

200)  
67x  
no. 645

SYNTHESIS AND PROPERTIES OF  
CARNOTITE AND ITS ALKALI ANALOGUES

By Paul B. Barton, Jr.

---

Trace Elements Investigations Report 645

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY





(200)  
7672

Copy 1  
IN REPLY REFER TO:

UNITED STATES  
DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY  
WASHINGTON 25, D. C.

February 27, 1958

AEC-397/8

Mr. Robert D. Nininger  
Assistant Director for Exploration  
Division of Raw Materials  
U. S. Atomic Energy Commission  
Washington 25, D. C.

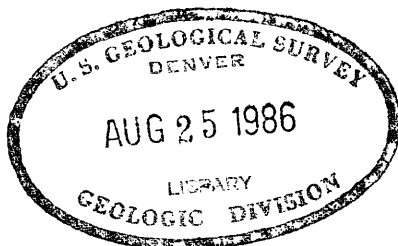
Dear Bob:

Transmitted herewith are three copies of TEI-645, "Synthesis and properties of carnotite and its alkali analogues," by Paul B. Barton, Jr., December 1957.

We plan to submit this report for publication in American Mineralogist.

Sincerely yours,

John H. Eric  
for W. H. Bradley  
Chief Geologist



JAN 25 2001

Geology and Mineralogy

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

SYNTHESIS AND PROPERTIES OF CARNOTITE AND ITS ALKALI ANALOGUES\*

By

Paul B. Barton, Jr.

December 1957

Trace Elements Investigations Report 645

This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.



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

USGS - TEI-645

## GEOLOGY AND MINERALOGY

<u>Distribution</u>	<u>No. of copies</u>
Division of Raw Materials, Albuquerque.....	1
Division of Raw Materials, Austin.....	1
Division of Raw Materials, Casper.....	1
Division of Raw Materials, Denver.....	1
Division of Raw Materials, Rapid City.....	1
Division of Raw Materials, Salt Lake City.....	1
Division of Raw Materials, Spokane.....	1
Division of Raw Materials, Washington.....	3
Exploration Division, Grand Junction Operations Office.....	6
Grand Junction Operations Office.....	1
Technical Information Service Extension, Oak Ridge.....	6
U. S. Geological Survey:	
Foreign Geology Branch, Washington.....	1
Fuels Branch, Washington.....	1
Geochemistry and Petrology Branch, Washington.....	12
Geophysics Branch, Washington.....	1
Mineral Deposits Branch, Washington.....	1
A. L. Brokaw, Grand Junction.....	2
N. M. Denson, Denver.....	1
R. L. Griggs, Albuquerque.....	1
W. R. Keefer, Laramie.....	1
H. W. Lakin, Denver.....	1
E. M. MacKevett, Menlo Park.....	1
L. R. Page, Washington.....	1
P. K. Sims, Denver.....	1
Q. D. Singewald, Beltsville.....	1
A. E. Weissenborn, Spokane.....	1
D. E. White, Menlo Park.....	1
TEPCO, Denver.....	2
TEPCO, RPS, Washington, (including master) .....	2

## CONTENTS

	Page
Abstract.....	4
Introduction.....	5
Previous work on synthesis.....	5
Precipitation of carnotite from aqueous solutions.....	7
Crystal chemistry.....	15
Synthesis.....	17
Aqueous methods.....	17
Fusion methods.....	20
Properties of carnotite and related compounds.....	25
Acknowledgments.....	32
References.....	33

## ILLUSTRATION

Figure 1. Relation of rate of precipitation of carnotite to concentration of various pentavalent vanadium species..	10
---	----

## TABLES

Table 1. Summary of fusion experiments.....	23
2. Unit-cell data for carnotite and related compounds.....	26
3. X-ray powder data for carnotite and its alkali analogues	28
4. Optical data for synthetic compounds related to carnotite	32

## SYNTHESIS AND PROPERTIES OF CARNOTITE AND ITS ALKALI ANALOGUES

By Paul B. Barton, Jr.

## ABSTRACT

Carnotite and its Na, Rb, Tl, Cs, and  $\text{H}_3\text{O}(\text{?})$  analogues have been synthesized in several different ways in attempts to obtain crystals suitable for single crystal structural investigations. Aqueous methods failed to produce usable crystals, but a simple fusion technique using metavanadate fluxes proved highly satisfactory. Work in progress by D. E. Appleman has shown that carnotite is composed of  $[(\text{UO}_2)_2\text{V}_2\text{O}_8]_{n-2n}$  layers bound together by alkali ions with or without water. Studies of the rate of precipitation of carnotite from aqueous solution as a function of pH suggest that the reaction involves interaction between uranyl, alkali, and metavanadate ( $\text{V}_4\text{O}_{12}^{-4}$ ) ions, though this is not the only possible interpretation of the data. The X-ray and optical properties of the synthetic compounds are presented. The similarity of the a and b dimensions in metatyuyamunite, sengierite, and the alkali analogues of carnotite shows that the same  $[(\text{UO}_2)_2\text{V}_2\text{O}_8]_{n-2n}$  layer is present in all of these compounds. The Na analogue of carnotite is less stable than the other carnotites, and it is not expected that the pure Na variety would occur in nature.

## INTRODUCTION

This report records the results of experiments dealing with the synthesis of carnotite and its alkali analogues. The work was primarily concerned with the preparation of single crystals suitable for detailed structural analysis, though some insight into the chemistry of the precipitation of carnotite was obtained.

## PREVIOUS WORK ON SYNTHESIS

Carnotite is named for M. Adolphe Carnot, French chemist and mining engineer. Carnot (1887) unknowingly synthesized the ammonium analogue of carnotite when he noted that uranyl salts quantitatively precipitate vanadate from aqueous solution as ammonium uranyl vanadate. The mineral was not described until 1899.

Canneri and Pestelli (1924) synthesized anhydrous carnotite,  $K_2(UO_2)_2V_2O_8$ , and anhydrous sodium carnotite,  $Na_2(UO_2)_2V_2O_8$ , by fusing a uranyl salt with an excess of the appropriate alkali metavanadate. Their chemical analyses show that the compound is equivalent to anhydrous carnotite. Canneri and Pestelli obtained well developed, diamond-shaped, platy crystals which they reported to be fluorescent. It was suggested that the crystals were orthorhombic, but no X-ray or morphological work was done. They proposed that the crystals were salts of a uranovanadic anion,  $(UO_2VO_4)^{-1}$ .

Hillebrand (1924) formed carnotite by exchanging the calcium in tyuyamunite,  $Ca(UO_2)_2V_2O_8 \cdot nH_2O$ , for potassium in a potassium-mercuric iodide solution.

Sundberg and Sillén (1949) followed the vanadate fusion procedure of Canneri and Pestelli; but, because Sundberg and Sillén were unable to obtain sufficiently large crystals by this method, they fused a mixture of potassium carbonate, vanadium pentoxide and ammonium uranate (diuranate?) in an excess of potassium carbonate. After slow cooling the resulting crystals were washed free of the flux with water and dilute nitric acid and were then used for the determination of the preliminary structure of  $KUO_2VO_4$ . Sundberg and Sillén also recorded the formation of at least one other potassium-uranium-vanadium phase, but they did not define it.

