	lines faint	
1.556	3		
1.488	4	1.486	2
1.336	2		

Table 9.--Identification of X-ray powder diffraction photographs of carnotite samples

Sample	Carnotite	Pattern similar to synthetic Ba carnotite	Quartz	Calcite	Other lines in A
1	x		x		8.3; 4.23
9		x			10.0; 3.34; 3.22
12		x			
13	x		x		
19		x	x		10.0; 3.34; 3.22
20	x		x		10.0; 3.34; 3.22
25	x				2.98
28	x				10.0; 3.34; 3.22
61	x				
62	x			x	
63	x				3.90;2.73
64					10.0; 3.34; 3.22

x Indicates pattern present

APPENDIX 4

Electron Microscopy

Purpose.--Electron microscopy presents a means of solving some of the problems associated with the study of the very fine grained material in the Colorado carnotite ores. The RCA-50KV-EMU instrument at the National Bureau of Standards was used in the preliminary survey of the different forms of material in the high-grade ores and of synthetic compounds having chemical compositions similar to natural carnotite and tyuyamunite. By using the electron microscope, size and shape of the different particles could be observed. This exploratory survey of the fine-grained material has aided in the interpretation of results of optical, alpha-plate, and X-ray diffraction studies and has served as a visible means of controlling different separation techniques.

The practical limit of resolution of the commercial electron microscope is at present about 100 angstrom units. The useful range of magnification of the EMU instrument is 2,000 to 20,000 diameters.

Procedure.--The methods of specimen preparation which were used on the - 200-mesh fraction of the carnotite ores and the two synthetic compounds were as follows:

1. Some samples were prepared by dispersing the material in a drop of collodion or Formvar and milling it together between two glass slides. The dry smear is then floated off on water and picked up on a 200-mesh screen and allowed to dry. A variation of this technique involves milling resin plus material in a small mortar and

dispersing a drop of the slurry on a still water surface.

2. Some samples were prepared by placing a drop of material in suspension on 200-mesh screens covered with Formvar or collodion films. The material in the drop is then allowed to settle and dry.

3. Metallic shadow-casting is used to add contrast as well as to indicate the height of the particles. Approximate height measurements may be made if a metal such as gold or chromium is evaporated obliquely at a known angle on the specimen mounts.

One of the most immediate problems is that of separation and dispersal of the sample. The technique of electrostatic separation is being tried. Methods of heavy liquid separation, ultracentrifugation, and ultrasonic dispersion may also offer means of solution for this problem.

Data.--Electron micrographs of synthetic carnotite and synthetic tyuyamunite show two distinctly different forms which seem to correspond to the different forms found in the naturally occurring minerals. The micrographs have also been helpful in determining the shapes of fine inclusions in the sericitic material associated with the carnotite. Interfacial angles of carnotite crystals too small to be resolved by the optical microscope were determined with the electron microscope.

Evaluation.--The techniques of specimen preparation must be considered in the interpretation of the results obtained so far. Chemical reactions may result from the association of the ores with organic solvents and water. In addition, the samples were dessicated and subjected to electron bombardment. When exposed to these conditions some of the components showed evidence of "boiling". It is not known whether the water lost was water of crystallization or adsorbed water.

Plates 13 through 26, following this page, are electron micrographs of the material studied. The magnifications listed are original magnifications. These plates are representative of types of material in the - 200-mesh fraction except where noted.

PLATE 13

Synthetic carnotite: $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 8 \pm H_2O$

These figures are representative of some of the forms present in synthetic carnotite.

A. The euhedral nature of the synthetic carnotite is shown. The predominant form is diamond-shaped plates. A natural occurrence of this form is shown in plate 21. The interfacial angles which have been measured correspond closely with those results published for natural megascopic crystals. The crystalline nature can be observed only with higher magnifications, and it should be noted that even these minute crystals are relatively opaque to the electron beam. This opacity is due in part to the presence of elements of high atomic number.

B. The transparency of the diamond-shaped crystal in the center of the micrograph is probably due to its extreme thinness.

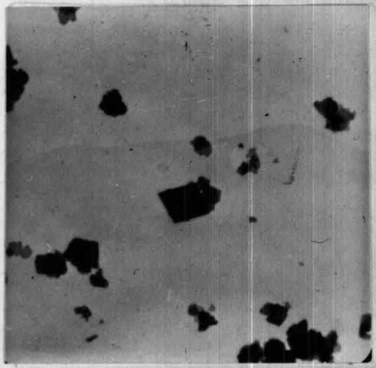
C. A shadowed specimen in which the ratio of the length of the shadow to the height of the particle is 4/1. The three-dimensional nature of these crystals is apparent from the long shadows cast. At higher magnifications sharp focus on the crystal edges was not possible, and the hazy outlines are thought to be the result of hydration of the crystal while dispersed in water. The specimen preparation for plate 13, A and B, avoided long exposure to water. The particles were dispersed in the collodion substrate.

D. The similarity between the natural microcrystalline carnotite shown in plates 18 and 24 and the synthetic carnotite shown here is noteworthy. The magnifications in each photograph are the same.

PLATE 13

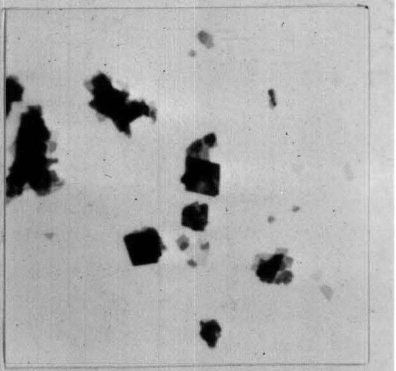
SAMPLE LRS/70/48

A



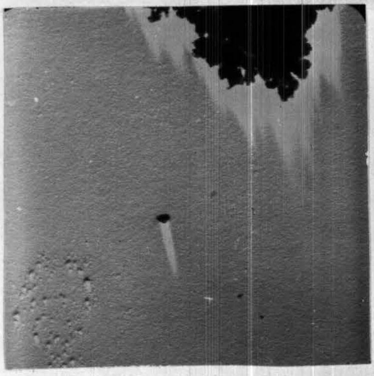
X 18500

B



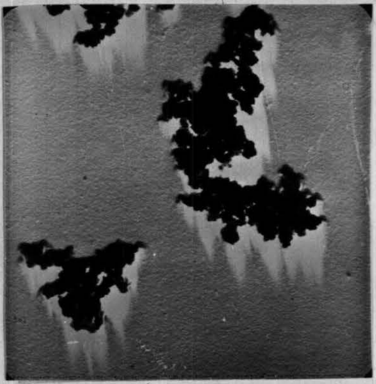
X 18500

C



X 6800

D



X 6800

PLATE 14

Synthetic tyuyamunite: $CaO \cdot 2UO_3 \cdot V_2O_5 \cdot 8 \pm H_2O$

These figures are representative of some of the different crystal forms of synthetic tyuyamunite.

A. A triangular-shaped plate of synthetic tyuyamunite. This mineral develops as large plates in contrast with the synthetic carnotite which occurs in a microcrystalline form. The naturally occurring tyuyamunite is also more coarsely crystalline than the naturally occurring carnotite. The thin platy nature is apparent from the semi-transparent tip at the right of this partly developed crystal.

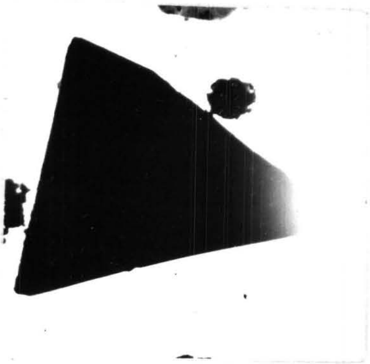
B. A euhedral crystal of synthetic tyuyamunite.

C. and D. Shadowed specimens in which the ratio of the length of the shadow to the height of the particle is 4/1. The short shadow is evidence of the thin platy nature of the crystal. The opacity to the electron beam is due in part to the presence of elements of high atomic number.

PLATE 14

SAMPLE LRS/71/48

A

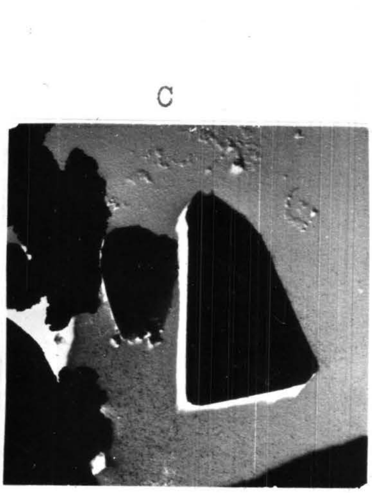


x 4500

B

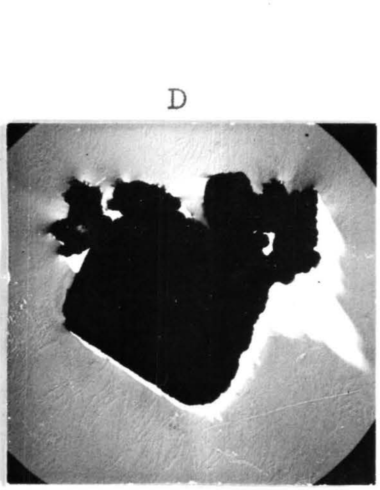
x 6000

C



x 3800

D



x 3800

PLATE 15

Sample 1 -Parco mine, Yellow Cat group, Grand County, Utah.

A. Well-developed plates are shown, but the crystal outline is not apparent.

B. A poorly developed crystalline form which possibly serves as matrix for either embedded inclusions or superimposed opaque particles. This aggregate may be the highly radioactive material found in the alpha-plate studies. (See section on alpha-plate analysis)

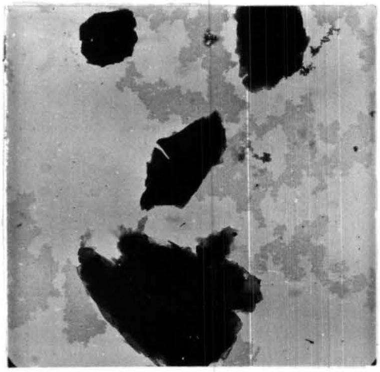
C. Well-developed plates similar to forms shown in plates 17 and 26.

D. A shadowed specimen in which the ratio of the length of the shadow to the height of the particle is 4/1. The platy nature of the large particle is substantiated by the short shadow cast. The smaller opaque particle casts a much longer shadow, and the opacity of the particle is due to its apparent greater thickness and/or atomic density.

PLATE 15

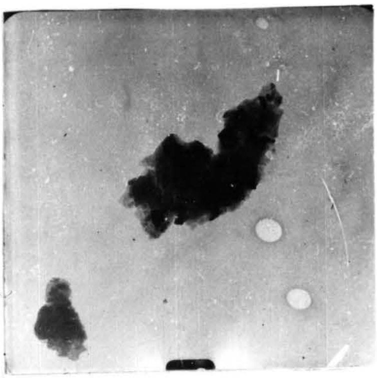
SAMPLE LRS/1/48

A



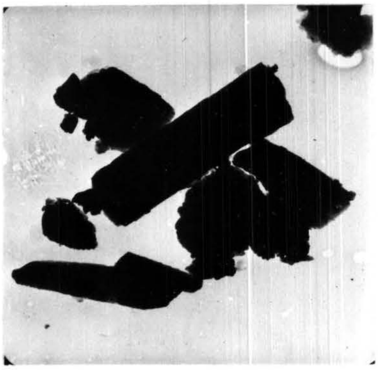
X 6800

B



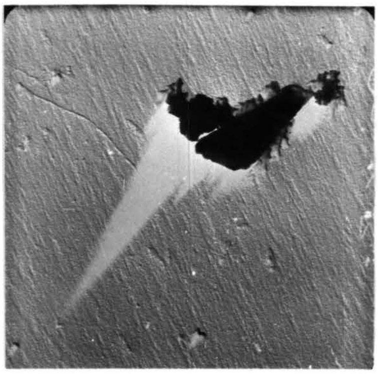
X 6800

C



X 6800

D



X 6800

PLATE 16

Sample 9 -Monument No. 2 mine, Mexican Hat area, San Juan County, Utah.

A. The larger crystal is probably an example of the euhedral platy form of carnotite. This may be contrasted with plate 15, A, in which the euhedral outline is not developed. This sample also contains a platy form similar to plate 15, C.

B. A platy euhedral crystal containing inclusions or superimposed material.

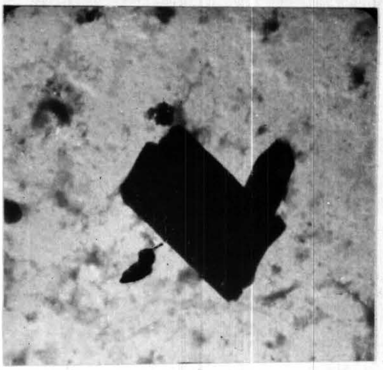
C. Small bladed crystals are shown. These are examples of clay minerals found in this ore.

D. A shadowed specimen in which the ratio of the length of the shadow to the height of the particle is 4/1. The larger mass is an example of the poorly developed crystalline form of the material. The two irregular particles below it are more opaque to the electron beam because of their greater thickness as shown by the length and irregularity of their shadows.

