RA NO. 51

RECLASSIFICATION AUTHORIZATION

In accordance with the authority delegated to me by memorandum from the General Manager, dated December 6, 1948, subject, "Security Procedures and Policies relating to the Domestic Raw Materials Program" and based on the criteria for determining classification, as outlined in Appendix A attached thereto, the document listed below is reclassified as indicated.

	Present Classification	Revised Classification
TEI-107 USGS-TELI Report 9 "Synthesis, Base Exchange, and Photosensitivity of Carnotite, Tyuyamunite, and Related Minerals" by K. J. Murata, E. A. Cisney, L. R. Stieff, and E. V. Zworykin, dated March 1950.	RESTRICTED	UNCLASSIFIED

March 31, 1950
Date

Jesse C Johnson
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Manager
Raw Materials Operations

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SYNTHESIS, BASE EXCHANGE, AND PHOTOSENSITIVITY OF CARNOTITE, TYUYAMUNITE, AND RELATED MINERALS

By

K. J. Murata, E. A. Cisney, L. R. Stieff, and E. V. Zworykin

(J) (abs.) Geol. Soc. Am. Bull. v. 61, no. 12, pt. 2
p. 1489, 1950.

U. S. Department of the Interior
Geological Survey
Washington, D. C.
August 1949

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SYNTHESIS, BASE EXCHANGE, AND PHOTOSENSITIVITY OF CARNOTITE, TYUYAMUNITE, AND RELATED MINERALS

by

K. J. Murata, E. A. Cisney, L. R. Stieff, and E. V. Zworykin

ABSTRACT

Hydrated uranyl vanadates of potassium, sodium, ammonium, calcium, strontium, and barium were synthesized as part of a mineralogic study of carnotite and tyuyamunite. Microscopic and electron-microscopic examination show the crystals to be diamond-shaped plates with micaceous cleavage.

On the basis of X-ray powder patterns, these compounds may be classified into four structural types:

Type 1. Potassium compound (carnotite) and ammonium compound.
Type 2. Sodium compound.
Type 3. Calcium compound (tyuyamunite).
Type 4. Strontium and barium compounds.

Compounds of type 1 differ from those of the other three types in being much less hydrated, containing, in the air-dried state, one molecule of water compared to 6-8 molecules in the others. The higher hydration of compounds of types 2-4 may be correlated with the presence of low-angle, basal reflections in their X-ray powder patterns. It is believed that the water molecules and alkali and alkaline earth ions occur between uranyl vanadate layers, a condition analogous to that found in the clay mineral montmorillonite. There is a progressive decrease in the interlayer spacing as water is removed by heating.

Compounds of types 2-4, when treated with solutions of potassium salts, rapidly exchange their cations for potassium, and are converted to carnotite. This also would result in the collapse of the postulated uranyl vanadate layers as the lower hydration of type 1 structure is attained. The reverse process, the conversion of carnotite to compounds of types 2-4, would involve the expansion of the interlayer space, and takes place much less readily.

When natural tyuyamunite is exposed to sunlight, its color changes from canary yellow to dark green. This solarization was first noted by Chirvinsky in the mineral from the type locality in Turkestan. W. T. Schaller has observed the same color change in a sample from Colorado, and he has further shown that the irradiated mineral slowly recovers the original color when kept in the dark. Among the synthetic compounds, all except those of type 1 solarize. The mechanism of solarization has not yet been determined, but chemical and spectrophotometric data indicate that a valence change in vanadium is involved.

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INTRODUCTION

Twenty years ago, J. G. Fairchild and W. T. Schaller (1) of the Geological Survey published a paper on synthesis and base exchange properties of a large number of alkali and alkaline-earth uranyl phosphates that comprise the autunite group of minerals. This work has been the inspiration for a similar approach to the study of the uranyl vanadate minerals, carnotite and tyuyamunite, which are important uranium minerals in our uranium deposits of the Colorado Plateau.

METHOD OF SYNTHESIS

The simple salting-out technique used successfully by Fairchild for synthesizing autunites unfortunately does not work for the uranyl vanadates. The high acidities involved causes the precipitation of vanadic oxide as an undesirable side reaction. The general method of synthesis that has been worked out consists of the following 3 steps:

Step 1. The preparation of alkali or alkaline-earth pyrovanadates by low-temperature sintering of the respective carbonates with vanadium pentoxide. For the ammonium compound, ammonium vanadate is used directly.

Step 2. Dissolving the pyrovanadates to obtain water solutions. The alkali pyrovanadates dissolve readily in water, but those of the alkaline-earths require careful treatment with successive portions of 3% nitric acid. The pH of all solutions is then adjusted to 6.