Murata, Cisney, Stieff, and Zworykin (1950) studied base exchange among the potassium, barium, calcium, strontium, and sodium analogues of carnotite and tyuyamunite. They mixed solutions of alkali or alkaline earth pyrovanadates with solutions of uranyl nitrate; the pH was adjusted to 6 with varying amounts of the oxide or hydroxide of the alkali or alkaline earth used. Following the development of the precipitate the pH was lowered to 3 and the preparation was digested for two weeks on a steam bath. Platy crystals of the calcium preparation, that is, tyuyamunite, were visible under the optical microscope; the other preparations showed crystals only under the electron microscope.

Morachevskii and Belyaeva (1956) revived the idea of Canneri and Pestelli (1924) of a uranovanadic anion. By spectrophotometric methods in the 250-400 mμ region Morachevskii and Belyaeva noted that dilute solutions (less than  $5 \times 10^{-5}$  M in uranovanadate) had a much higher optical density than either the uranyl or the vanadate solutions alone, and from this they concluded the existence of some complex ion. They cited no evidence that

the uranovanadate solution was not colloidal. Insoluble salts formed by the reaction of the uranovanadic anion with the divalent cations  $\text{Pb}^{+2}$ ,  $\text{Ba}^{+2}$ , and  $\text{UO}_2^{+2}$  contained 6 to 8 percent  $\text{H}_2\text{O}$  (they also made a  $\text{Mg}^{+2}$  compound but gave no analysis). They assigned to these salts the structural formula  $\text{Me}[\text{UO}_2(\text{OH})_2\text{VO}_3]_2 \cdot n\text{H}_2\text{O}$ . By analogy they give the same general formula to carnotite, tyuyamunite, and sengierite. Morachevskii and Belyaeva give no X-ray data, but it seems much more likely that they prepared the  $\text{Pb}^{+2}$ ,  $\text{Ba}^{+2}$ , and  $\text{UO}_2^{+2}$  analogues of metatyuyamunite which would also contain about 6 to 8 percent  $\text{H}_2\text{O}$  but whose general structural formula would be  $\text{Me}[(\text{UO}_2)_2\text{V}_2\text{O}_8] \cdot 3\text{H}_2\text{O}$ .

Recently R. F. Marvin, U. S. Geological Survey, (personal communication, 1956) has synthesized carnotite and rauvite (a poorly defined hydrous uranyl vanadate having V:U greater than 1:1) in aqueous solution; the rauvite formed in the pH range from approximately 1.5 to 2.0. The products were very fine grained.

Because carnotite is very easily prepared, it is probable that many other investigators have also created this compound; but to my knowledge, there is no procedure described to form carnotite crystals satisfactory for single crystal X-ray work from aqueous solution.

#### PRECIPITATION OF CARNOTITE FROM AQUEOUS SOLUTIONS

Carnotite usually occurs in nature as a microcrystalline yellow powder impregnating sandstones or coating joints and fractures. Crystals of suitable size for single crystal X-ray work (largest dimension greater than 0.1 mm) are extremely rare. This is due, at least in part, to the very low solubility of carnotite, less than 1 ppm in pure water

at pH 7 (R. F. Marvin, personal communication), which causes it to precipitate in a very fine grained or colloidal state. As shown below, the reactions involved in the precipitation of carnotite are very complicated, and this fact, also, may contribute to the very fine grain size in most natural carnotites.

At room temperature carnotite is precipitated from aqueous solutions as the stable phase when stoichiometric proportions of potassium, uranyl, and vanadate ions are mixed in the pH range from 2 to 9.5. Above pH 9.5 another phase of unknown composition precipitates at a more rapid rate than does carnotite, but the unknown compound apparently converts to carnotite on standing. In the pH range from 1.5 to 2 a brown phase, identified through its comparatively diffuse X-ray powder pattern as rauvite, precipitates from solutions greater than about 0.01 M in uranyl and vanadate ions. It is not known whether rauvite is metastable with respect to carnotite. Below pH 1.5 the uranium is not precipitated, but  $V_2O_5 \cdot nH_2O$  may form if the vanadate concentration exceeds 0.001 M. The pH ranges and concentrations given above are only approximate as the attainment of equilibrium is extremely slow at 25° C.

The uranyl ion,  $UO_2^{+2}$ , exists as the predominant uranium species in aqueous solution below pH 3.5 (Miller, 1955). Above this pH various hydrolysis products become predominant, eventually leading to the precipitation of uranyl hydroxides at about pH 4.5. In the presence of anions such as sulfate, acetate, and especially carbonate, the degree of hydrolysis is reduced through the formation of complex ions, and uranium-bearing solutions are stable at higher pH values (up to 11 or 12 with the carbonate). These complexes must be destroyed to precipitate carnotite,

but even the very stable carbonate complexes seem to have little effect in retarding precipitation (though they undoubtedly increase the solubility of carnotite to some extent).

H. T. Evans, Jr., and R. M. Garrels (U. S. Geological Survey, personal communication, 1956) have summarized the available chemical and thermodynamic data on vanadium in aqueous solution. On acidification, an alkaline aqueous solution on pentavalent vanadium goes through a complex series of polymerization reactions which are shown in the lower two-thirds of figure 1. The lower part of the diagram illustrates approximately how the concentrations of the different vanadate species vary with pH, the central part shows the predominant ion at any given pH. The formulas assigned to the various vanadate species are believed by Evans and Garrels to give the best agreement with the diffusion, cryoscopic and titration studies recorded in the literature, but these data merely reflect the average degree of polymerization and other, undefined, ionic species may be present in significant amounts. Likewise, the coordination of the vanadium by oxygen, a factor which is reflected in the ratio of vanadium to oxygen in the various ions, may reasonably be assumed to be 4, or 5, or possibly even some intermediate values in the cases of ions having vanadium in both degrees of coordination. Because the ionization constants are not known, all of the anionic species with the exception of the polyvanadates are written without attached hydrogen ions. Thus figure 1 presents a gross simplification of the aqueous chemistry of pentavalent vanadium. The chemical formula for carnotite,  $KUO_2VO_4 \cdot nH_2O$ , suggests that it is an orthovanadate, but new X-ray diffraction studies clearly show that it is not.