PLATE 16

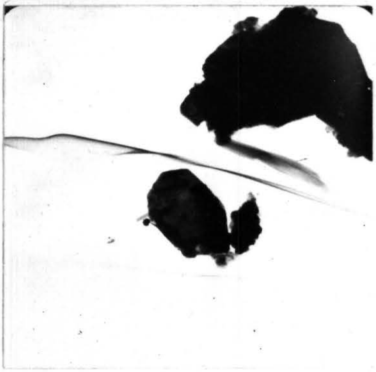
SAMPLE LRS/9/48

A



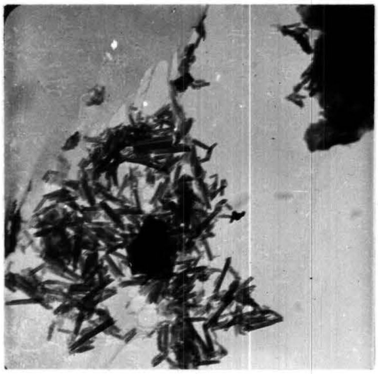
X 6800

B



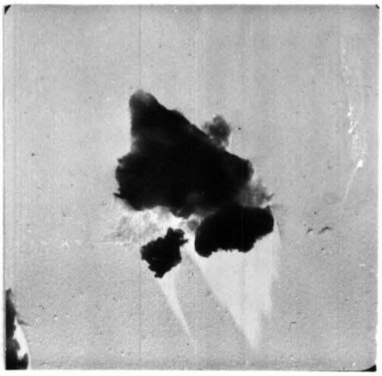
X 6800

C



X 13000

D



X 6800

PLATE 17

Sample 12 - Jo Dandy mine, Jo Dandy group, Montrose County, Colorado.

A, B, and C. Examples of the abundant bladed crystals which are found in this sample. On the basis of X-ray powder diffraction studies this sample was found to be similar in structure to barium "carnotite." The synthetic barium "carnotite" will be studied to see if the morphologies of the two materials are similar. The sandstone from which this sample was obtained was badly weathered, and it is possible that the presence of abundant bladed crystals is a result of recent recrystallization.

D. A shadowed specimen in which the ratio of the length of the shadow to the height of the particle is 5/1. The thin platy nature of these crystals is indicated by the very short shadows cast. The opacity of the crystal is probably due not only to its thickness but also to the presence of elements of high atomic number which scatter electrons more than the lighter elements. The particle casting the long shadow is evidently much thicker and is probably an aggregate of plates and irregularly shaped particles.

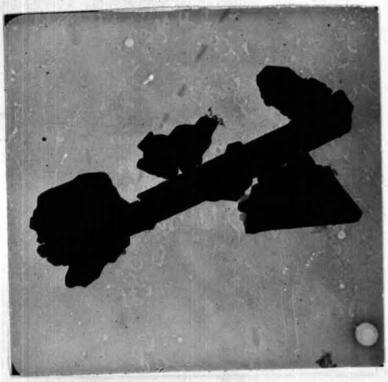
PLATE 17

SAMPLE LRS/12/48

A

X 6800

B

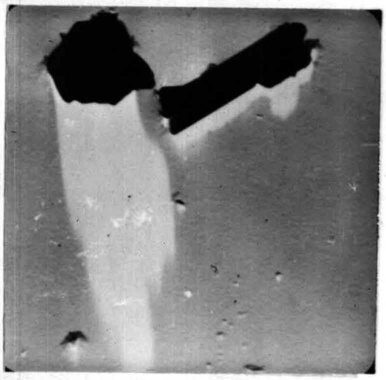


X 6800

C

X 6800

D



X 6000

PLATE 18

Sample 13 - Jo Dandy mine, Jo Dandy group, Montrose County, Colorado.

A and B. Examples of the finely divided (probably microcrystalline) form of this material. Many of the smallest particles are opaque to the electron beam. However, traces of a less opaque platy form are apparent.

C. The finely divided material is shown and also a semitransparent form which contains either denser inclusions or superimposed opaque particles. This sample has not been weathered. Comparison between the figures shown on this plate and plate 17 indicates possible differences between the microcrystalline and coarsely crystalline forms.

D. A shadowed specimen in which the ratio of the length of the shadow to the height of the particle is 5/1.

PLATE 18

SAMPLE LRS/13/48

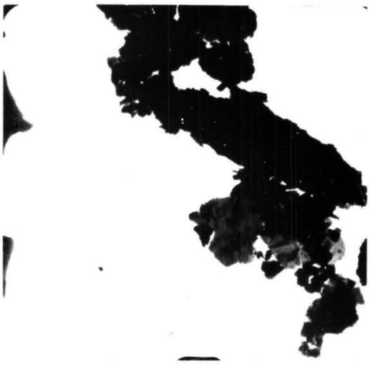
A

X 6800

B

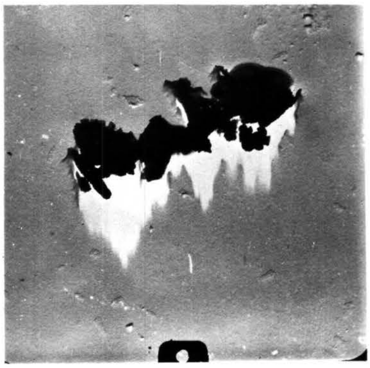
X 6800

C



X 6800

D



X 6000

PLATE 19

Sample 19 - Radium No. 6 mine, Radium group, San Miguel County, Colorado.

A. An example of two forms of the material. The finely divided opaque variety and the semitransparent poorly developed crystalline form. This sample is moderately weathered.

B. An example of material, similar to that shown in plate 19, A, which shows either inclusions or superimposed opaque particles.

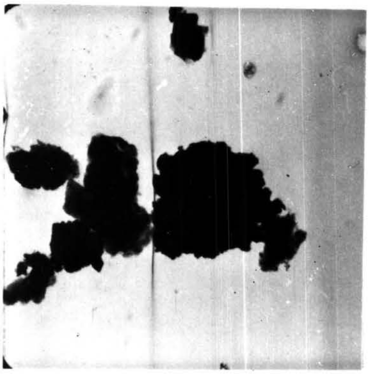
C. Another example of the poorly developed crystalline form of this material.

D. A shadowed specimen in which the ratio of the length of the shadow to the height of the particle is 5/1. The bladed crystal shown in this figure is similar to the crystalline material in plate 17. From the shadow cast at the lower left end of the crystal it can be seen that the blade is thin. The opacity is, therefore, due in part to the presence of elements of high atomic number.

PLATE 19

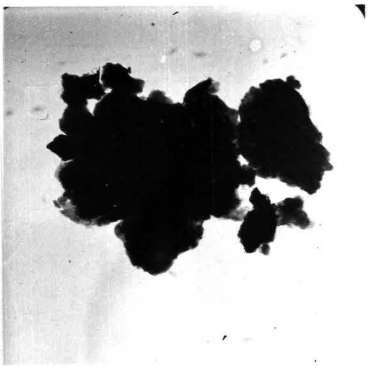
SAMPLE LRS/19/48

A



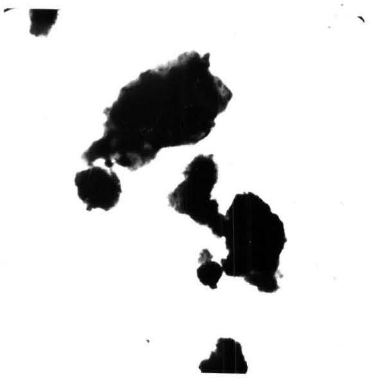
X 6800

B



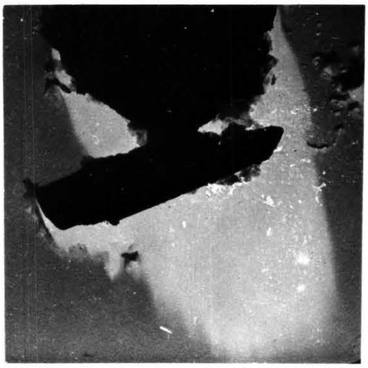
X 6800

C



X 6800

D



X 6800

PLATE 20

Sample 20 - Radium No. 6 mine, Radium group, San Miguel County, Colorado.

A. An example of the matrix material having inclusions or superimposed opaque particles. This sample does not show any of the larger bladed forms. On this basis it may be inferred that this material has not been subject to appreciable recrystallization.

B. A finely divided opaque (probably microcrystalline) form and a platy form are shown.

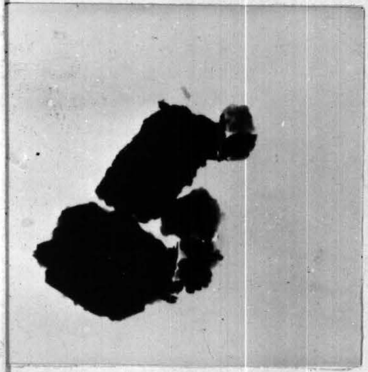
C. An example of the semitransparent matrix which appears to enclose many of the opaque particles.

D. A shadowed specimen in which the ratio of the length of the shadow to the height of the particle is 5/1. It can be seen that the small opaque particle at the left of the micrograph is very thin. The most probable interpretation is that its opacity is due in part to elements of high atomic number.

PLATE 20

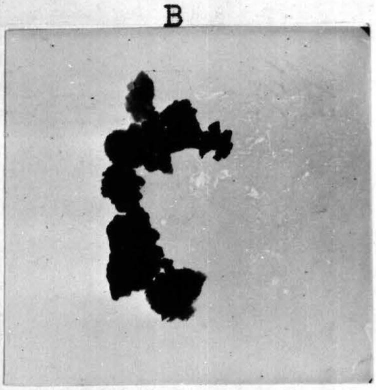
SAMPLE LRS/20/48

A



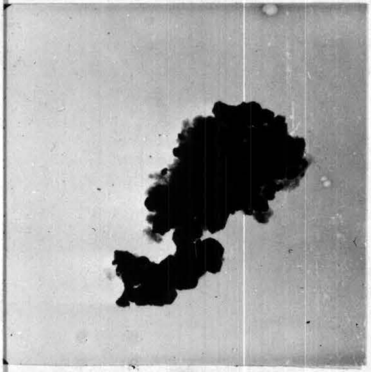
X 6800

B



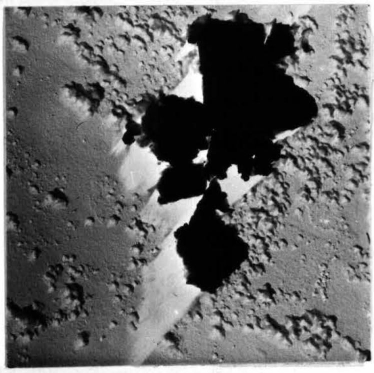
X 6800

C



X 6800

D



X 6000

PLATE 21

Sample 25 - Calamity No. 13 mine, Gateway area, Mesa County, Colorado.

A. The small discrete diamond-shaped crystals in this micrograph are strikingly similar to the crystal form of synthetic carnotite in plate 13. The square shapes of some of these crystals are probably due to the tilting of the crystal. Even the smallest diamond-shaped crystals are opaque, and this may be contrasted with the relative transparency of the other material in the micrograph. The sample from which this material was taken was unweathered. Large bladed crystals are not apparent in this sample.

B. Many of the opaque inclusions shown have a suggestion of crystal outline similar to those shown in plate 21, A. The matrix of this material shows slight crystalline structure.

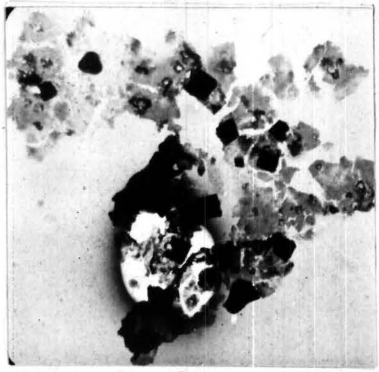
C. The finely divided (probably microcrystalline) form of the material is shown.

D. A shadowed specimen in which the ratio of the length of the shadow to the height of the particle is 4/1. The large mass seems to be uniform in opacity and structure.

PLATE 21

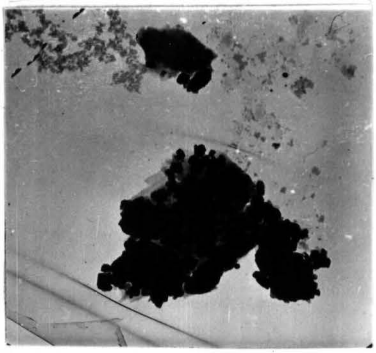
SAMPLE LRS/25/48

A



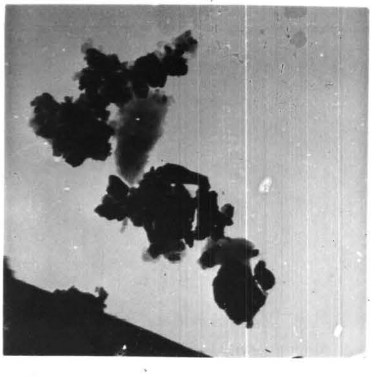
X 6800

B



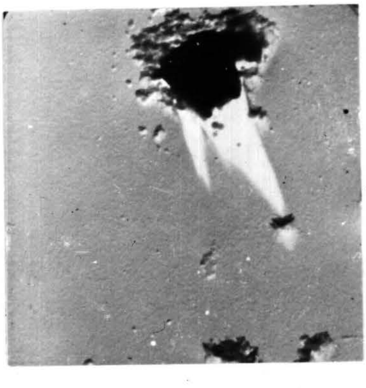
X 6800

C



X 6800

D



X 6800

PLATE 22

Sample 28 - Calamity No. 13 mine, Gateway area, Mesa County, Colorado.