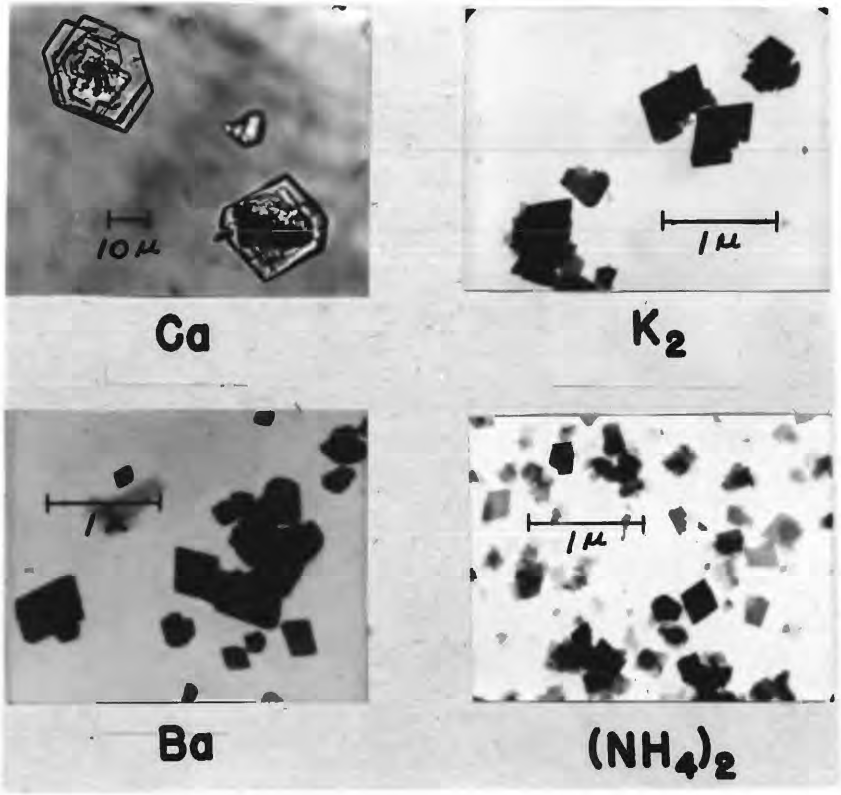
Step 3. Precipitation of the desired uranyl vanadate by addition of a stoichiometric quantity of uranyl nitrate. A gelatinous precipitate forms immediately. The pH is then adjusted to 3, and the preparation digested on the steam bath for two weeks.

Slide 1 (pl. 1) shows the general appearance of some of the synthetic products. Crystals of tyuyamunite or the calcium compound are notably coarser than those of all others. They were photographed at a magnification of 555, whereas the other compounds required the use of the electron microscope at a magnification of 15,000. All compounds crystallize as rhombic plates with good basal cleavage. Tyuyamunite shows a well developed (010) face, truncating the acute angles of the rhomb.

Because of the extremely small size of the crystals, both the natural and synthetic minerals are most conveniently identified by means of their X-ray powder diffraction patterns. Where mixtures are involved, supplementary spectrographic analysis for the alkalies and alkaline-earths is helpful.

CLASSIFICATION BASED ON X-RAY POWDER PATTERNS

X-ray powder patterns indicate that the several compounds may be classified into four structural types shown on the next slide (pl. 2). The compositions are in agreement with the general formula already established for carnotite and tyuyamunite with the exception of the sodium compound. The composition of the sodium compound, with its additional molecule of vanadic oxide, is anomalous,


10 μ
1 μ
Ca
K$_2$
1
1 μ
Ba
(NH$_4$)$_2$

CLASSIFICATION OF URANYL VANADATES, BASED ON X-RAY POWDER PATTERNS

Type 1	$K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot H_2O \pm$ (carnotite) $(NH_4)_2O \cdot 2UO_3 \cdot V_2O_5 \cdot H_2O \pm$
Type 2	$Na_2O \cdot 2UO_3 \cdot 2V_2O_5 \cdot 6H_2O$?
Type 3	$CaO \cdot 2UO_3 \cdot V_2O_5 \cdot 8.5H_2O \pm$ (tyuyamunite)
Type 4	$SrO \cdot 2UO_3 \cdot V_2O_5 \cdot 6.5H_2O \pm$ $BaO \cdot 2UO_3 \cdot V_2O_5 \cdot 6H_2O \pm$

and needs further study. Its 6 molecules of water would ally the sodium compound with those of the alkaline earths rather than with those of potassium and ammonium.