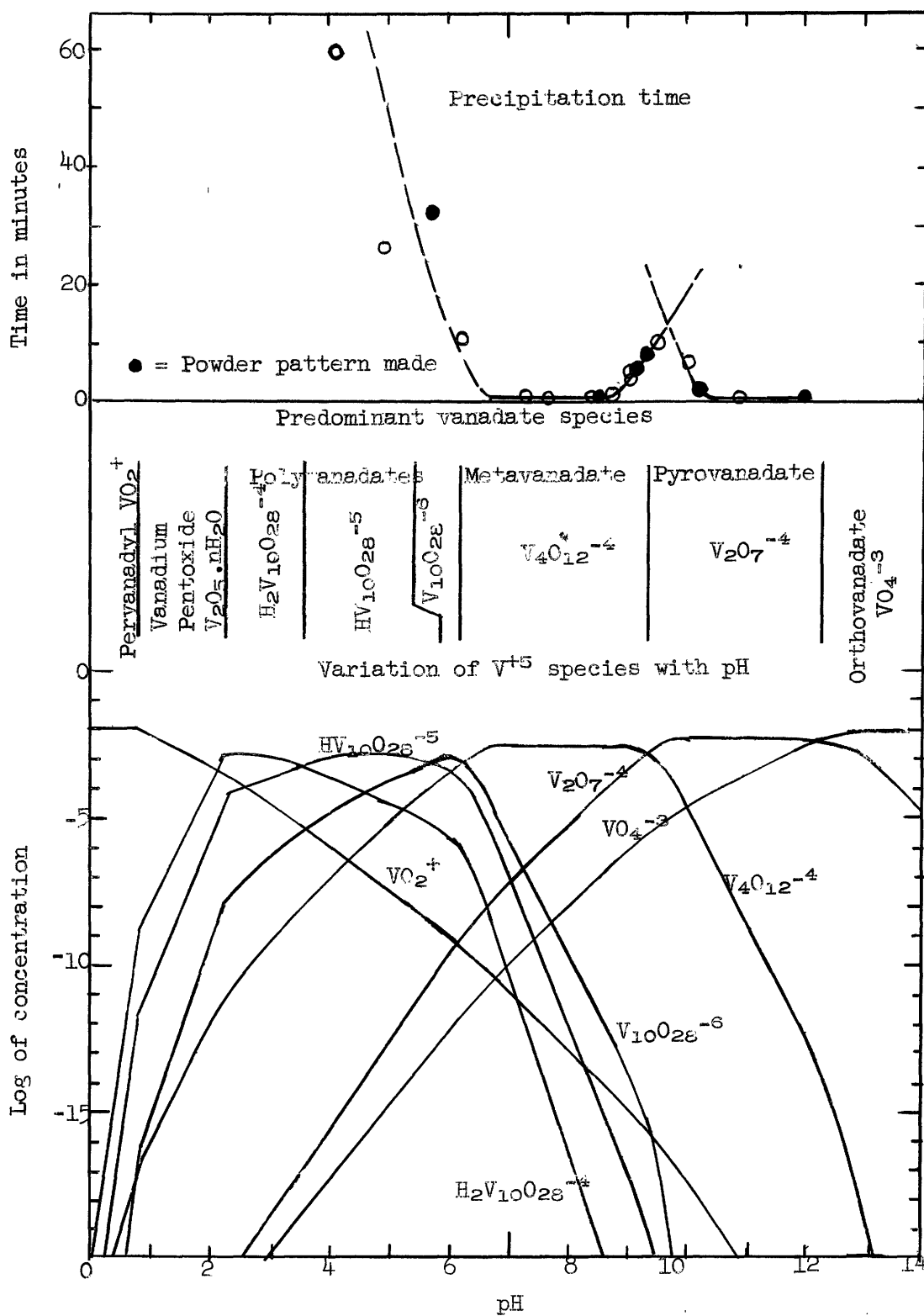


Figure 1.--Relation of rate of precipitation of carnotite to concentration of various pentavalent vanadium species.

D. E. Appleman (U. S. Geological Survey, personal communication, 1957) has done preliminary work on the structure of carnotite, using material synthesized in the course of the investigation described by this report, and has shown that the structure proposed by Sundberg and Sillén (1949) is in error so far as the coordination and position of the oxygen and vanadium atoms are concerned. The new work on the structure of carnotite has shown that the vanadium occurs in "divanadate" groups,  $V_2O_8^{-6}$ . The vanadium is in fivefold coordination with oxygen, so that the resulting polyhedra are distorted trigonal bipyramids; two such bipyramids share an edge to form the  $V_2O_8^{-6}$  ion. This ion is similar in structure to two links from the five-coordinated  $V_nO_{3n}^{-n}$  chains found in the compound potassium metavanadate monohydrate,  $KVO_3 \cdot H_2O$  (Christ, Clark, and Evans, 1954). The linear uranyl ion is coordinated in a fairly regular way by five oxygens from three  $V_2O_8^{-6}$  groups, forming  $[(UO_2)_2V_2O_8]_n^{-2n}$  sheets, with the axes of the uranyl ions nearly normal to the sheets. The alkali ions fit between the sheets as in the case of the micas. As will be discussed later, water molecules may also fit between the sheets, but they are not essential to the structure nor do they greatly affect the cell dimensions except for the interlayer spacing. The structural formula is  $K_2(UO_2)_2V_2O_8 \cdot nH_2O$  with 2 formula units per unit cell.

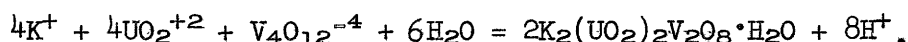
The rate of precipitation of carnotite as a function of pH was determined, and the results are plotted in the upper part of figure 1. In the rate experiments 20 ml aliquots of 0.01 M  $NaVO_3$  were mixed with 20 ml portions of a solution 0.009 M in  $Na_4UO_2(CO_3)_3$  and 0.5 M in  $K_2SO_4$ . Before mixing, the pH of each portion was adjusted to the desired value

with KOH or  $\text{HNO}_3$ . The solutions were well mixed and the pH recorded. The time for precipitation was defined as the time required to obtain the first noticeable cloudiness in the solution. Obviously, refinements could be made in the experimental techniques, but the present results are satisfactory for this study. The scatter of points in the acid range (fig. 1) is due in part to difficulty in detecting the beginning of precipitation; however, disequilibrium is a more important factor. Because adjusting the acidity upsets the equilibrium between the various condensed vanadate species and because the depolymerization reactions are sluggish in the pH range 4 to 8, the measured pH values do not necessarily reflect the concentrations of the various vanadate species. Due to the presence of considerable amounts of  $\text{Na}^+$ , it is probable that the carnotite contained at least a small amount of sodium although the powder patterns of the precipitates have spacings very similar to those of the pure potassium carnotite.

The rapid increase in rate of precipitation up to pH 7 shows that precipitation involves reaction with a species of ion that increases in concentration with pH. The decrease in rate from pH 9 to 9.5 suggests that the reaction involves the ionic species predominant in the pH range 7 to 9, that is the metavanadates. The return to instantaneous precipitation at the highest pH values suggests that another compound may be forming instead of carnotite above pH 9.5. Powder patterns of the low pH precipitates (below 9.5) show diffuse but definite carnotite lines, whereas precipitates from the high pH region (above 9.5) show weaker carnotite lines plus a faint, fuzzy line at about 11 Å. One precipitate that formed at pH 7.4 also had the line at 11 Å, but this

line was weak compared to the carnotite lines. The differences between the powder patterns are not pronounced, and the high pH phase cannot be characterized with certainty from the powder patterns; but the X-ray diffraction work does lend permissive support to the interpretation that a poorly crystallized uranyl vanadate of uncertain composition precipitates more rapidly than does carnotite at pH above 9.5 and that this phase converts to carnotite on standing. At lower pH carnotite precipitates directly from solution.