A and B. These micrographs show the finely divided opaque particles and the apparently noncrystalline matrix in which the particles are held. Although this sample and the sample shown in plate 21 are from the same mine and have been subjected to the same alteration since deposition, this material does not show well-developed diamond-shaped crystals. However, there is some evidence of subhedral opaque crystals. In general, this material is more representative of a microcrystalline form of the carnotite than it is of a recrystallized form.

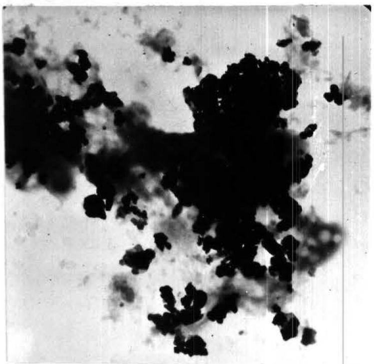
C. An example of the finely divided opaque particles. This material does not show well-developed crystal outline.

D. A shadowed specimen in which the ratio of the length to the height of the particle is 4/1. A well-terminated plate appears in the upper right hand corner of the micrograph. The opacity of the crystal is due in part to elements of high atomic number as the plate is quite thin.

PLATE 22

SAMPLE LRS/28/48

A

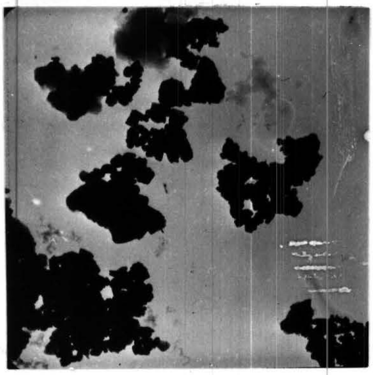


X 6800

B

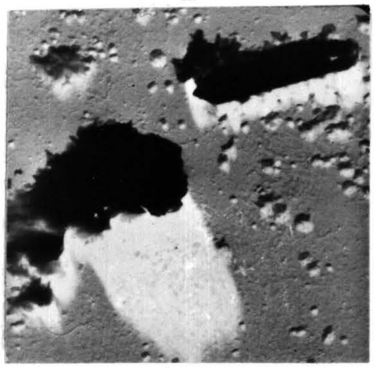
X 6800

C



X 6800

D



X 6800

PLATE 23

Sample 61 - Club mine, Uravan, Montrose County, Colorado.

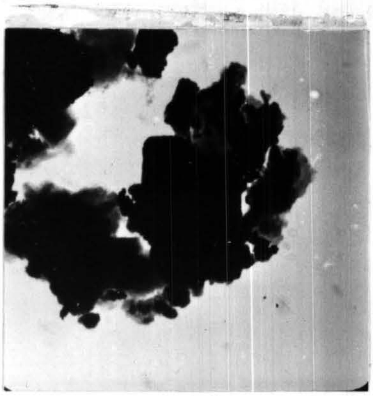
A, B, and C. The two principle forms of this sample are the finely divided opaque particles and the more transparent material which may be the matrix and some of which has distinct platy structure. In general, the opaque particles do not have good crystal outlines. Specimens shown in plates 23, 24, and 25 were collected from the same stope. They have been subjected only to alteration by the action of ground water. The bladed forms associated with recrystallized carnotites have not been observed in this material. The finely divided opaque particles are probably microcrystalline carnotite.

D. A shadowed specimen in which the ratio of the length of the shadow to the height of the particle is 5/1. The variations in the density of the particles of this micrograph can be interpreted as variations in thickness. In some particles there is evidence that the more opaque material is an inclusion.

PLATE 23

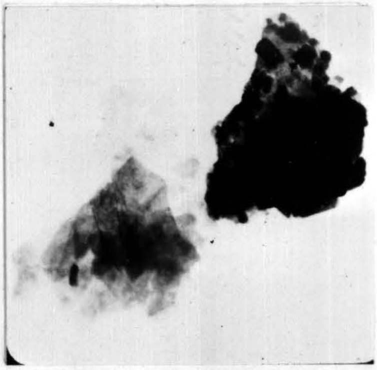
SAMPLE LRS/61/48

A



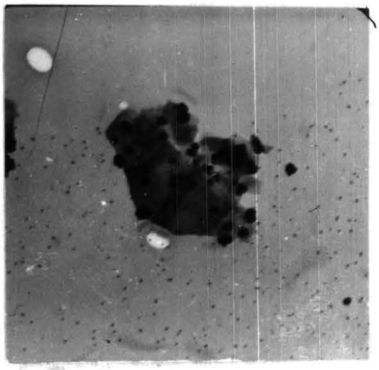
X 6800

B



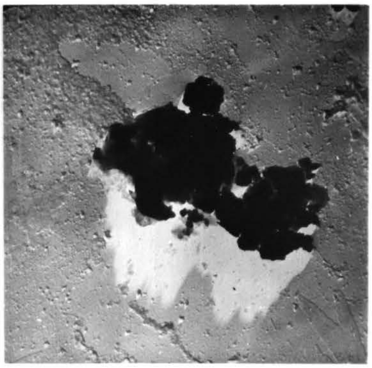
X 8300

C



X 13000

D



X 6000

PLATE 24

Sample 62 - Club mine, Uravan, Montrose County, Colorado.

A. This sample differs from plate 23 in that opaque, apparently hexagonal, crystals are exhibited.

B. In addition to the normal finely divided opaque form, there is a partly developed hexagonal plate at the left of the micrograph.

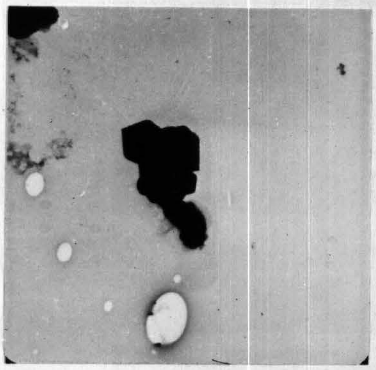
C. The platy nature of one of the more transparent forms is clearly shown. The center area consists of thin uniform overlapping plates. The poorly defined outline of the opaque mass in the center suggests that it is a dense inclusion.

D. A shadowed aggregate of opaque particles in which the ratio of the length of the shadow to the height of the particle is 4/1.

PLATE 24

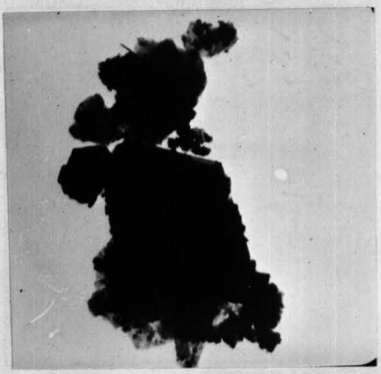
SAMPLE LRS/62/48

A



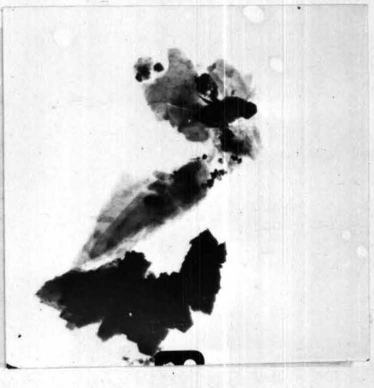
X 6800

B



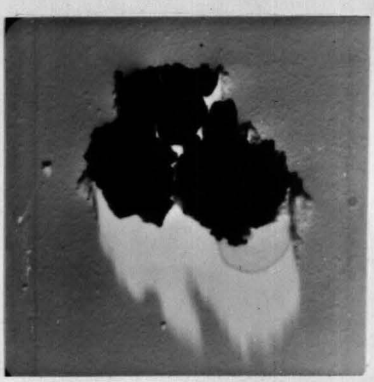
X 6800

C



X 6800

D



X 6800

PLATE 25

Sample 63 - Club mine, Uravan, Montrose County, Colorado.

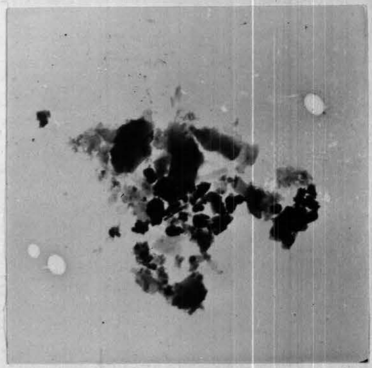
A, B, and C. This sample consists mainly of an opaque, finely divided form which does not show well-developed crystalline outline. The more transparent form may be the matrix. This material is similar to the microcrystalline carnotite which has been previously described.

D. A shadowed specimen in which the ratio of the length of the shadow to the height of the particle is 4/1. The irregular outline of the shadows cast implies the presence of discrete structures which project above the surface. Fine material may be partly embedded in the transparent matrix.

PLATE 25

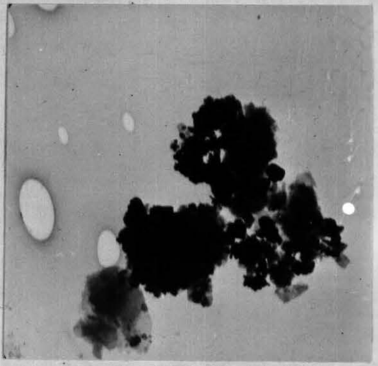
SAMPLE LRS/63/48

A



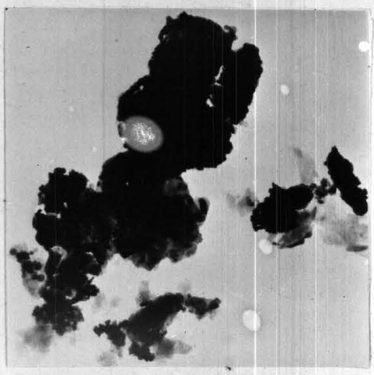
X 6800

B



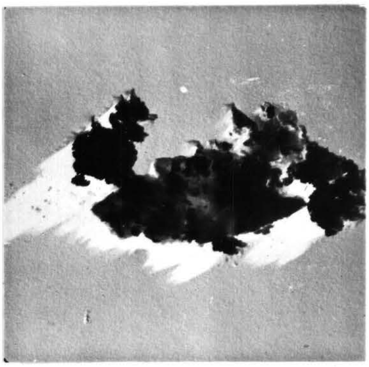
X 6800

C



X 6800

D



X 6800

PLATE 26

Sample 64 - Bob Tail mine, Monogram group, Paradox Valley, Montrose County, Colorado.

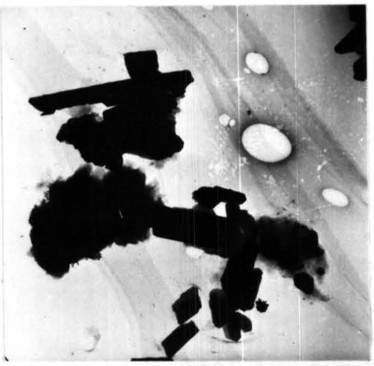
A, B, and C. This sample consists of plates many of which are well-terminated and of less dense and more poorly defined material. Many opaque inclusions are found. The similarity between this specimen and the crystals in plate 17 is striking. This sample was collected from the same general area as the material described in plate 17, but the weathering of sample 64 was not as extensive.

D. A shadowed specimen in which the ratio of the length of the shadow to the height of the particle is 5/1. The platy nature of these crystals is evident from the extremely short shadows that they cast. The lack of irregularities in the shadows indicates that the surfaces of the plates are smooth.

PLATE 26

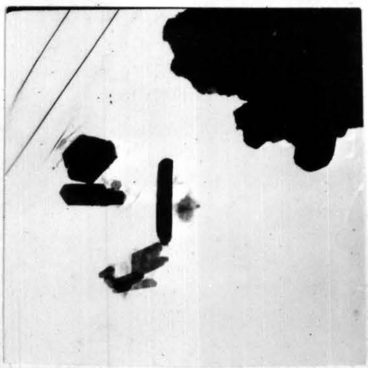
SAMPLE LRS/64/48

A



X 6800

B

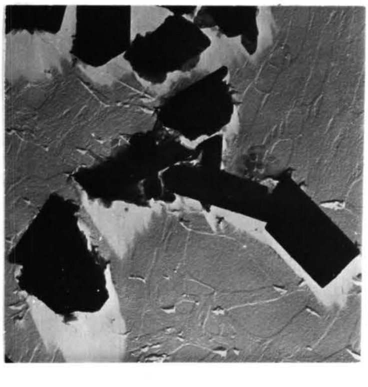


X 6800

C

X 6800

D



X 6000

APPENDIX 5

Determination of Calcium, Potassium, and Sodium in the High-grade Carnotite Samples

A 250-mg portion of the - 200-mesh fraction of each of the 12 high-grade carnotite samples was digested on the steam bath with 20 ml of 1 + 1 nitric acid. The solution was evaporated to 5 ml. Distilled water was added to the solution before filtering. The volume of the filtrate was made to 50 ml, and the insoluble portion was ignited and weighed.