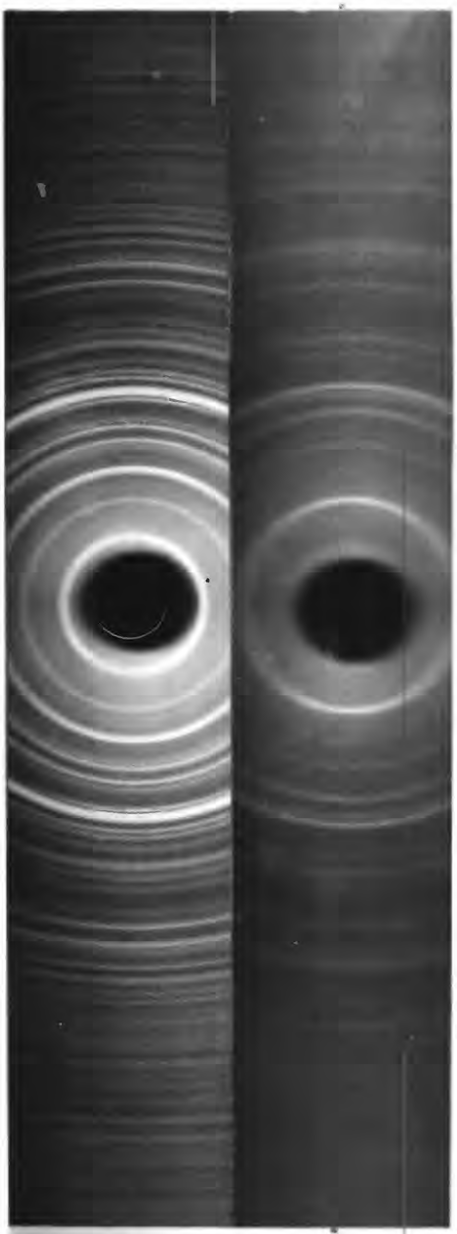
The X-ray powder patterns [illegible] of compounds of types 2-4 are characterized by a strong line occurring at low angles to the incident beam. This line has been correlated with the high water content of these compounds, and can be interpreted as a basal reflection from a fundamental uranyl vanadate layer structure. The reality of such a layer structure is strongly suggested by the platy habit, the micaceous cleavage, and the optical properties of the crystals.

The next slide (pl. 3) shows the low-angle basal reflection in the X-ray powder pattern of tyuyamunite. In contrast to the other compounds, the corresponding strong line in the carnotite pattern is at a much greater angle. The general appearance of the X-ray powder patterns of all of these compounds is largely controlled by the characteristic amounts of water in the compounds. In illustration of this point, tyuyamunite was partly dehydrated by heating to 58°C the resulting pattern then closely simulates the pattern of the barium compound. Such similarities are further evidence that all of these compounds have the same fundamental structure.

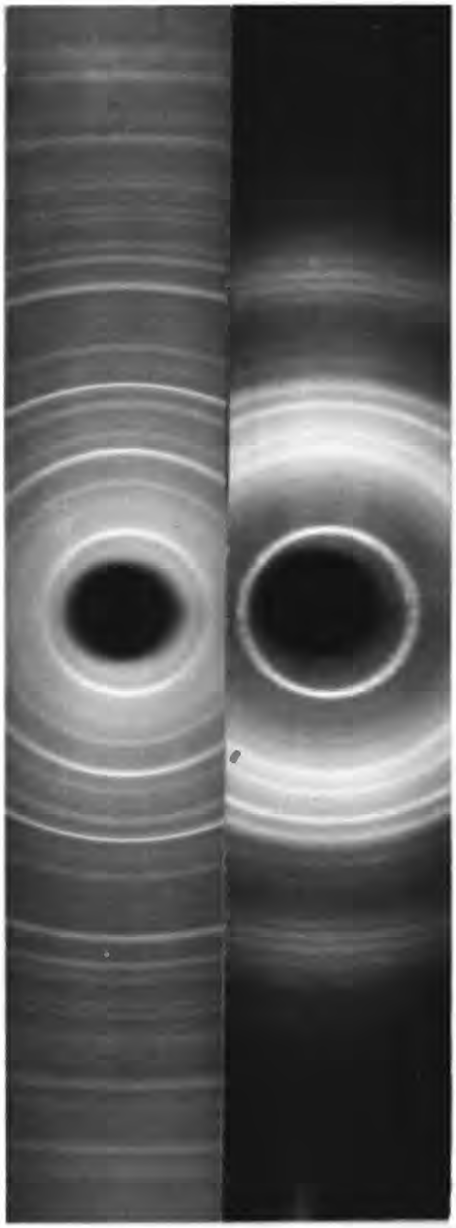
HYDRATION CHARACTERISTICS

Hillebrand (2) in 1924 was first to notice that the water content of tyuyamunite and carnotite fluctuates with the prevailing humidity and temperature. His observations were confirmed by Hode (3).