There are several possible reactions by which carnotite can be precipitated while fulfilling the restrictions placed upon the precipitation by the rate study. The upper part of figure 1 shows that the rate-determining reaction is controlled by a species that has its maximum abundance in the pH range 7.0 to 9.5. The work of Evans and Garrels shows that metavanadate, perhaps  $V_4O_{12}^{-4}$ , is predominant in the pH range 7.0 to 9.5; thus there is a strong possibility that the precipitation reaction is of the sort:



However, this is not the only possible reaction. Simple calculations show that any ion of the type  $(H_{2n}V_mO_{3m+n})^{-m}$ , which includes  $H_2VO_4^-$ ,  $H_2V_2O_7^{-2}$ ,  $H_4V_2O_8^{-2}$ , and others, will have its maximum concentration in exactly the same region as the metavanadate plateau because the formula  $(H_{2n}V_mO_{3m+n})^{-m}$  is merely the general formula for hydrated metavanadate ion,  $(H_{2n}V_4O_{12+n})^{-4}$ . There are no experimental data to indicate which of the possible ionic species determines the rate of reaction. Whatever the formula of the metavanadate, there will be other possible ions corresponding to the hydrated metavanadates

discussed above so that we cannot be certain of the identity of the ionic species that reacts to precipitate carnotite. The rapidity of the precipitation in the metavanadate region suggests, but certainly does not prove, that the metavanadate ion contains at least some 5-coordinated vanadium atoms. The available data are too poor to permit evaluation of the order of the rate-determining reaction in terms of metavanadate concentration.

It may be noted that the metavanadate ( $V_4O_{12}^{-4}$ ) plateau in the lower part of figure 1 is slightly broader than the region of rapid precipitation of carnotite shown at the top of this diagram. Although the metavanadate plateau is plotted as if it represents only one species, it probably represents several species such as  $V_4O_{12}^{-4}$ ,  $HV_4O_{12}^{-3}$ ,  $H_2V_4O_{12}^{-2}$ ; and  $H_3V_4O_{12}^{-1}$ ; and possibly several  $V_3O_9^{-3}$ ,  $V_2O_6^{-2}$ , or other species. This situation is parallel to that in the polyvanadates, except that some of the ionization constants are known for the polyvanadates and therefore they may be plotted as separate ions. It seems likely that the rate-determining reaction for the formation of carnotite does not involve all of the possible metavanadate species; thus the composite metavanadate pH range is wider than the pH range of rapid precipitation.

If the reaction does involve metavanadate ion, there must be some sort of interaction at the crystal-solution interface by which metavanadate is depolymerized to divanadate,  $V_2O_8^{-6}$ , because the crystal structure contains  $V_2O_8^{-6}$  ions. Under these circumstances the problem arises of how the initial carnotite nuclei originate. It is possible that the initial carnotite nuclei may form from a small amount of aqueous divanadate ion (if it exists in appreciable concentration

in aqueous solution), or perhaps some other vanadate species may provide a transient seed phase on which the carnotite crystallizes. The line at 11 Å in the powder pattern of the precipitate obtained at pH 7.4 suggests that this transient phase may be the same one that precipitates at a high pH, but there are few data at present to justify such a conclusion.

### CRYSTAL CHEMISTRY

The composition of carnotite reflects the unique crystal structure of the  $[(\text{UO}_2)_2\text{V}_2\text{O}_8]_n^{-2n}$  layers. Because of its coordination in the dumbbell-shaped uranyl ion,  $\text{UO}_2^{+2}$ , the uranium is not likely to be replaced by any other ion. The asymmetric, fivefold coordination of the vanadium is not similar to that found in any other ion; therefore, elements such as phosphorous and arsenic, which sometimes form isomorphous series with tetrahedrally coordinated vanadate compounds (pyromorphite-mimetite-vanadinite), will not proxy for vanadium in the carnotite structure. The tendency for vanadium to occur in peculiar coordination may also explain the absence of naturally occurring vanadium analogues to torbernite, autunite, zeunerite, and abernathyite. Isomorphous substitution in the carnotite-type structure is very likely limited to the interlayer sites, that are occupied by potassium in carnotite and by calcium in tyuyamunite.

Natural carnotite contains from 1 to 3 moles of water per formula weight (Palache, Berman, and Frondel, 1951). The synthetic material on which the present structural work was done was originally entirely anhydrous (see description of synthesis below), yet this synthetic material, when kept anhydrous by immersion in mineral oil, gave an X-ray powder pattern practically identical to that of natural carnotite. Luedemann and Bates (1957) show that the curve for weight loss versus temperature for natural carnotite is smooth, with no sharp breaks, and their differential thermal analysis curve shows no pronounced endothermic or exothermic peaks. If carnotite is heated to 1100° to 1200° C, it will melt and recrystallize as carnotite (unless held at the high temperature for several days, in which case it decomposes through loss of oxygen to  $U_3O_8$  and other as yet unidentified compounds). Therefore, none of the water in natural carnotite is essential to the structure. Under normal laboratory humidity the amount of water in carnotite is sufficiently low so that there is little variation in the cell dimensions, although Donnay and Donnay (1955) have shown that some natural material (table 2) may show a considerable range in the c dimension, presumably due to variation in water content. Carnotite does not seem to hydrate in a stepwise fashion as do autunite and tyuyamunite. X-ray diffraction examination shows that the natural carnotite crystals are noticeably disordered, especially in the c direction, as would be expected if there is disorder in stacking of the layers or variation in water content.

## SYNTHESIS

In this work several techniques were used in attempts to obtain well-crystallized carnotite. Aqueous systems from room temperature to 200° C were tried without success, and therefore it was necessary to resort to fusion methods.

## Aqueous methods

In aqueous systems at low temperatures it is difficult, if not impossible, to avoid the precipitation of carnotite from a solution containing appreciable amounts of potassium, hexavalent uranium, and pentavalent vanadium from pH 2 to pH 9.5. Beyond these pH limits other phases precipitate. (See discussion of precipitation from aqueous solution above.) The rapid precipitation from cold aqueous solution produces a carnotite which is very poorly crystallized, as is indicated by its diffuse X-ray powder pattern. Sharp powder patterns, but no crystals distinguishable at 500x magnification, are obtained by prolonged digestion of the precipitate on the steambath or by placing it for a few days in a closed tube with water at temperatures as high as 200° C. Variations in pH, concentration, and relative proportions of reagents seemed to make little improvement in the crystallization of the carnotite. A single experiment in which fine-grained carnotite was aged in an approximately neutral solution in an autoclave at 150° C and about 35 atmospheres CO<sub>2</sub> pressure failed to improve the crystallinity of the carnotite measurably.

It was thought that perhaps the very slow mixing of uranyl and vanadate solutions might permit the growth of single crystals. Excellent crystals of many insoluble compounds can be grown by slow mixing of reactants by diffusion through silica jelly. When uranyl (or uranyl carbonate) and vanadate solutions containing potassium are introduced into the opposite sides of a U-tube partly filled with silica jelly, a precipitate forms at the contact of the diffusing ions. The precipitates develop in 2 to 20 days and often show rhythmic Liesegang banding but, unfortunately, no visible crystals. When the solutions have a low pH (about 2), two distinctly different phases result. On the uranium side is a bright yellow precipitate of carnotite which gives a sharp X-ray pattern, while on the vanadium side there is a brown cryptocrystalline material identified as rauvite through its relatively diffuse pattern. At the higher pH (about 8) investigated by this method only carnotite appears. Because of the buffering action of the silica jelly (prepared by mixing 5 volumes of 2 percent  $\text{H}_2\text{SO}_4$  with 8 volumes of 1:6 sodium silicate) the exact hydrogen ion concentration at the point of precipitation is unknown. At the lower pH the predominant ions are  $\text{UO}_2^{+2}$ ,  $\text{V}_{10}\text{O}_{28}^{-6}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{H}^+$ , and  $\text{SO}_4^{-2}$ ; at the higher pH they are  $\text{UO}_2(\text{CO}_3)_3^{-4}$ ,  $\text{V}_4\text{O}_{12}^{-4}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{-2}$ .