Calcium was determined in the 50-ml solution using a Beckman flame photometer. The calcium wave length used was 620 mμ. Each calcium emission was bracketed by comparison with two standard solutions.

Aliquots of the 50-ml solution were diluted 10 times with distilled water after which potassium and sodium determinations were made in a similar manner to the calcium determinations previously outlined. The wave lengths used were 767 mμ for potassium and 589 mμ for sodium.

The results of these analyses are given in table 10.

Table 10.--Results of chemical analyses of 12 high-grade carnotite samples and synthetic carnotite and tyuyamunite

Analyst, C. A. Kinser, Geological Survey.

Sample	Percent insoluble in HNO_3	Percent K_2O	Percent Na_2O	Percent CaO	Percent UO_3	UO_3/K_2O	UO_3/CaO
1	39.58	5.18	0.16	1.29	32.7	6.32	25.3
9	14.64	0.76	0.14	1.92	45.6	60.0	23.8
12	48.88	0.17	0.12	5.34	24.0	141.0	4.5
13	3.40	6.52	0.32	2.15	37.4	5.73	17.4
19	27.97	1.50	0.42	1.06	26.1	17.4	24.6
20	18.68	2.46	0.19	1.24	39.2	15.9	31.6
25	14.36	6.12	0.25	0.52	39.1	6.40	75.2
28	12.24	5.82	0.24	0.56	43.3	7.45	77.5
61	5.23	7.16	0.47	1.25	38.7	5.40	31.0
62	6.27	3.38	1.04	14.24	17.8	5.26	1.25
63	5.55	5.10	1.22	1.79	30.5	5.99	17.0
64	34.08	0.67	0.17	1.23	41.6	62.1	33.8
Synthetic [a] carnotite		9.88			64.60	6.55	
Synthetic [a] tyuyamunite				5.41	54.33		10.0

[a] Chemical analysis, Analyst, J. J. Rowe

Table 11.--Published analyses of carnotite and tyuyamunite
(Arranged in order of increasing CaO percentages)

	← Carnotite →			← Tyuyamunite →		
	1 La Sal Mts., Utah	2 Temple Mt., Utah	3 Roc Creek, Montrose County, Colo.	4 Turkestan	5 Turkestan	6 Paradox Valley, Montrose County, Colo.
	Hess and Foshag (1927)	Hillebrand (1924)	Hillebrand and Ransome (1905)	Hillebrand (1924)	Melkov (1945)	Hillebrand (1924)
UO_3	66.51	63.29	61.70	58.45	56.72	60.7
V_2O_5	21.41	20.91	20.78	18.76	19.28	20.5
As_2O_5	None		Tr.			
P_2O_5	Tr.		0.90			Tr.
K_2O	9.71	10.16	7.33	0.18	1.38	0.1
Na_2O	0.35	0.16	0.15	0.21	Present	0.2
CaO	0.65	0.67	3.04	5.02	5.79	6.4
BaO	None		1.01			1.3
H_2O	1.37	4.57	5.09	17.38	16.83	10.8
	100.00	100.00	100.00	100.00	100.00	100.0

W. T. Schaller, Geological Survey, recalculated all analyses to 100 percent after deducting impurities.

Notes:

1. Original analysis included 0.32 insoluble; 0.22 MgO; 0.16 Al_2O_3; 0.04 Fe_2O_3; tr. CuO.
2. Original analysis included insoluble; 0.30 MgO; 0.07 CuO; tr. MoO_3; 0.55 Fe_2O_3; 0.26 SO_3.
3. Original analysis included 7.10 insoluble; 0.02 SrO; 0.13 PbO; 0.22 MgO; 0.15 CuO; 0.18 MoO_3; 0.15 SiO_2; 0.03 TiO_2; 0.09 Al_2O_3; 0.21 Fe_2O_3; 0.56 CO_2; tr. Li_2O.
4. Original analysis included insoluble; 0.09 MgO; 0.10 CuO; 0.13 Fe_2O_3; tr. Li, Tl.
5. Na_2O not separated.
6. Original analysis included 0.2 PbO; 0.2 MgO; 3.7 CuO; 0.4 Al_2O_3 + Fe_2O_3.

References:

Hess, F. L., and Foshag, W. F., 1927, Crystalline carnotite from Utah: U. S. Nat. Mus. Proc., vol. 72, art. 12, pp. 1-6.

Hillebrand, W. F., and Ransome, F. L., 1905, On carnotite and associated vanadiferous minerals in western Colorado; U. S. Geol. Survey Bull. 262, pp. 9-31.

Hillebrand, W. F., 1924, Carnotite and tyuyamunite and their ores in Colorado and Utah: Am. Jour. Sci., 5th ser., vol. 8, pp. 201-216.

Melkov, V. G., 1945, Oe iranovanadate igh medorozhdenia Mayli-Sy v. Kergizhud: Soc. russe minéralogie Mem. vol. 74, pp. 41-47.

Table 12.--Optical and physical properties of carnotite and related minerals

Samples (See note at end of table)	Color (in natural light)	Pleochroism	Cleavage	Optical character	Habit	Axial angle	Indices		
							X	Y	Z
1	Pale-yellow to medium-yellow	Gray to yellow-green?	(001) When evident	Biaxial (-)	Rhombic plates and aggregates	Medium	>1.89	>1.89	---
2	Clear pale yellow	?	(001)	Biaxial (-)	Rhombic plates and aggregates	Medium	>1.89	>1.89	---
3	Light lemon-yellow to green-yellow	Nearly colorless to yellow	(001) Imperfect	Biaxial (-)	Rhombic plates	35° ±	1.90 ± (est)	1.93 ± (est.)	---
4	Very pale yellow	None	---	---	Microcrystalline	---	---	1.835±	---
5	Yellow	---	(001) Micaceous	Biaxial (-)	Rhombic plates (001), shreds	39°-44°	1.750	1.895 1.925	1.92 1.95
6	Yellow	Grayish yellow to lemon-yellow	(001) Perfect	Biaxial (-)	Rhombic plates	Small	2.06	---	2.08

Samples (See note at end of table)	Color (in natural light)	Pleochroism	Cleavage	Optical character	Habit	Axial angle	Indices		
							X	Y	Z
7	Yellow	Nearly colorless to canary yellow to darker canary yellow	(001) Micaceous	Biaxial (-)	Plates (001) elongated or rhombic	36°	1.670	1.870±	1.895
8	Yellow	Nearly colorless to canary yellow to darker canary yellow	(001) Micaceous	Biaxial (-)	Plates (001) elongated or rhombic	40°-55°	1.77	1.93 ±	1.97

1. Synthetic carnotite prepared by K. J. Murata.
2. Synthetic tyuyamunite prepared by K. J. Murata.
3. Natural carnotite, sample 1.
4. Natural carnotite, sample 25.
5. Natural carnotite, Larsen, E. S. and Berman, Harry, The microscopic determination of the nonopaque minerals: U. S. Geol. Survey Bull. 848, p. 205, 1934.
6. Natural carnotite (op. cit., p. 208).
7. Natural tyuyamunite (op. cit., p. 204).
8. Natural tyuyamunite (op. cit., p. 205).

The first 4 samples have not been completely analyzed chemically; this will be done. The results of the analyses may change the identifications.

Table 13.--Optical and physical properties of natural carnotites

Sample	Color (in natural light)	Cleavage	Optical character	Habit	Axial angle	Indices of refraction X	Indices of refraction Y	Indices of refraction Z
1	Light lemon-yellow to green-yellow	(001) Imperfect	Biaxial (-)	Predominantly crystalline. Rhombic plates and splinters; also radial aggregates	2V = 35°±	(>1.90) est.	(1.93) est.	---
9	Light lemon-yellow to green-yellow	(001) Imperfect	Biaxial (-)	Predominantly crystalline. Rhombic plates and very fine crystalline material	Medium	(>1.90) est.	(1.93) est.	---
12	Pale-yellow	Not evident	---	Predominantly crystalline. Splinters often growing as fan-shaped aggregates	---	---	---	---
13	Pale-to medium-yellow and yellow-green (tending to dark)	Not evident	---	Predominantly microcrystalline. Splintery crystals and flakes	---	---	---	---
19	Medium-yellow	Imperfect	Biaxial (-)	Predominantly microcrystalline. Radial clumps of splintery crystals; a few plates	35° ±	(>1.90) est.	(1.93) est.	

Table 13.--Optical and physical properties of natural carnotites (continued)

Sample	Color (in natural light)	Cleavage	Optical character	Habit	Axial angle	Indices of refraction X	Y	Z
20	Clear pale-yellow to medium-yellow	(001) Imperfect	Biaxial (-)	Predominantly crystalline, Rhombic plates and small masses	Medium	---	---	---
25	Medium-yellow	---	---	Predominantly microcrystalline. Splinters and radial clumps of microcrystalline material	---	---	Microcrystalline 1.835 ±	---
28	Clear pale- to medium-yellow	Imperfect	---	Plates, splinters and microcrystalline	---	---	---	---
61	Light lemon-yellow to medium-yellow	Imperfect	---	Predominantly microcrystalline. Plates and splinters	---	---	Microcrystalline 1.835 ±	---
62	Pale-yellow to amber	(001) Imperfect	Biaxial (-)	Rhombic plates and microcrystalline material	Medium	Rhombic plates (1.91) est. Microcrystalline ---	(1.94) est. 1.835 ±	--- ---

Table 13.--Optical and physical properties of natural carnotites (continued)

Sample	Color (in natural light)	Cleavage	Optical character	Habit	Axial angle	Indices of refraction		
						X	Y	Z
63	Light lemon-yellow to amber	(001) Imperfect	Biaxial (-)	Predominantly microcrystalline. Rhombic plates and microcrystalline	Medium	Rhombic plates >1.89 Microcrystalline ---	 >1.89 1.84 ±	 --- ---
64	Light lemon-yellow to amber	---	---	Rhombic plates, splinters, radial aggregates, and microcrystalline	---	---	---	---

APPENDIX 9

Petrographic Analysis

Hand specimens and thin sections of the carnotite-bearing sandstones were studied under petrographic and binocular microscopes. Colors listed below under major and minor constituents are colors observed in transmitted white light. These are the preliminary results of the study of only one thin section for each sample, as the rock specimens are very friable and therefore thin-section material was difficult to obtain. The pieces sectioned may not be representative of the specific sample location, but when they are considered collectively some general relationships seem to exist. The sections were studied especially for clues to the occurrence, age relationships, and possible origin of the carnotites. Following is a detailed description of the samples studied with the exception of sample 28 for which no thin section could be made.

Sample 1 Parco mine, Yellow Cat group, Grand County, Utah.

Rock type Carnotite-bearing sandstone, Salt Wash sandstone member of the Morrison formation.

Description

A. Megascopic

The rock is a fine-grained, yellow, quartz sandstone with carnotite-encrusted grains. The quartz grains are usually fresh and glassy with crystal faces visible.

B. Microscopic

The major constituents are quartz (75%) and carnotite (20%). The quartz grains in the - 200-mesh fraction are subangular, have broken edges, a glassy luster, and are coated with carnotite. There is apparently some secondary quartz.

Carnotite occurs in secondary quartz and between grains. Many small grains are in a sericite matrix. Some large carnotite grains grade into indistinct red-brown areas in the centers of the grains. Rhombic plates and acicular crystals of carnotite are present.

The minor constituents (less than 1% each) are plagioclase in altered grains, zircon in small angular fragments and crystals, and sericite in flaky masses.

C. Age relationships

Carnotite is apparently later than the sericite and is earlier or equal in age to the secondary quartz.

Sample 9 Monument No. 2 mine, Mexican Hat area, San Juan County, Utah.

Rock type Carnotite-bearing sandstone, Shinarump conglomerate.

Description

A. Megascopic

The rock is a fine-grained, yellow, quartz sandstone with carnotite-encrusted grains.

B. Microscopic

The major constituents are quartz (60%) and carnotite (35%). The quartz grains are subangular, commonly fractured, and contain bubble inclusions. Carnotite occurs as fine material in thin cracks in quartz grains. Many small, flaky, rhombic crystals are associated in fractures with sericite. The minor constituents (less than 1% each) are biotite in quartz, rutile in quartz, sericite in cracks associated with carnotite, and opaque material (black anhedral crystals).

C. Age relationships

Carnotite seems to be replacing quartz.

Sample 12 Jo Dandy mine, Jo Dandy group, Montrose County, Colorado.

Rock type Carnotite-bearing sandstone, Salt Wash sandstone member of the Morrison formation.

Description

A. Megascopic

The rock is a gray and yellow fine-grained quartz sandstone with carnotite-encrusted grains. Carnotite crystals occur in vugs surrounded by quartz grains.

B. Microscopic

The major constituents are quartz (70%) and carnotite (20%). The quartz grains are fractured and have a glassy luster.

The carnotite occurs between grains and in cracks in the quartz. Clear yellow, splintery carnotite crystals grow in vugs in fan-shaped or radial patterns.

The minor constituents (less than 1% each) are calcite in large interstitial grains, unaltered grains of microcline, ilmenite as a large skeleton crystal and small slightly rounded detrital grains which seem to have a leucoxene coating, and rutile or hewettite in small, red-brown, slightly rounded grains.

Sericite (5%) occurs as spherulitic aggregates of flaky crystals coated with carnotite some of which shows rhombic outlines.

C. Age relationships

Carnotite is later than the sericite and may be an alteration of hewettite.

Sample 13 Jo Dandy mine, Jo Dandy group, Montrose County, Colorado.

Rock type Carnotite-bearing sandstone, Salt Wash sandstone member of the Morrison formation.

Description

A. Megascopic

The rock is a yellow-gray, fine-grained, quartz sandstone.

B. Microscopic

The major constituents are quartz (65%) and carnotite (25%). The quartz grains are subangular, fractured and have either a glassy luster or are frosted. The carnotite occurs as green-yellow acicular and darker flaky crystals in bands enclosing plagioclase, sericite, and quartz. Dark indistinct centers in some of the grains indicate a possible earlier mineral (hewettite?) which is replaced by carnotite.

The minor constituents are plagioclase (5%) in subangular, partly altered grains, sericite (3%), rutile (< 1%) as needles in quartz grains, hewettite (< 1%) as dark-reddish masses in carnotite grains, and subrounded opaques (< 1%).

C. Age relationships

The presence of groups of small quartz grains which are optically continuous indicates that replacement of a larger original quartz grain may have occurred. Relatively large grains of microcrystalline sericite material are encrusted by carnotite. The carnotite seems to be the youngest mineral in this assemblage.

<u>Sample 19</u> Radium No. 6 mine, Radium group, San Miguel County, Colorado

<u>Rock type</u> Carnotite-bearing sandstone, Salt Wash sandstone member of the Morrison formation.

Description

A. Megascopic

The rock is a yellow-gray, fine-grained, quartz sandstone.

B. Microscopic

The major constituents are quartz (85%) and carnotite (>10%). The quartz grains show straining, a glassy luster, and are subangular. Some grains are carnotite-encrusted. The carnotite occurs as acicular crystals growing in radial clumps presenting a "toothed" appearance and as a few pale-yellow interstitial plates. The minor constituents (less than 1% each) are sericite associated with carnotite crystals, hewettite as dark red-brown, irregularly shaped grains, and rutile.

C. Age relationships

The carnotite occurs as fillings in fractured quartz grains and as coatings on sericitized feldspar grains.

Sample 20 Radium No. 6 mine, Radium group, San Miguel County, Colorado.

Rock type Carnotite-bearing sandstone, Salt Wash sandstone member of the Morrison formation.

Description

A. Megascopic

The rock is a yellow fine-grained quartz sandstone with abundant quartz and carnotite crystals visible on the surface.

B. Microscopic

The major constituents are quartz (75%) and carnotite (20%). The quartz grains are subangular, have a glassy luster and bubble inclusions.

The carnotite occurs as rhombic crystals and as small masses associated with flakes of sericite enclosing quartz grains.

The minor constituents (less than 1% each) are sericite in aggregates, hewettite in red-brown masses associated with carnotite, and rutile in well-formed crystals.

C. Age relationships

The association of carnotite with quartz grains indicates the possibility of replacement of the quartz.

<u>Sample 25</u> Calamity No. 13 mine, Gateway area, Mesa County, Colorado.

<u>Rock type</u> Carnotite-bearing sandstone, Salt Wash sandstone member of the Morrison formation.

<u>Description</u>

A. Megascopic

The rock is a yellow, fine-grained, quartz sandstone with carnotite encrustation.

B. Microscopic

The major constituents are quartz (70%) and carnotite (25 to 30%). The quartz grains are subangular and have a glassy luster. The carnotite crystals are growing in radial clumps in association with a dark-appearing hewettite (?).

The minor constituents are sericite ($<3\%$), hewettite (?) ($<1\%$) as dark red-brown flecks in the carnotite, and rutile (?) ($<1\%$).

C. Age relationships

Hewettite in this section may be altering to carnotite.

<u>Sample 61</u> Club mine, Uravan, Montrose County, Colorado.

<u>Rock type</u> Carnotite-bearing sandstone, Salt Wash sandstone member of the Morrison formation.

<u>Description</u>

A. Megascopic

The rock is a yellow-gray, fine-grained, earthy sandstone with carnotite encrustations.

B. Microscopic

The major constituents are quartz (65%) and carnotite (30%). The quartz grains are small, have a glassy luster and bubble inclusions. The carnotite grains and aggregate grains are mixed in fracture fillings with sericitic material.

The minor constituents are sericite (5%), zircon ($<1\%$) in well-developed crystals, and opaque material ($<1\%$; ilmenite and/or magnetite).

C. Age relationships

The carnotite seems to be younger than the sericite. The relationship of the carnotite to the quartz grains indicates the possibility of replacement of the quartz.

Sample 62 Club mine, Uravan, Montrose County, Colorado.

Rock type Carnotite-bearing sandstone, Salt Wash sandstone member of the Morrison formation.

Description

A. Megascopic

The rock is a yellow, very fine grained, quartz sandstone with carnotite encrustations.

B. Microscopic

The major constituents are quartz (60%), calcite (25%), and carnotite (10%). The quartz grains are subrounded, and many are coated with carnotite. The calcite is interstitial and slightly altered. Carnotite occurs as small rhombic plates between quartz and feldspar grains and as microcrystalline material. The minor constituents are sericite (2%) and rounded plagioclase grains (2%) embedded in the calcite matrix.

C. Age relationships

Quartz sandstone was apparently cemented by calcite (replacement of part of sandstone possible). There was later deposition of carnotite, possibly by replacement.

Grains of quartz and feldspar are more rounded in this sample than in the other samples described, possibly indicating more abrasion before deposition.

Sample 63 Club mine, Uravan, Montrose County, Colorado.

Rock type Carnotite-bearing sandstone, Salt Wash sandstone member of the Morrison formation.

Description

A. Megascopic

The rock is a yellow-gray, very fine grained quartz sandstone with carnotite-encrusted grains.

B. Microscopic

The major constituents are quartz (65%) and carnotite (30%). The quartz grains are fractured and slightly altered.

Carnotite occurs both as a coating of rhombic plates on grains of quartz and feldspar and as acicular crystals. The microcrystalline type is also present. The minor constituents are sericite (2%), hewettite (1%), rutile (<1%), and opaque material (1%).

C. Age relationships

The relationship of the carnotite to the quartz in the banded areas suggests that carnotite may have replaced quartz.

Sample 64 Bob Tail mine, Monogram group, Montrose County, Colorado.

Rock type Carnotite-bearing sandstone, Salt Wash sandstone member of the Morrison formation.

Description

A. Megascopic

The rock is a yellow- andgray-banded, medium- to fine-grained, quartz sandstone.

B. Microscopic

The major constituents are quartz (65%) and carnotite (25%). The quartz grains are subrounded, fractured, and have a glassy luster.

Carnotite in the form of rhombic plates and radial aggregates encloses grains of quartz and plagioclase feldspar.

The minor constituents are sericite (5%), altered plagioclase feldspar (<4%), rutile (1%) in very small crystals, and hewettite (1%) in red-brown patches associated with carnotite.

C. Age relationships

Carnotite may be an alteration of hewettite.

APPENDIX 10

Synthesis of Carnotite and Related Compounds

The following procedure was used in the synthesis of the carnotite and related compounds:

1. 0.009 mole of the appropriate carbonate of K, Na, Ca, Sr, or Ba was mixed in a mortar with 0.0045 mole of V_2O_5
2. The mixture was gently sintered at as low a temperature as possible
3. The sintered mass was removed, thoroughly crushed, and mixed and re-sintered. This procedure was repeated three times
4. The sintered mass was dissolved by several treatments with 5 percent HNO_3. The alkali compounds are soluble in water
5. The pH was adjusted to 6 with either dilute HNO_3 or the appropriate hydroxide
6. The volume was adjusted to about 800 cc
7. The solution was heated to boiling and 0.009 mole of hydrous uranyl nitrate dissolved in 100 ml of water added
8. A gelatinous precipitate formed immediately
9. The material was then digested on a steam bath for from 2 to 3 weeks
10. The solution was filtered, and the precipitate was washed and dried at room temperature

APPENDIX 11

Alpha-plate Analysis

Eastman Kodak Nuclear Track Plates, type NTA, are cut to the size of a microscope slide (1-7/8 by 1-1/4 inches). The cut plate is soaked in water to soften the emulsion so that it is better able to trap small grains. About 5 mg of finely divided material (- 200-mesh) is dispersed in water and put in a Petri dish. The NTA plate is immersed emulsion side up in the dish. For five minutes the radioactive material is allowed to settle out on the emulsion of the plate. The plate is then taken out and placed in a vacuum system to remove the excess water, harden the emulsion, and thus trap the material on the plate. A Kodak safelight filter, Wratten Series OA, is used. The exposure given to the plate is based on the radioactivity of the material. Too long an exposure makes the tracks too numerous, and it is hard to locate the source particle; if the exposure is too short, not enough tracks are produced to determine the relative activity of the material. The plate is exposed according to the following scheme:

Percent equivalent U_3O_8	Days exposed
10.0 or over	5
5.0 to 10.0	7
1.0 to 5.0	10
0.51 to 1.0	14
0.1 to 0.51	17
0.0 to 0.1	21

The plates are developed in Kodak developer D-19 at about 20°C. for three minutes and then fixed in hypo at approximately 20°C. for

10 minutes. The plates are studied under a petrographic microscope with an oil-immersion lens (95X) and a 10X ocular which give a magnification of approximately 950 diameters. A medical-type binocular microscope was also used to study the plates.

Methods of viewing through the microscope are extremely fatiguing to the eyes, and only a few hours a day can be spent at the microscope with this high magnification. An alternative method might be to project the field of view on a screen. This method would probably give satisfactory results for long-continued study.

APPENDIX 12

Chemical U_3O_8 Determinations

Purpose

Many chemical determinations for U_3O_8 were made for the purpose of (1) computing the amount of radium that should be in equilibrium with the uranium in the sample, (2) computing the amount of uranium present at the time the enclosing sandstone was deposited, assuming no leaching and late Jurassic deposition, (3) computing the age of the uranium mineral from the lead-uranium ratio, and (4) comparing the chemical and radiometric analyses.

Procedure

The following is a detailed outline of the procedure used under the direction of F. S. Grimaldi, Geological Survey:

1. Weigh 1.0-g sample and transfer to porcelain crucible
2. Add 3 to 5 g $KHSO_4$ and fuse. Heat until mixture appears to be homogeneous
3. Cool. Add enough hot water to remove hardened material from crucible. Rinse crucible's contents with distilled H_2O into 250-ml beaker
4. Add 5 ml of concentrated H_2SO_4 and heat on hot plate for 10 minutes
5. Add distilled H_2O to make solution up to 100 ml. Digest for 10 minutes and set aside for 1 hour
6. Filter off gangue and insoluble sulfates; wash with water

7. Add 17 ml of concentrated HCl to filtrate and adjust the volume of the solution to 170 ml with distilled H_2O
8. Cool solution in ice water until cold
9. Transfer solution to 600-ml separatory funnel
10. Add 100 ml chilled 6% cupferron solution (6 g + 100 ml of H_2O)
11. Shake funnel for a few seconds
12. Add 200 ml of chilled ethyl acetate. Shake for 1 minute
13. Drain H_2O layer into beaker and reserve. Save acetate layer in another beaker
14. Rinse funnel with ethyl acetate and drain it into ethyl acetate beaker
15. (a) Repeat step 12 with the water layer, using 100 ml of chilled ethyl acetate
    (b) Pour ethyl acetate layers together and set aside. Save H_2O layer and set aside
16. Place ethyl acetate layers in separatory funnel; add 50 ml of cold 8% HCl and shake
17. Allow layers to settle. Draw off aqueous layer and save. Reject ethyl acetate layer
18. Wash H_2O layer from step 17 with 50 ml of ethyl acetate in separatory funnel. Save H_2O layer and reject ethyl acetate layer
19. Combine H_2O layers (from steps 15 and 18); place beaker on steam bath and evaporate to one-half its volume
20. Add 20 ml of concentrated HNO_3

21. Evaporate to volume of 25 ml on steam bath
22. Transfer solution to 125-ml Erlenmeyer flask
23. Evaporate solution on hot plate to H_2SO_4 fumes
24. Cover with a small watch glass and fume for 5 minutes
25. Add 1 to 3 ml of fuming HNO_3 and fume for at least 5 minutes (or for a short time after nitrous fumes disappear)
26. Repeat step 25
27. Repeat step 25
28. Cool thoroughly. Dilute to 40 ml and digest on steam bath
29. Filter if necessary. Make volume to 50 ml and cool in ice bath until cold
30. Add 15 ml of cold 6% cupferron solution, and extract 3 times with 50, 25, and 25 ml of cold ethyl acetate, washing as before
31. Evaporate water layer to small volume. Add 15 ml of concentrated HNO_3 and take to fumes of H_2SO_4
32. Repeat steps 25, 26, and 27
33. Add 50 ml of H_2O and take to fumes of H_2SO_4
34. Repeat step 33
35. Repeat step 33. These steps insure the removal of nitrate
36. Add 3 ml of H_2SO_4 and then bring volume up to 100 ml
37. Pass solution through Jones reductor at rate of 40 ml per minute

38. Wash beaker with 15 ml of dilute H_2SO_4 (1 + 19) and then with H_2O
39. Aerate the solution for 5 minutes
40. Titrate with 0.1N $KMnO_4$ (to a pinkish-yellow end point)

Evaluation

The results of the chemical determinations are in sufficiently close agreement to permit their use in equilibrium and age calculations. The analyses which differ are now being rechecked. With one exception the results of the National Bureau of Standards were used when the analyses were in disagreement. By using the lower results the conclusions are modified in degree only. In no instance would the conclusions be materially altered.