Most natural carnotite was apparently precipitated from solutions derived from sources containing tetravalent uranium and tri- and tetravalent vanadium compounds; this suggests another method of precipitation in which vanadate and uranyl solutions could be combined very slowly. Tetravalent vanadium and hexavalent uranium do not precipitate each other from solution. Tetravalent vanadium is

amphoteric; the vanadyl ion,  $\text{VO}^{+2}$ , is stable in solutions up to about pH 3 where  $\text{V}_2\text{O}_4$  hydrate precipitates; above a pH of about 8.2 the  $\text{V}_2\text{O}_4$  redissolves as the vanadite ion, possibly  $\text{V}_4\text{O}_9^{-4}$ .

Two types of experiment were set up in an attempt to duplicate the natural method of crystal growth. In the first, sulfur dioxide was bubbled through a solution of potassium sulfate and sodium vanadate so that the vanadium was reduced to the tetravalent state. Hexavalent uranium in molecular excess of the vanadium was then added to the vanadite solution and the mixture was permitted to drip at the rate of about one drop per hour on a sloping piece of filter paper where the sulfur dioxide either escaped as a gas or was converted to sulfate by air oxidation. The vanadium slowly oxidized to the pentavalent state. The pH of the solution before loss of sulfur dioxide was about 3. A yellow film of carnotite developed in a few days but even after two months there were no crystals visible under 80 power magnification.

The second experiment involved diffusion of ions through U-tubes. A silica jelly containing sodium, potassium, and hexavalent uranium was prepared. Vanadyl sulfate was introduced into one limb of the tube and potassium peroxydisulfate (a strong oxidizing agent) was placed in the other. Small, well formed, yellow crystals in the shape of roughly equant plates developed after a few days, especially along the glass-jelly contact. These were at first thought to be carnotite which had had its tendency to form diamond-shaped plates suppressed by the interference of the jelly. But the appearance of penetration twinning and the fact that the crystals later redissolved proved

that the crystals were not carnotite. X-ray data suggest that the crystals are a potassium uranyl sulfate. Later, the usual bands of cryptocrystalline rauvite and carnotite appeared.

There is another mechanism through which the well crystallized natural carnotites may have been formed, but this has not been tried in the laboratory because of the success of the fusion techniques which are described later. Tyuyamunite (or metatyuyamunite), being considerably more soluble than carnotite, occurs in nature as visible crystals much more frequently than does carnotite. It is also possible to synthesize suitable crystals of tyuyamunite (Murata and others, 1950). Such crystals could then be converted to carnotite by treatment with a solution containing a high concentration of  $K^+$  relative to  $Ca^{++}$  (Hillebrand, 1924). A possible drawback to this method is that the base exchange process might well result in random stacking of the layers. As is discussed later, the natural carnotite crystals commonly exhibit stacking disorder.

#### Fusion methods

By following the procedure developed by Canneri and Pestelli (1924) carnotite crystals up to a centimeter across were obtained. The same technique also provided the Na, Rb, Tl, and Cs analogues of carnotite as crystals which were suitable for single crystal X-ray work. The crystals of the K and Cs compounds were also sufficiently well developed for goniometric work (D. E. Appleman, personal communication).

The procedure used to crystallize carnotite and its alkali analogues is very simple, although the size to which the individual crystals grow is, as yet, controlled more by luck than science. Ammonium metavanadate,  $\text{NH}_4\text{VO}_3$ , and an alkali hydroxide, chloride, carbonate or nitrate were fused together in a platinum crucible to give the alkali metavanadate. The reactions were quite rapid, especially with the hydroxides. Usually one or two percent  $\text{NH}_4\text{VO}_3$  in excess of the stoichiometric amount was used in order to prevent the possibility of excess hydroxide which might react with the crucible. Then a small amount of uranyl nitrate or acetate, or uranium trioxide hydrate was added to the alkali metavanadate and the mixture was fused. On cooling, beautiful, yellow, rhombic plates could be seen to grow rapidly at the surface of the melt just before the main mass of the metavanadate crystallized. The crystals were then separated by handpicking, or the flux was dissolved away with water or dilute nitric acid. If the acid used was too strong,  $\text{V}_2\text{O}_5$  hydrate precipitated and was then redissolved in a solution of the appropriate alkali.

In an attempt to perform the synthesis in the manner of Sundberg and Sillén (1949), stoichiometric amounts of uranyl nitrate and potassium metavanadate were fused in a great excess of potassium carbonate. This technique gave orange, tabular, pseudotetragonal (orthorhombic) crystals with three mutually perpendicular cleavages. The (001) cleavage is micaceous, the other two are good. The unit-cell dimensions, determined by Joan R. Clark, U. S. Geological Survey, are 4.33, 4.33, and 13.21 Å, or possibly some multiples thereof. The

intensity distribution on X-ray patterns of the compound shows that the two short axes are not equivalent. The crystals break down rapidly in contact with atmospheric moisture, but they can be preserved under mineral oil or toluene. The optical character of the crystals changes with hydration from sensibly uniaxial to biaxial with  $2V$  of  $10^\circ$  to  $15^\circ$ , and the crystals soon become disordered. The powder patterns of the hydrated material show some carnotite lines; the other lines present cannot be indexed on either the carnotite or the above-mentioned pseudotetragonal cell. A more detailed study of this very interesting phase has thus far been prevented by its instability. Similar sodium and rubidium compounds have been prepared using melts of the appropriate alkali carbonate, but no X-ray work has been done on these. Attempts to make the thallium member have been unsuccessful, presumably due to the difficulty of preventing the thermal decomposition of the thallos carbonate.

Besides the carbonate and vanadate fluxes some other types of flux were tried. As described above, uranyl salt was added to the vanadate fluxes; to the other fluxes (table 1) a small amount of the appropriate alkali analogue of previously prepared synthetic carnotite was added. The mixtures were fused and allowed to cool slowly. In general, there were only two types of uranium-bearing crystals formed: carnotite, and the previously described orange, orthorhombic compound. Table 1 summarizes the results of the fluxing experiments.