The difference in chemical determinations shown in table 14 may be due to one or several of the following factors:

1. Inhomogeneities in the sample
2. Changes in the weight of the sample due to loss or gain of water
3. Differences in chemical procedure
    A. Use of different titrating standards
    B. Variations in aeration methods
    C. Different end points
4. Failure to remove completely
    A. Nitrates
    B. Vanadium
5. Contamination

Table 14.--Chemical U_3O_8 content of high-grade carnotite samples

Sample no.	Percent U_3O_8 [a]	Percent U_3O_8 [b]	Percent U_3O_8 [c]	Weighted percent U_3O_8 average	Percent U average	Theoretical percent U 130 million years ago
1	31.24[d]	32.04	32.13	32.1	27.2	27.8
9	43.78	43.85[d]	44.66	44.7	37.9	38.7
12	23.33	---	23.88	23.6	20.0	20.4
13	36.54	36.52	37.06	36.7	31.1	31.7
19	25.46	25.53	25.91	25.6	21.7	22.1
20	37.79	38.43	38.64	38.5	32.6	33.3
25	36.98	37.95	38.58	38.3	32.5	33.2
28	41.81	42.24	42.46	42.4	36.0	36.7
61	36.00	36.37	38.02	38.0	32.2	32.9
62	17.25	17.47	17.68	17.5	14.8	15.1
63	28.73	31.73	29.88	29.9	25.4	25.9
64	37.35	37.79	40.76	40.8	34.6	35.3

a) Analysts, L. R. Stieff and M. N. Girhard, Geological Survey
b) Analysts, T. W. Stern and M. N. Girhard, Geological Survey
c) Analyst, W. A. Peavy, Jr., National Bureau of Standards; average of two determinations
d) Average of two determinations

APPENDIX 13

Radium Determinations

The radium determinations were made at the National Bureau of Standards by Mr. J. J. Tregoning, Mr. L. L. Stockman, and Mr. W. A. Peavy, Jr., using the following procedure: one-gram sample of the - 200-mesh fraction was dissolved in nitric acid and filtered. The residues were then treated with hydrofluoric acid and fused with sodium carbonate. This material was dissolved in nitric acid and added to the acid leach remaining from the first step.

The solution was then transferred to a flask fitted with a reflux condenser. De-emanation was induced by boiling the solution at a reduced pressure of about one-half atmosphere while nitrogen was bubbled through it for about 20 minutes. The flask was then closed at atmospheric pressure by stopcocks, allowing the radon to collect for a convenient time (usually about one day).

The radon was transferred by reboiling the solution and passing the nitrogen (containing radon) into an evacuated ion chamber. Purification of the nitrogen was accomplished by passing through hot reduced copper to remove oxygen, through Drierite and P_2O_5 to remove water vapor, and through Ascarite to remove CO_2. The radon was allowed to remain in the chamber for at least three hours so that it would come to equilibrium. An amplifier, scaler, and traffic recorder were used to make the count. (The instruments are calibrated by using standard radium solutions.)

The foregoing procedure is described in detail by Curtiss and Davis (1943) of the National Bureau of Standards.

APPENDIX 14

Quantitative Determination of Lead

The procedure for the determination of lead in carnotite used by R. G. Milkey of the Geological Survey consisted of four main steps.

a. Solution of the sample in aqua regia and elimination of insoluble residue

b. Precipitation of lead as the sulfide in 0.3N HCl

c. Solution of the lead sulfide and precipitation of the lead as $PbSO_4$

d. Finally, solution of $PbSO_4$ in ammonium acetate solution and subsequent precipitation of $PbCrO_4$, which was dried at 110°C. and weighed

Detailed Procedure

a. One gram of the ore sample was weighed and deposited in a 100-ml beaker. Twenty ml of aqua regia were added, and the mixture was digested (covered) on the steam bath until vigorous effervescence had ceased. The cover was then replaced by a Speedyvap, and the solution allowed to evaporate to dryness.

Six ml of 1 + 1 HCl were added to the residue, and the sample was digested on the steam bath for 1 to 1½ hours. Thirty ml of H_2O were then added, and after a few minutes, the mixture was filtered through a "slow" filter on a filter funnel equipped with a stopcock in the stem.

H_2SO_3 was added to the filtrate in sufficient amount to obtain a perceptible odor of SO_2. The solution was then boiled until the SO_2 odor was no longer evident. To the insoluble matter on the filter funnel were added 3- to 6-ml portions of hot ammonium acetate solution (20 g NH_4 OAc + 3 ml HOAc per 100 ml of solution), the stopcock closed off, and the liquid allowed to remain in contact with the insoluble matter for a few minutes. These portions of wash solutions were then added to original filtrate. Volume of liquid was then made up to 100 cc. In case basic salts began to precipitate from the solution after the addition of the ammonium acetate solution, enough HCl was added from a dropping bottle to obtain a clear solution.

b. After heating to boiling, the solution in a 150-ml Erlenmeyer flask was gassed with H_2S for 15 minutes. The gas was allowed to flow at a moderate rate, and the rate of bubbling was controlled by inserting a flask of distilled water between the solution and the source of H_2S.

After the metallic sulfides were precipitated, the Erlenmeyer flask was stoppered with a rubber stopper and left overnight.

c. The sulfides were filtered through a "slow" 7-cm filter paper and the flask and filter paper rinsed with 0.3 N HCl saturated with H_2S. After the washing was considered sufficient, the precipitate and filter paper were removed from the funnel, folded, and placed in a 30-ml beaker. To the beaker were added 15 ml of concentrated HNO_3 and 1.5 ml of concentrated H_2SO_4. The solution was then evaporated on the steam bath and later on the hot plate to fumes of H_2SO_4. After strong fumes of sulfuric acid were established, fuming HNO_3 was added by means of a dropper down the sides of the beaker, taking care to keep the beaker well covered. Fuming HNO_3 was added until all of the carbonaceous material and sulfur had been oxidized. Afterward the sides of the beaker and cover were washed down with a stream of water and the solution diluted to 20 ml. Once again the H_2SO_4 solution was evaporated to strong fumes of sulfuric acid and the solution diluted to 20 ml with vigorous stirring. The precipitate of $PbSO_4$ was allowed to stand for several hours.

d. The precipitate of $PbSO_4$ was filtered on a platinum Monroe crucible and washed with a 2-percent solution of H_2SO_4. The crucible was then partly filled with solid ammonium acetate, and hot ammonium acetate solution (20 g $NH_4OAc + 3$ cc HOAc per 100 ml solution) was added to the crucible and allowed to remain in contact with the precipitate for several minutes. Two or at the most three such treatments were sufficient to extract the $PbSO_4$. After the ammonium acetate treatment, some solid residues still remained on the Monroe filter. In order to establish without doubt the completeness of the extraction, a representative sample of this residue for sample 20 was taken for a spectrographic analysis.

Its composition was found to be:

Si - about 3 percent

Pt - about 1 percent

Pb - about 0.01 percent or less

Mg - trace

Al - trace

Fe - trace

The extraction solution was transferred to a 50-ml beaker and adjusted to a volume of 35 to 40 ml. The acidity was adjusted to the end point of methyl red, and 4 to 5 drops of acetic acid added in excess. After heating the solution to gentle boiling, 3 cc of $K_2Cr_2O_7$ solution (3 cc = 0.1 g $K_2Cr_2O_7$) were added and the gentle boiling continued for some minutes. Subsequently, the solution was digested on the steam bath until the precipitate had settled.

After all of the lead sulfate had been extracted by means of the hot saturated solution of NH_4OAc, one further treatment of the residue yielded a solution from which a yellow-chromate precipitate slowly settled after the addition of the $K_2Cr_2O_7$ reagent. Upon heating the solution to boiling, the solid went into solution completely, contrary to the behavior of $PbCrO_4$, and a spectrographic analysis of the material showed the following:

Cr - approximately 50 percent

Pb - 1 to 5 percent

$$\left.\begin{matrix}\text{Fe}\\ \text{Cu}\\ \text{Mg}\\ \text{Si}\end{matrix}\right\}\ \text{trace}$$

In the absence of any cations, it was thought that the solid was composed of $(NH_4)_2CrO_4$, whose solubility was perhaps greatly diminished in a nearly saturated solution of NH_4OAc with HOAc and alcohol from a methyl-red indicator present.

The precipitate of $PbCrO_4$ was filtered on a platinum Monroe crucible, washed with water at room temperature, dried in an oven at 110°C., and weighed.

$$\text{wt.} \times 0.6411 = \%\ \text{Pb}$$

An alternate and quicker method was later used, and results on samples 20, 25, 62, and 63 were found to check with results from the longer procedure. The precipitate of sulfides was filtered through a Monroe platinum crucible. Hot 1 + 1 HNO_3 was then added to the crucible and allowed to remain in contact with the precipitate until all the soluble material present had dissolved.

The solution of lead was then evaporated to dryness on the steam bath to get rid of the nitric acid and the residue extracted with hot 20-percent ammonium acetate and filtered through a fine filter paper. The filtrate was then made slightly acid with acetic acid, and $PbCrO_4$ precipitated.

Table 15.--Lead content of high-grade carnotite samples[a]

Sample	g $PbCrO_4$ per g sample	g $PbCrO_4$ per g sample	g $PbCrO_4$ per g sample	g $PbCrO_4$ per g sample	Recommended average g $PbCrO_4$ per gram sample	g Pb per g sample
1	0.0000	---	---	---	0.0000	0.0000
9	0.0024	---	---	---	0.0024	0.0015
12	0.0000	0.0000	---	---	0.0000	0.0000
13	0.0013	0.0012	---	---	0.00125	0.0008
19	0.0010	0.0008	---	---	0.0009	0.0006
20	0.0025	0.0023	0.0024	---	0.0024	0.0015
25	0.0052	0.0052	0.0057	0.0052	0.0052	0.0033
28	0.0061	0.0059	0.0057	---	0.0059	0.0038
61	0.0052	0.0048	---	---	0.0050	0.0032
62	0.0052	0.0055	0.0048	0.0049	0.0051	0.0033
63	0.0046	0.0045	0.0051	0.0054	0.0049	0.0031
64[b]	0.0021	0.0022	---	---	0.00215	0.0014

a) Analyst, R. G. Milkey, Geological Survey
b) Second separation of sample 64

APPENDIX 15

Spectrographic Analysis

Purpose

The high-grade carnotite samples were analyzed spectrographically for elements which might interfere with the quantitative lead determinations.

Procedure

Mr. K. J. Murata of the Geological Survey made the analyses with a large Jarrell-Ash spectrograph. A 15,000 line per inch grating with a dispersion of 5A per mm in the first order was used in the region of 2280 A to 4600 A. Eastman type III-O plates were used. The plates were evaluated by visual and densitometric methods.

Standards were prepared for each element in amounts of 1 percent, 0.1 percent, and 0.01 percent. Oxides of the elements were used for these standards. The material was analyzed for the following elements: Cu, Ag, As, Pb, Mn, Mo, Zn, Co, Ni, Bi, Sn, Sb, Tl, and Hg. Both the samples and the standards were burned to completion in the d. c. arc operated at 16 amperes. Before arcing, the samples and the standards were mixed with carbon in the proportion of one to one.

The analyses are given in table 16. The possible interfering elements were not found in sufficient amounts to require specific modification of the analytical method used.

Future Program

A complete spectrographic analysis should be made of all the samples. Information on the elements which occur in trace emounts would be useful in recognizing similar source areas for the carnotite and in interpreting the effects of weathering and leaching.

Table 18. Results of spectrographic analyses
in carnotite and related minerals (in percent)

Dashes in the columns mean not detected

Sample no.	Cu	Ag	As	Pb	Mn	Mo	Zn	Co	Ni
1	0.0X	---	---	---	0.X	0.00X	---	0.X	0.0X
9	---	---	---	0.0X	---	---	---	---	---
12	0.0X	---	0.0X	0.0X	---	---	---	---	---
13	---	---	---	0.X	---	0.0X	---	---	---
19	0.X	---	0.0X	0.X	0.00X	0.00X	0.X	---	---
20	0.X	---	---	0.X	---	---	---	---	---
25	0.00X	---	0.0X	0.X	---	---	---	0.0X	0.0X
28	---	---	0.0X	0.X	---	---	---	---	---
61	0.X	0.00X	0.X	0.X	0.0X	---	0.X	0.0X	0.0X
62	0.X	0.00X	0.X	0.X	0.X	---	0.X	0.X	0.X
63	0.0X	0.00X	0.X	0.X	0.00X	---	0.X	0.0X	0.0X
64	0.0X	---	0.0X	~~0.0X~~	---	---	---	---	---
Limit	(0.003)	(0.0005)	(0.05)	(0.01)	(0.005)	(0.005)	(0.1)	(0.01)	(0.01)

The following elements were looked for but not found: Bi (0.05), Sn (0.01), Sb (0.1), Tl (0.5), and Hg (1.0). Figures in parentheses are lower limits of detection for this material and are in general higher than for non-uranium-bearing materials.

APPENDIX 16

Radiometric Determinations

Purpose.--Radiometric determinations for percentage equivalent U_3O_8 were made to study the factors influencing the emanating power of the high-grade carnotite samples and to establish by a simple and rapid means the extent to which the radium in the samples is in radioactive equilibrium with uranium. In addition, the results obtained have aided in the selection of the best method of chemical analysis for the particular sample.

Procedure.--Ten grams of the - 200-mesh material were compressed by a pressure of about 8,000 to 10,000 pounds per square inch into a cylindrical pellet one inch in diameter and approximately 0.3 inch thick. This pellet was then accurately positioned by means of an adjustable platform in a lead chamber, and an aluminum filter was placed between the material and the Geiger-Müller counter. Primary alpha and beta particles were absorbed by the aluminum filter. The time required to count a predetermined number of gamma photons was accurately recorded. Percentage equivalent U_3O_8 was computed by comparison with the counting rate of pitchblende samples that were known to be in equilibrium (Rodden, 1949, p. 327).

Table 17 contains the results of seven sets of percentage equivalent U_3O_8 determinations by Mr. Imirie, National Bureau of Standards. A comparison of the chemical U_3O_8 and the highest percentage equivalent U_3O_8 determinations is given in table 18. A comparison of the highest percentage equivalent U_3O_8 and the U_3O_8 in equilibrium with the radium in the samples is given in table 19. A sample of the calculations used in preparing tables 18 and 19 is given in appendix 18.

Discussion.--Radiometric determinations for U_3O_8 standardized against pitchblende should agree with the chemical determinations of U_3O_8 if the two following conditions can be satisfied:

1. The emanating power of the samples is zero.
2. The samples are in radium-uranium equilibrium.

1. The emanating power (Hahn, 1936, p. 191) of a radioactive substance has been defined as the ratio of the amount of emanation escaping spontaneously from the substance to the total amount of emanation formed in the substance. This ratio varies with the mineral, surface area, temperature, and the pressure and relative humidity (Hahn, 1936, pp. 205-229). Radon and its isotopes are the daughter products which escape by emanation from a radioactive substance.

The variations in the percentage equivalent U_3O_8 determinations shown in table 17 are, in general, systematic and are greater than those which could be attributed to the instrumental error of ± 2 percent. Systematic observational or mathematical errors were not found. The differences in count per minute with respect to changes in humidity conditions under which the samples were stored could not be a result of the lack of radium-uranium equilibrium. However, a loss of radon with changes in the state of hydration of the carnotite could explain the differences shown in table 17.

For the following reasons it is thought that the differences in the count per minute with changes in humidity are a measure of the emanating power of the samples. First, carnotite and its analogues are noted for the fact that their water content varies from day to day with changes in the temperature or humidity (Hillebrand, 1924, p. 205). The solubility of radon in water is greater than that of any other noble gas. Finally, Mr. J. T. Bracken and Mr. W. R. Champion measured the alpha-particle activity of water exposed to emanation from a pellet of high-grade carnotite, and their results suggest that the alpha activity was largely produced by radon and actinon.

A strong correlation exists between the maximum difference in equivalent U_3O_8 for any one sample and its chemical composition. The samples which contain the smallest amounts of potassium and which therefore contain the least carnotite (see appendix 5) have the greatest differences in count. The published analyses of carnotite and tyuyamunite show that tyuyamunite contains at least twice as much water as does carnotite (appendix 6). The behavior of these analogues of carnotite suggeststhat the rapid emanation of radon is in some way related to their crystal structure and high water content. The maximum difference in equivalent U_3O_8 with changes in humidity of crystalline carnotite (sample 1) is slightly less than the maximum difference in count of such microcrystalline samples as 28 or 61. This agrees with the predicted increase of emanating power as the particle size decreases.

2. By controlling the humidity (and the emanating power) it is possible to increase markedly the counts per minute of many of the high-grade samples. The remaining difference (table 18) between the maximum count and the chemically determined U_3O_8 was assumed to be due to the

lack of radium-uranium equilibrium. This assumption was tested by computing the amount of uranium which would be in equilibrium with the radium in the samples, as determined by the National Bureau of Standards, and comparing these amounts with the maximum equivalent U_3O_8 determinations. (See table 19.)

The good agreement between columns 2 and 3 of table 19 for samples 13, 19, 20, 28, and 63 suggests that the remaining difference was due to the lack of radium-uranium equilibrium. The somewhat greater differences for samples 25, 61, and 64 may be due to small cumulative instrumental errors or to the count contributed by the uranium in excess of the uranium in equilibrium with the radium in the samples. If the radium analyses for samples 1,9,12, and 62 are correct, some other phenomenon is needed to explain these large deficiencies.

<u>Evaluation</u>.-- A study of the variation in count of small samples with changes in humidity indicates that the effects of emanating power on the determination of equivalent U_3O_8 cannot be ignored. In addition, the assumption that small samples of carnotite are in radium-uranium equilibrium is known to be incorrect. Therefore, equivalent U_3O_8 determinations which are not corrected for these two factors will not give accurate indications of the actual U_3O_8 content of the sample.

The radiometric study of the high-grade samples also suggests that a simple and rapid method of determining the approximate radium content may be developed by counting solid samples. The radium content of the samples may be computed from the equivalent U_3O_8 determinations if the emanating power of the material has been minimized and if samples are compared to material known to be in radium-uranium equilibrium.

Table 17.--Variation of count of high-grade carnotite samples with humidity (figures in percentage equivalent U_3O_8)

Date counted	11/4/48	12/1/48	12/28/48	12/30/48	2/7/49	2/9/49	2/10/49
Conditions	In laboratory, not covered	In laboratory, not covered	In laboratory, not covered	In desiccator over H_2O for 2 days	In desiccator over $CaCl_2$ for 39 days	In desiccator over $CaCl_2$ for 2 days	In desiccator over H_2O for 1 day
Sample no.							
1	18.5	18.6	18.9	18.6	19.6	20.0	19.2
9	26.0	25.9	28.5	25.7	33.2	33.9	28.5
12	11.3	11.0	11.0	11.2	17.2	12.4	11.8
13	27.3	27.2	28.0	26.9	29.7	30.1	28.0
19	20.5	19.1	21.3	18.9	24.7	25.4	20.6
20	32.9	30.9	34.4	31.3	38.3	39.7	34.0
25	32.9	31.7	32.5	31.5	33.7	35.3	32.6
28	34.6	34.2	35.5	33.8	37.5	39.0	35.9
61	29.4	30.9	31.5	30.6	32.6	33.3	31.4
62	15.2	14.1	14.5	14.1	15.1	15.4	14.5
63	25.0	23.8	24.4	23.5	25.7	25.7	24.0
64	18.4	19.5	26.2	20.5	32.2	32.9	25.2

Table 18.--Difference between highest equivalent U_3O_8 and chemical U_3O_8

Sample no.	Highest equivalent U_3O_8 (in percent)	Chemical U_3O_8 (in percent)	Difference chemical-radiometric	Difference (in percent)
1	20.0	32.1	12.1	38
9	33.9	44.7	10.8	24
12	12.4	23.6	11.2	47
13	30.1	36.7	6.6	18
19	25.4	25.6	0.2	0.8
20	39.7	38.5	excess 1.2	excess 3
25	35.3	38.3	3.0	8
28	39.0	42.4	3.4	8
61	33.3	38.0	4.7	12
62	15.4	17.5	2.1	12
63	25.7	29.9	4.2	14
64	32.9	40.8	7.9	19

Table 19.--Comparison of the percentage U_3O_8 determined chemically, the percentage equivalent U_3O_8, and the percentage U_3O_8 in equilibrium with the radium in the samples

	Column 1	Column 2	Column 3
Sample no.	Weighted U_3O_8, chemical	U_3O_8 in equilibrium with Ra present	Highest equivalent U_3O_8, counter
1	32.1	9.2	20.0
9	44.7	27.1	33.9
12	23.6	1.6	12.4
13	36.7	30.3	30.1
19	25.6	26.1	25.4
20	38.5	40.1	39.7
25	38.3	37.6	35.3
28	42.4	39.4	39.0
61	38.0	30.7	33.3
62	17.5	6.3	15.4
63	29.9	25.5	25.7
64	40.8	30.1	32.9

APPENDIX 17

Lead-isotope Determinations

The lead-isotope determinations were made in the Schenectady Laboratory of the General Electric Company by Mr. G. P. Schacher.

The procedure used in the isotopic determination of the carnotite leads was divided into two main parts:

1. The extraction of the lead from the sample and the preparation of lead iodide
2. The analysis of the lead iodide in the General Electric mass spectrograph

The lead iodide samples were prepared by Irving May of the Geological Survey.

The preparation of lead iodide was completed in seven operations (glass-distilled water and reagents were used).

1. Solution of the sample in concentrated HNO_3
2. Precipitation of $PbSO_4$ from a dilute solution of H_2SO_4 after removal of nitrates by fuming with H_2SO_4
3. Leaching of the $PbSO_4$ with acetic acid and ammonium-acetate solutions
4. Precipitation of PbS from the leach
5. Digestion of PbS in 1 to 1 HNO_3 followed by filtering and evaporation to dryness
6. Lead salts converted to PbI_2 in small volume of cold KI solution

7. PbI_2 washed and dried at 110°C.

The isotopic analyses of the lead iodides were made on the General Electric mass spectrograph. This spectrograph is similar in design to the 60-degree mass spectrometer first made by A. O. Nier.

A small glass tube containing approximately 1 mg of PbI_2 was sealed to the sample inlet of the spectrograph tube. The pressure in the tube was reduced to less than 10^{-5} mm of mercury. The tube was allowed to pump until the mercury vapors from the diffusion pump, which included the Hg^{204} isotope, had almost disappeared. The temperature of the sample was then raised to approximately 320°C. (the temperature of the spectrometer tube) and 15°C. above the melting point of PbI_2. At this temperature, some PbI_2 vapor could pass into the spectrometer tube without condensing. The isotopic analyses were repeated until reproducible results were obtained.

The spectrograph is cleaned by baking and by flushing the tube with iodine vapors.

APPENDIX 18

Sample Calculations

Sample calculation for radioactive equilibrium computed from chemical U_3O_8 content and radiometric percentage equivalent U_3O_8 content

For sample 1

Highest percent equivalent U_3O_8 content $= 20.0\%$

Chemical U_3O_8 content $= 32.1\%$

Difference chemical - counter $= 12.1\%$

$$\text{Percentage difference} = \frac{12.1}{32.1} \times 100 = 38\%$$

Sample calculation for chemical U_3O_8 content of high-grade carnotite sample

For sample 1

Chemical U_3O_8 content $= 31.24\%$

Chemical U_3O_8 content $= 32.04\%$

Chemical U_3O_8 content $= 32.13\%$

The 31.24% is believed to be in error as two analyses by the National Bureau of Standards and one by the Geological Survey gave markedly higher results. A weighted average of 32.1% was selected.

Sample calculation for percent U from percentage U_3O_8 and amount of uranium present 130 million years ago

Gravimetric factor U_3O_8 to U = 0.84802

$32.1 \times 0.84802 = 27.2\%U$

$n = n_o e^{-\lambda t}$

$\lambda = \frac{\ln 2}{T} = \frac{0.693}{T}$ (Mattauch and Fluegg, 1946)

where n = amount of U at time of analysis = 0.272 g U/g sample

n_o = amount of U initially present

T = half-life of $U^{238} = 4.51 \times 10^9$ years

λ = decay constant

t = assumed age of mineral = 13×10^7 years

All logarithms are natural (naperian) logarithms.

$$\lambda = \frac{0.693}{4.51 \times 10^9} = 0.154 \times 10^{-9}/\text{year}$$

$$n = n_o e^{-\lambda t}$$

$$\ln n = \ln n_o - \lambda t$$

$$\ln n_o = \lambda t + \ln n$$

$$\ln n_o = (0.154 \times 10^{-9})(13 \times 10^7) + \ln 0.272$$

$$\ln n_o = 2.002 \times 10^{-2} + (-1.30195)$$

$$\ln n_o = -1.28193$$

$$n_o = \underline{\underline{27.8\%\ U}}$$

Sample calculation for radium content and equilibrium conditions

For sample 1

Average percent U = 27.2% = 0.272 g U/g sample

One g U contains 3.32×10^{-7} g Ra when in equilibrium

Therefore, $(0.272)(3.32 \times 10^{-7}) = \underline{\underline{9.03 \times 10^{-8} \text{ g Ra/g sample}}}$

Experimental radium determined by the National Bureau of Standards = 2.60×10^{-8} g Ra/g sample. Difference between theoretical and experimental radium content:

$(9.03 \times 10^{-8}) - (2.60 \times 10^{-8}) = 6.43 \times 10^{-8}$ g Ra/g sample.