Table 1.--Summary of fusion experiments

Flux	Melting point °C of pure flux	Nature of uranium-bearing phase
KVO <sub>3</sub>	650 (estimated)	yellow carnotite crystals
K <sub>2</sub> CO <sub>3</sub>	891	orange orthorhombic crystals
K <sub>2</sub> CO <sub>3</sub> :KVO <sub>3</sub> (2:1)	600 (estimated)	orange orthorhombic crystals
K <sub>2</sub> CO <sub>3</sub> :KF (5:1)	750 (estimated)	orange orthorhombic crystals
K <sub>2</sub> SO <sub>4</sub>	1,076	orange, poor crystals
KCl	776	orange pseudomorphs of original yellow carnotite crystals
KNO <sub>3</sub>	334	yellow, no recrystallization
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	60	yellow, no recrystallization
V <sub>2</sub> O <sub>5</sub>	690	no micaceous uranium-bearing (carnotite requires alkali)
KHSO <sub>4</sub>	210	orange melt turns yellow on cooling; no crystals, too acid
NaVO <sub>3</sub>	630	yellow Na carnotite crystals
Na <sub>2</sub> CO <sub>3</sub>	851	orange orthorhombic (?) crystals
TlVO <sub>3</sub>	424	yellow Tl carnotite crystals
Tl <sub>2</sub> SO <sub>4</sub>	632	yellow Tl carnotite crystals
Tl <sub>2</sub> CO <sub>3</sub>	273	unsuccessful due to oxidation of Tl; requires further work
RbVO <sub>3</sub>	500 (estimated)	yellow Rb carnotite crystals
Rb <sub>2</sub> CO <sub>3</sub>	837	orange orthorhombic (?) crystals
CsVO <sub>3</sub>	500 (estimated)	yellow Cs carnotite crystals
LiVO <sub>3</sub>	600 (estimated)	very fine grained insoluble greenish yellow material that gives carnotite-like pattern after washing with water

In the course of the fusion synthesis experiments the preparation of the lithium analogue was tried. An insoluble compound with a greenish-yellow sheen, too fine grained to be resolved under the microscope, was retained after the leaching away with water of the lithium metavanadate flux. The compound gave a powder pattern that was practically identical to that of carnotite. This was tentatively explained as due to the base exchange of  $\text{Li}^+$  by  $\text{H}_3\text{O}^+$  during the washing, so as to yield a hydronium carnotite practically identical to the natural carnotite in cell dimensions ( $r_{\text{K}^+} = 1.33 \text{ \AA}$ ;  $r_{\text{H}_3\text{O}^+} \approx r_{\text{O}^{2-}} = 1.40 \text{ \AA}$ ). It is unlikely in terms of modern crystal chemical theory to find the small  $\text{Li}^+$  ion ( $r_{\text{Li}^+} = 0.68 \text{ \AA}$ ) in the same structural position as  $\text{K}^+$  or  $\text{Cs}^+$ . The  $[(\text{UO}_2)_2\text{V}_2\text{O}_8]_n^{2n-}$  layers may exist in the Li compound, but the  $\text{Li}^+$  would not occupy the same position as does the  $\text{H}_3\text{O}^+$  which replaces it.

It was not possible to make the ammonium analogue of carnotite by the fusion technique because the ammonia was lost on heating. Fine grained ammonium carnotite prepared by K. J. Murata by aqueous methods gave a powder pattern very similar to that of natural carnotite ( $r_{\text{NH}_4^+} = 1.43 \text{ \AA}$ ).

The synthesis of the Na carnotite from the  $\text{NaVO}_3$  melts could not be repeated at will as some as yet undetermined factor often prevented the formation of visible crystals. Murata and others (1950) record a peculiar formula, in which there is an excess of  $\text{V}_2\text{O}_5$ , for their Na "carnotite," and they suggest that further investigation on the nature of this compound be carried out. They report that the Na compound is also readily base exchanged in  $\text{K}^+$  bearing solutions

with the formation of K carnotite. In addition, the present study showed that Na carnotite dissolves in acid much more rapidly, and at a slightly higher pH than the other carnotites. These observations indicate that Na carnotite is relatively unstable compared to the carnotites which contain larger alkali cations. It seems unlikely that pure Na carnotite would occur in nature because sufficient amounts of  $K^+$  are present in most natural solutions to base exchange the  $Na^+$  by  $K^+$ . Apparently the decrease in stability of Na carnotite relative to K carnotite is related to the decrease in ionic size of  $Na^+$  relative to  $K^+$  ( $r_{Na^+} = 0.97$ ;  $r_{K^+} = 1.33$  Å).

#### PROPERTIES OF CARNOTITE AND RELATED COMPOUNDS

Table 2 presents the unit-cell data for natural and synthetic carnotite, its alkali analogues, and some related natural compounds. The new data were obtained using filtered molybdenum radiation ( $\lambda_{K\alpha} = 0.7107$  Å) with a precession camera; corrections were made for film shrinkage. The cell dimensions of the synthetic compounds show systematic variation with the ionic radius of the alkali cation. The similarity of the a and b dimensions of carnotite, sengierite, and metatyuyamunite (and tyuyamunite) suggests that all have essentially the same  $[(UO_2)_2V_2O_8]_n^{-2n}$  layer structure with only the interlayer cations and the degree of hydration accounting for the differences. Tyuyamunite and metatyuyamunite contain  $2[(UO_2)_2V_2O_8]_n^{-2n}$  layers per unit cell and are orthorhombic; whereas carnotite and sengierite have only one such layer and are monoclinic. Further evidence for the similarity of the layers in these minerals is furnished by the similarity in physical properties (Palache, Berman,

Table 2.--Unit-cell data for carnotite and related compounds

Material	a (in Å)	b (in Å)	c (in Å)	$\beta$	Specific gravity	
					Calculated	Observed
$\text{Na}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$	10.39 $\pm$ 0.03	8.39 $\pm$ 0.03	6.14 $\pm$ 0.10	100°10' $\pm$ 30'	5.16	
$\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$	10.47 $\pm$ 0.02	8.41 $\pm$ 0.01	6.59 $\pm$ 0.01	103°50' $\pm$ 05'	4.99	4.95 $\pm$ 0.05
$\text{Tl}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$	10.48 $\pm$ 0.02	8.41 $\pm$ 0.02	6.82 $\pm$ 0.01	105°15' $\pm$ 10'	6.76	6.58 $\pm$ 0.05
$\text{Rb}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$	10.49 $\pm$ 0.02	8.43 $\pm$ 0.02	6.93 $\pm$ 0.02	105°25' $\pm$ 10'	5.29	5.14 $\pm$ 0.05
$\text{Cs}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$	10.51 $\pm$ 0.02	8.45 $\pm$ 0.01	7.32 $\pm$ 0.01	106°05' $\pm$ 05'	5.52	5.48 $\pm$ 0.05
Carnotite 1/	10.48 $\pm$ 0.03	8.37 $\pm$ 0.02	6.75 $\pm$ 0.05	104°20' $\pm$ 1°		
Carnotite 2/	10.47 $\pm$ 0.03	8.39 $\pm$ 0.02	6.63 $\pm$ 0.03	103°50' $\pm$ 15'		
Carnotite 3/	10.47	8.41	6.91	103°40' $\pm$ 10'	4.91	4.70 $\pm$ 0.05
$\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8 \cdot n\text{H}_2\text{O}$ 4/	10.46	8.40	6.59	103°40' $\pm$ 20'	5.00	4.80 $\pm$ 0.05
$\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$ 5/	10.43	8.40	6.59	104°12'	5.03	
Sengierite 6/	10.62	8.10	10.11	103°36' $\pm$ 10'	3.99	4.41
Metatyuyamunite 7/	10.63	8.36	16.96	orthorhombic	4.04	3.92 $\pm$ 0.05
Metatyuyamunite 8/	10.54	8.49	17.34	orthorhombic		3.61 $\pm$ 0.05
$\text{Ca}(\text{UO}_2)_2\text{V}_2\text{O}_8 \cdot 3\text{--}5\text{H}_2\text{O}$ 9/	10.38	8.46	17.02	orthorhombic		