The equilibrium conditions may be determined by:

$$\frac{(\text{Theoretical Ra content}) - (\text{Experimental Ra content})}{\text{Theoretical Ra content}} \times 100$$

expressed in percentage.

Thus, $\dfrac{6.43 \times 10^{-8}}{9.03 \times 10^{-8}} \times 100 = \underline{\underline{71\%}}$

Sample calculation for percentage U and U_3O_8 in radioactive equilibrium with the radium in the sample

For sample 1

g Ra/g sample = 2.60×10^{-8}

g Ra in equilibrium with 1 g U = 3.32×10^{-7}

Thus, $3.32 \times 10^{-7} : 1.0 \text{ g U} = 2.60 \times 10^{-8} : X \text{ g U}$

$X \text{ g U} = \dfrac{2.60 \times 10^{-8}}{3.32 \times 10^{-7}} = 0.0783 \text{ g U} = \underline{\underline{7.83\% \text{ U}}}$

Gravimetric factor U to U_3O_8 = 1.1792

$0.0783 \times 1.1792 = 0.0923 \text{ g } U_3O_8\text{/g sample} = \underline{\underline{9.23\% \ U_3O_8}}$

Sample calculation for lead content of high-grade carnotite sample

For sample 20

g $PbCrO_4$/g sample = 0.0025, 0.0023, and 0.0024

Recommended average g $PbCrO_4$/g sample = 0.0024

Gravimetric factor $PbCrO_4$ to Pb = 0.6411

So (0.0024) (0.6411) = $\underline{\underline{0.0015 \text{ g Pb/g sample}}}$

Sample calculation for correcting for common (nonradiogenic) lead

$$\frac{\text{Abundance Pb}^{208}}{\text{Abundance Pb}^{204}} = \frac{52.29}{1.5} = 34.9$$

$$\frac{\text{Abundance Pb}^{207}}{\text{Abundance Pb}^{204}} = \frac{22.64}{1.5} = 15.1$$

$$\frac{\text{Abundance Pb}^{206}}{\text{Abundance Pb}^{204}} = \frac{23.59}{1.5} = 15.7$$

Isotopic-abundance ratios for sample 20

Pb^{204} = 0.1

Pb^{206} = 87.3

Pb^{207} = 6.5

Pb^{208} = 6.0

As Pb^{204} is nonradiogenic lead, a correction for Pb^{206}, Pb^{207}, and Pb^{208} may be made by subtracting proportional quantities from the Pb^{206}, Pb^{207}, and Pb^{208} isotopic-abundance ratios.

For Pb^{206}	For Pb^{207}	For Pb^{208}
87.3	6.5	6.0
- 1.6	- 1.5	- 3.5
85.7	5.0	2.5

Recasting these isotopic-abundance ratios on basis of 100%

$85.7 + 5.0 + 2.5 = 93.2$

$$\frac{85.7}{93.2} \times 100 = \underline{\underline{92.0}};\ \frac{5.0}{93.2} \times 100 = \underline{\underline{5.3}};\ \frac{2.5}{93.2} \times 100 = \underline{\underline{2.7}}$$

Therefore the corrected isotopic-abundance ratios are:

$Pb^{206} = 92.0\%$

$Pb^{207} = 5.3\%$

$Pb^{208} = \underline{2.7\%}$

$\phantom{Pb^{208} =} 100.0\%$

Sample calculation for age of carnotite on basis of Pb^{206}/U^{238}, Pb^{207}/U^{235}, and Pb^{207}/Pb^{206}

For sample 20, Pb^{206}/U^{238}

0.0014 g Pb/g sample (radiogenic)

Isotopic abundance for $Pb^{206} = 92.0\%$

g U/g sample $= 0.326$

Isotopic-abundance ratio for $U^{238} = 99.3\%$

$$\frac{Pb^{206}}{U^{238}} = \frac{(0.0014)\ (0.920)}{(0.326)\ (0.993)} = \frac{0.00129}{0.324} = 0.00398$$

Enter nomograph Pb^{206}/U^{238} by Wickman (1939, p.7) and opposite 3.98×10^{-3} read <u>30.0 million years</u>.

For sample 20, Pb^{207}/U^{235}

$$\lambda_{235} = \frac{\ln 2}{T} \quad \text{where } T = \text{half-life}, \ln 2 = 0.69315$$

$$\lambda_{235} = \frac{0.69315}{7.07 \times 10^8} = 0.098 \times 10^{-8}/\text{ year}$$

$U = 32.6\%$ Abundance ratio for $U^{235} = 0.72\%$

$U^{235} = (32.6)\ (0.0072) = 0.2347\%$

Pb = 0.0015 g/g sample but 6.8% is common lead, so

(0.0015 g) (0.068) = 0.000102 g; 0.0015 g -0.0001 g =

0.0014 g radiogenic lead

g Pb^{207} = (0.0014) (isotopic ratio for Pb^{207})

(0.0014) (0.053) = 0.0000742 g Pb^{207}

Then,

$207 : 6.02 \times 10^{23} = 0.0000742 : x$

where x = number of atoms of Pb^{207}

$x = 2.158 \times 10^{17}$ atoms of Pb^{207}

Also,

$235 : 6.02 \times 10^{23} = y : 2.158 \times 10^{17}$

where y = g U^{235}

y = 0.00008424 g U^{235}

U^{235} now present = 0.002347 g

U^{235} transformed to Pb^{207} = 0.0000842 g

U^{235} originally present = 0.0024312 g

$$u_o = ue^{\lambda t}$$

where u_o = weight of U^{235} initially present

u = weight of U^{235} at time of analysis

λ = disintegration constant for U^{235}

t = age of mineral

All logarithms are natural (naperian) logarithms.

$$t = \frac{\ln u_0 - \ln u}{\lambda}$$

$$t = \frac{(-1.41469) - (-1.44817)}{0.098 \times 10^{-8}}$$

$$t = 34.2 \times 10^6 = \underline{\underline{34.2 \text{ million years}}}$$

For sample 20, Pb^{207}/Pb^{206}

Isotopic ratio Pb^{207}/isotopic ratio Pb^{206}

$5.3/92.0 = 0.0576$

Enter Wickman (1939, p. 8) nomograph for Pb^{207}/Pb^{206} and opposite 0.0576 read $\underline{\underline{\text{520 million years}}}$.

REFERENCES CITED

Boltwood, B. B., 1904, On the ratio of radium to uranium in some minerals: Am. Jour. Sci., 4th ser., vol. 18, pp. 97-103.

_________, 1908, On the radioactivity of uranium minerals: Am. Jour. Sci., 4th ser., vol. 25, pp. 269-298.

Butler, B. S., 1920, The ore deposits of Utah: U. S. Geol. Survey Prof. Paper 111.

Crook, T., and Blake, G. S., 1910, On carnotite and an associated mineral complex from South Australia: Mineralog. Mag., vol. 15, pp. 271-284.

Curtiss, L. F, and Davis, F. L., 1943, A counting method for the determination of small amounts of radium and radon: Nat. Bur. Standards Research Paper RP 1557.

Dunning, J. R., 1949, Atomic structure and energy: Am. Scientist, vol. 37, p. 511.

Fischer, R. P., 1942, Vanadium deposits of Colorado and Utah: U. S. Geol. Survey Bull. 936-P, pp. 363-394.

_________, 1949, Origin of the Colorado Plateau vanadium deposits: Abstr., Washington Acad. Sci. Jour., vol. 39, p. 109.

_________, 1950, Uranium-bearing sandstone deposits of the Colorado Plateau: Econ. Geology, vol. 45, pp. 1-11.

Friedel, Charles, and Cumenge, E., 1899, Sur une nouvelle espéce minérale, la carnotite: Soc. chim. Paris Bull., 3d, ser., vol. 21, pp. 328-331.

Gleditsch, Ellen, 1911, Sur le rapport entre l'uranium et le radium dans les minéraux actifs: Le Radium, tome 8, pp. 256-273.

Goldschmidt, V. M., 1924, Über die Umwandlung krystallisierter Minerale in den metamikten Zustand (Isotropisierung): Videns. Skrift. I. Mat.-nat. Kl. Kristiania, no. 5, pp. 51-58.

Hahn, Otto, 1936, Applied radiochemistry, Ithaca, Cornell Univ. Press.

Hess, F. L., 1914, A hypothesis for the origin of the carnotite deposits of Utah and Colorado: Washington Acad. Sci. Jour., vol. 4, p. 236.

_________, 1922, Uranium-bearing asphaltite sediments of Utah: Eng. and Min. Jour-Press, vol. 114, p. 274.

_________, 1925, New and known minerals from the Utah-Colorado carnotite region: U. S. Geol. Survey Bull. 750, pp. 63-78.

_________, and Foshag, W. F., 1927, Crystalline carnotite from Utah: U. S. Nat. Mus. Proc., vol. 72, art. 12, pp. 1-6.

Hillebrand, W. F., 1924, Carnotite and tyuyamunite and their ores in Colorado and Utah: Am. Jour. Sci., 5th ser., vol. 8, p. 209.

Hodgman, C. D., 1949, Handbook of chemistry and physics, Cleveland, Chemical Rubber Publishing Co.

Holmes, Arthur, 1931, Age of the earth: Nat. Research Council Bull. 80, pp. 124-459.

_________, 1947, The age of the earth: Endeavour, vol. 4.

_________, 1948, The construction of a geological time-scale, in Marble, J. P., Chairman, Rept. Comm. Geol. Time 1946-1947, Nat. Research Council, pp. 39-46.

Kovarik, A. F., 1931, Age of the earth: Nat. Research Council Bull. 80, pp. 73-123.

Larsen, E. S., and Berman, Harry, 1934, The microscopic determination of the nonopaque minerals: U. S. Geol. Survey Bull. 848, pp. 1-266.

Lind, S. C., and Whittemore, C. F., 1915, The radium-uranium ratio in carnotites: U. S. Bur. Mines Tech. Paper 88, pp. 1-28.

McCoy, H. N., 1904, Ueber das Entstehen des Radiums: Ber. Deutsch. Chem. Gesell., Jahrg. 37, Bd. 4, pp. 2641-2656.

__________, 1905, Radioactivity as an atomic property: Am. Chem. Soc. Jour. vol. 27, p. 391.

Marckwald, W., and Russell, A. S., 1911a, Über den Radiumgehalt einiger Uranerze: Ber. Deutsch. Chem. Gesell., Jahrg. 44, Bd. 1, p. 771.

__________, 1911b, Über den Radium-gehalt von Uranerzen: Jahrb. Radioakt. Elektronik, Bd. 8, p. 457.

Mattauch, J., and Fluegge, Siegfried, 1946, Nuclear physics tables and an introduction to nuclear physics, New York, Interscience Publishers, Inc.

Melkov, V. G., 1945, Oe iranovanadate igh medorozhdenia Mayli-Sy v. Kergizhud: Soc. russe Minéralogie Mem., vol. 74, p. 47.

Nier, A. O., 1938, Variations in the relative abundance of the isotopes of common lead from various sources: Am. Chem. Soc. Jour., vol. 60, pp. 1571-1576.

__________, 1939a, The isotopic constitution of uranium and the half-lives of the uranium isotopes. I: Phys. Rev., vol. 55, pp. 150-153.

__________, 1939b, The isotopic constitution of radiogenic leads and the measurement of geological time. II: Phys. Rev., vol. 55, pp. 153-163.

Pollard, Ernest, and Davidson, W. L., Jr., 1946, Applied nuclear physics, New York, John Wiley and Sons.

Ransome, F. L., and Hillebrand, W. F., 1905, On carnotite and associated vanadiferous minerals in Western Colorado: U. S. Geol. Survey Bull. 262, pp. 9-31.

Richards, T. W., and Lembert, M. E., 1914, The atomic weight of lead of radioactive origin: Am. Chem. Soc. Jour., vol. 36, pp. 1329-1344.

__________, and Wadsworth, Charles, 3d, 1916, Further study of the atomic weight of lead of radioactive origin: Am. Chem. Soc. Jour., vol. 38, pp. 2613-2622.

Rodden, C. J., 1949, Determination of naturally occurring radioactive elements: Anal. Chemistry, vol. 21, pp. 327-338.

Rose, J. L., and Stranathan, R. K., 1936, Geological time and isotopic constitution of radiogenic lead: Phys. Rev., vol. 50, pp. 792-796.

Sloss, L. L., and Feray, D. E., 1948, Microstylolites in sandstone: Jour. Sedimentary Petrology, vol. 18, pp. 3-13.

Shimkin, D. B., 1949, Uranium deposits in the USSR: Science, new ser., vol. 109, pp. 58-60.

Webber, B. N., 1947, Geology and ore resources of uranium-vanadium depositional province of the Colorado Plateau region.

Wickman, F. E., 1939, Some graphs on the calculation of geological age: Sveriges geol. undersökning, arsbok 33, pp. 1-8.

__________, 1942, On the emanating power and the measurement of geological time: Geol. fören. förhandl., Bd. 64, pp. 465-476.

Yagoda, Herman, 1949, Radioactivity measurements with nuclear emulsions, New York, John Wiley and Sons.