- 1/ Carnotite from Cane Springs Pass, Utah.
- 2/ Carnotite from Congress Junction, Arizona.
- 3/ Carnotite from Cane Springs Pass, Utah, fully hydrated (Donnay and Donnay, 1955).
- 4/ Synthetic hydrated carnotite prepared by K. J. Murata (Donnay and Donnay, 1955).
- 5/ Synthetic anhydrous carnotite (Sundberg and Sillén, 1949).
- 6/ Sengierite from Haut-Katanga, Belgian Congo (Donnay and Donnay, 1955).
- 7/ Metatyuyamunite from May Day mine, Mesa County, Colorado (Donnay and Donnay, 1955).
- 8/ Metatyuyamunite from Small Spot mine, Mesa County, Colorado (Donnay and Donnay, 1955).
- 9/ Synthetic metatyuyamunite prepared by K. J. Murata. (Donnay and Donnay, 1955).

and Frondel, 1951) and by the ability of these compounds to convert to one another through base exchange (Hillebrand, 1924; Murata and others, 1950; and Donnay and Donnay, 1955).

The indexed powder patterns for the synthetic carnotites are shown in table 3. These data were calculated from measurements taken from powder patterns obtained using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Corrections for film shrinkage have been made. Because of the platy nature of the carnotite, it was almost impossible to avoid alinement of crystals in the spindle, thus the relative intensities of the various reflections were influenced by this preferred orientation. Intensities were visually estimated. The reflections were indexed on the basis of the unit cells of the synthetic crystals. The  $\text{NH}_4$  and  $\text{H}_3\text{O}(?)$  carnotites were indexed on the basis of the K carnotite cell. Lines with  $d$  values of less than  $2.0 \text{ \AA}$  were not indexed.

Single crystals of the natural carnotite commonly exhibit very diffuse, streaky spots in the  $h0l$  and  $0kl$  precession photographs, although the  $hk0$  patterns have fairly well defined spots. This indicates that the crystals are relatively disordered in the  $c$  direction, presumably due to disorder in the stacking of the layers or random variation in the water content so that the  $00l$  spacings are nonuniform.

The carnotite crystals are brilliant canary yellow to greenish yellow. Although most vanadates do not fluoresce, the Cs carnotite and a K carnotite that had been held at  $1000^\circ \text{ C}$  for three hours fluoresced yellow-green under ultraviolet light.

Twinning by reticular pseudomerohedry, as described (and erroneously recorded as reticular merohedry) by Donnay and Donnay (1955), was noted in the precession patterns from the K, Cs, Rb, and Tl carnotites.

Table 3.--X-ray powder data for carnotite and its alkali analogues.

(d in angstroms).  $\text{CuK}\alpha$ ;  $\lambda = 1.5418 \text{ \AA}$ 

Na Carnotite				K Carnotite			
<u>hkl</u>	<u>d(calc.)</u>	<u>d(obs.)</u>	<u>I</u>	<u>hkl</u>	<u>d(calc.)</u>	<u>d(obs.)</u>	<u>I</u>
110	6.49	6.47	W	110	6.48	6.46	W
001	6.04	6.04	VS	001	6.40	6.36	VS
200	5.11	5.12	M	200	5.08	5.06	W
$\bar{2}01$	4.30	4.29	VW	111	4.24	4.22	M
111	4.19	4.16	S	020	4.20		
201	3.603	3.579	VW	201	3.585	3.530	S
021	3.447	3.437	M	021	3.514		
220	3.243	3.222	W	220	3.240	3.207	S
310	3.159	3.140	M	002	3.199		
002	3.022	3.015	M	310	3.143	3.140	M
$\bar{2}21$	3.001	3.000	M	$\bar{3}11$	3.107	3.100	M
$\bar{2}12$	2.681	2.680	W	$\bar{2}21$	3.086		
311	2.628	2.612	M	112	2.709	2.705	W
410	2.445	2.437	M	311	2.602	2.600	VW
$\bar{3}12$	2.387	2.387	VW	$\bar{1}31$	2.549		
$\bar{4}02$	2.148	2.150	W	$\bar{3}12$	2.542	2.544	M
222	2.097	2.104	VW	400	2.542		
				202	2.456	2.453	VW
				230	2.455		
				330	2.160	2.156	VW
				$\bar{2}03$	2.160		
				003	2.133	2.140	W
				312	2.028	2.031	VW

Table 3.--X-ray powder data for carnotite and its alkali analogues.--Continued.

NH <sub>4</sub> Carnotite				TI Carnotite			
<u>hkl</u>	<u>d(calc.)</u>	<u>d(obs.)</u>	<u>I</u>	<u>hkl</u>	<u>d(calc.)</u>	<u>d(obs.)</u>	<u>I</u>
110	6.48			001	6.58	6.56	M
001	6.40	6.61	VS	200	5.06	5.05	M
111	4.24	4.19	M	210	4.33	4.33	M
020	4.20			111	4.27	4.29	M
201	3.585	3.534	M	020	4.21	4.23	W
021	3.514			211	4.06	4.06	M
211	3.297	3.314	W	021	3.543	3.535	S
220	3.240			002	3.289	3.285	VS
002	3.199	3.220	W	311	3.136		
310	3.140	3.132	M	310	3.128	3.128	M
311	3.107	3.115	M	221	3.116		
H <sub>3</sub> O(?) Carnotite				012	3.064	3.054	VW
110	6.48	6.48	M	212	2.961	2.956	VW
001	6.40	6.37	VS	130	2.701	2.705	W
200	5.08	5.05	VW	031	2.579	2.579	W
111	4.24			401	2.176	2.179	VW
020	4.20	4.20	M	330	2.155	2.154	W
021	3.514	3.507	M	222	2.133	2.130	VW
121	3.464	3.453	W	032	2.133		
220	3.240			232	2.098	2.098	W
002	3.199	3.215	M	312	2.032	2.032	W
121	3.194	3.193	W				
310	3.143	3.126	M				
311	3.107						
221	3.086	3.095	W				
112	2.709	2.698	VW				
311	2.602	2.589	W				
312	2.542						
400	2.542	2.543	VW				

Table 3.--X-ray powder data for carnotite and its alkali analogues.--Continued.

Rb Carnotite				Cs Carnotite			
<u>hkl</u>	<u>d(calc.)</u>	<u>d(obs.)</u>	<u>I</u>	<u>hkl</u>	<u>d(calc.)</u>	<u>d(obs.)</u>	<u>I</u>
001	6.68	6.70	VS	001	7.03	7.02	S
110	6.45	6.46	W	110	6.48	6.50	VW
200	5.06	5.08	M	200	5.05	5.04	W
$\bar{2}01$	4.67	4.68	W	111	4.39	4.37	M
111	4.30	4.30	M	210	4.33		
020	4.21	4.21	M	$\bar{2}11$	4.16	4.13	M
$\bar{2}11$	4.09	4.10	M	$\bar{1}21$	3.575	3.591	M
120	3.891	3.883	W	002	3.517	3.482	VS
021	3.565	3.562	S	$\bar{2}02$	3.354		
002	3.341	3.339	S	211	3.351	3.339	M
220	3.237	3.231	M	$\bar{1}12$	3.351		
310	3.130	3.137	S	220	3.240	3.220	M
$\bar{2}12$	2.997	2.988	W	$\bar{3}11$	3.176	3.170	M
221	2.736	2.726	VW	221	3.165		
130	2.707	2.702	M	$\bar{2}12$	3.118	3.102	M
$\bar{3}12$	2.631	2.625	M	112	2.884	2.867	W
$\bar{4}01$	2.605	2.603	M	$\bar{3}12$	2.708	2.706	M
$\bar{2}22$	2.552	2.543	VW	031	2.614	2.614	M
$\bar{4}11$	2.489	2.488	VW	230	2.460	2.458	M
230	2.457	2.452	M	212	2.460		
131	2.449			003	2.344	2.331	M
$\bar{3}22$	2.314	2.230	M	$\bar{1}13$	2.342		
321	2.292			$\bar{4}12$	2.298	2.294	VW
013	2.153	2.154	M	013	2.268	2.262	VW
040	2.107	2.108	W	222	2.196	2.193	VW
140	2.064	2.067	W	401	2.191		
132	2.034	2.036	W	$\bar{2}32$	2.157	2.153	M
				$\bar{4}22$	2.078	2.077	M
				132	2.075		
				023	2.052	2.037	M
				041	2.023		

VS very strong

S strong

M moderate

W weak

VW very weak

The micaceous (001) cleavage of carnotite is well developed in all of the synthetic and natural carnotites examined. A good cleavage parallel to (100) is seen in the larger crystals of the natural carnotite and in most of the synthetic crystals. Less frequently (010) and (110) cleavages appear. The diamond-shaped platy crystals are commonly bounded by {110} faces in addition to the (001) cleavage planes. The Cs carnotite also shows {010} and {100} faces. In the natural carnotite from Congress Junction, Arizona, the {110} faces are so well developed that the crystals are almost equant rather than tabular; however, there is much disorder in the  $\underline{c}^*$  direction in these crystals.

The optical data for various synthetic carnotites are presented in table 4. The crystals are biaxial (-), and the micaceous cleavage flakes give centered optic axis figures. The optic angles were measured on a universal stage using optic axis figures; the values are reproducible to within  $0.5^\circ$  or less. The optic angle of the thallium carnotite is too large to obtain a centered figure, but it was measured using a ruled eyepiece which was calibrated at lower angles. The optic plane is parallel to  $\underline{b}$  and, so far as can be determined (within a degree), lies in the  $\underline{bc}^*$  plane.

Table 4.--Optical data for synthetic compounds related to carnotite 1/

Material	$\alpha_2$	$\beta$	$\gamma$	2V (Na light)
$\text{Na}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$		$2.21 \pm 0.01$	$2.21 \pm 0.01$	$13^\circ \pm 1^\circ$
$\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$	$1.77 \pm 0.04$	$2.010 \pm 0.005$	$2.090 \pm 0.005$	$53^\circ 30' \pm 1^\circ$
$\text{Th}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$		$>2.70$	$>2.70$	$>64^\circ 40'$
$\text{Rb}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$	$1.86 \pm 0.04$	$2.125 \pm 0.0005$	$2.205 \pm 0.005$	$51^\circ 30' \pm 1^\circ$
$\text{Cs}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$	$<1.83$	$2.49 \pm 0.01$	$>2.70$	$45^\circ 30' \pm 1^\circ$

1/ The indices of refraction were determined by C. S. Ross, U. S. Geological Survey, using sulfur-selenium mixtures.

2/ Calculated values.

#### ACKNOWLEDGMENTS

I wish to thank many of my coworkers in the U. S. Geological Survey, especially D. E. Appleman, C. L. Christ, H. T. Evans, Jr., R. M. Garrels, R. F. Marvin, K. J. Murata, A. M. Pommer, and E. Roedder for discussion and suggestions throughout the study. Joan R. Clark measured the cell dimensions of the synthetic K carnotite and the orange orthorhombic phase. C. S. Ross measured the indices of refraction of the synthetic materials. Mary Mrose, Daphne Riska Ross, and Evelyn Cisney identified fine-grained materials by means of X-ray powder patterns.

This work was done by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

## REFERENCES

- Canneri, G., and Pestelli, V., 1924, La sintesi della carnotite: Gazz. chim. italiana, v. 54, p. 641-646.
- Carnot, M. Adolphe, 1887, Etude sur les reactions des vanadates au point de vue de l'analyse chimique: Acad. Sci. Paris Comptes Rendus, v. 104, p. 1850-1853.
- Christ, C. L., Clark, Joan R., and Evans, H. T., Jr., 1954, The crystal structure of potassium metavanadate monohydrate,  $KVO_3 \cdot H_2O$ : Acta Crystallographica, v. 7, p. 801-807.
- Donnay, Gabrielle, and Donnay, J. D. H., 1955, Contribution to the crystallography of uranium minerals: U. S. Geol. Survey TEI-507, 42 p., issued by U. S. Atomic Energy Comm., Tech. Inf. Service Extension, Oak Ridge, Tenn.
- Hillebrand, W. F., 1924, Carnotite and tyuyamunite and their ores in Colorado and Utah: Am. Jour Sci., 5th ser., v. 8, p. 201-216.
- Leudeman, Lois, and Bates, T. F., 1957, Mineralogical study of several hydrous vanadates: Pennsylvania State Univ., College of Mineral Industries, Tech. report no. 8 to Office of Naval Research. Available as microfilm or photocopy, Library of Congress, Washington, D. C.
- Miller, Leo J., 1955, Annual report for June 30, 1954 to April 1, 1955, Part 1. The chemical environment of pitchblende: U. S. Atomic Energy Comm. RME-3110(Pt. 1), 49 p., issued by U. S. Atomic Energy Comm. Tech. Inf. Service Extension, Oak Ridge, Tenn.
- Morachevskii, Yu. V., and Belyaeva, L. I., 1956, O sostave uranovanadatov [On the composition of the uranovanadates]: Geokhimiya, no. 7, p. 20-24.
- Murata, K. J., Cisney, E. A., Stieff, L. R., and Zworykin, E. V., 1950, Hydration and base-exchange properties of carnotite, tyuyamunite, and related compounds (abs.): Geol. Soc. America Bull., v. 61, no. 12, pt. 2, p. 1489-1490.
- Palache, C., Berman, H., and Frondel, C., 1951, Dana's system of Mineralogy, 7th ed., v. 2, New York, John Wiley and Sons, Inc.
- Sundberg, I., and Sillén, L. G., 1949, The crystal structure of  $KUO_2VO_4$ : Arkiv for Kemi, v. 1, p. 337-351.