Plate 3



TYUY. **CAR.**



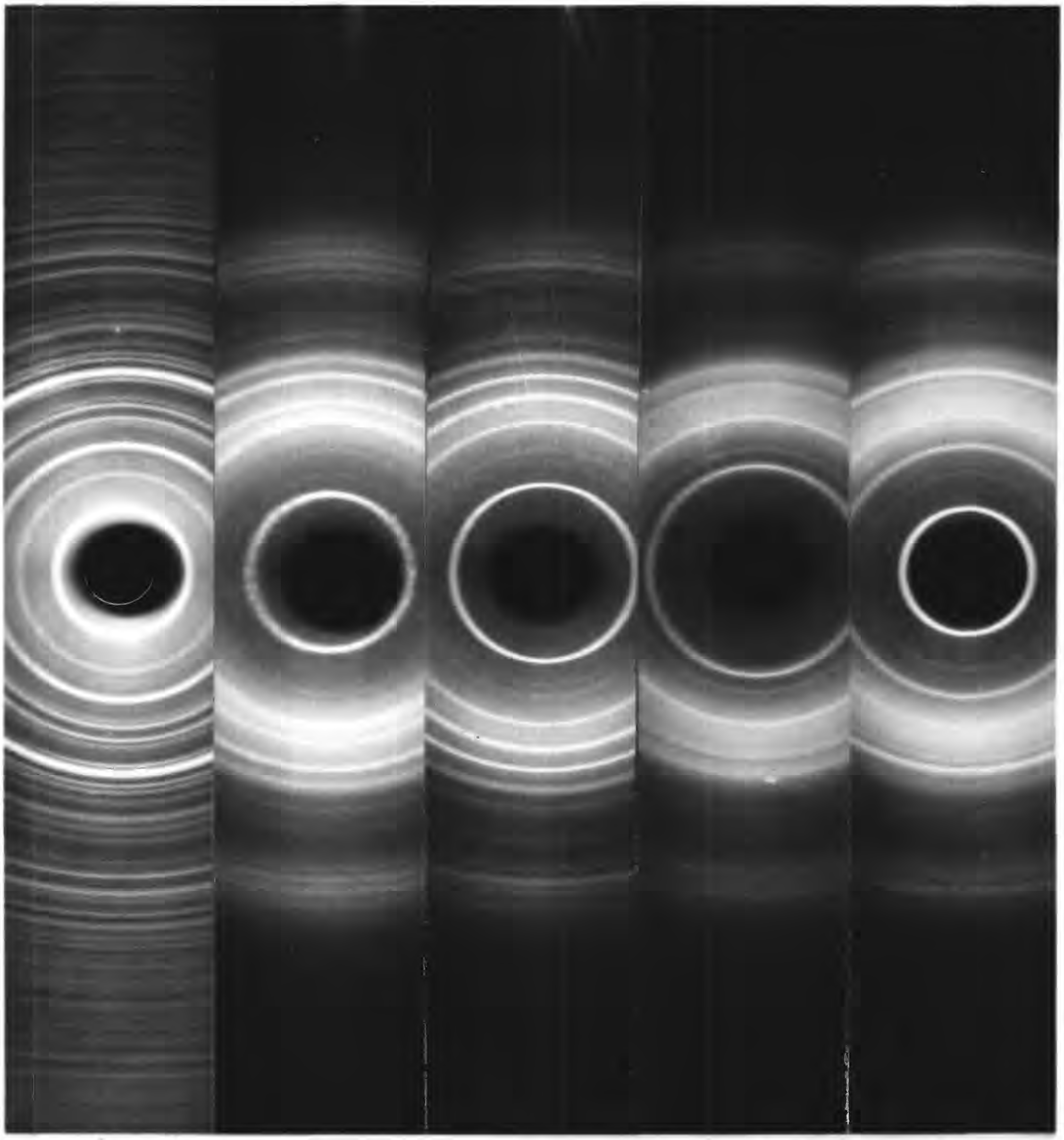
Ba. **TYUY.-52°**

Merwin (4) showed that the density of tyuyamunite increases as the mineral is dehydrated. The modern technique of X-ray diffraction has enabled us to follow this reversible dehydration of tyuyamunite in greater detail.

A series of X-ray powder patterns taken of tyuyamunite as it was dehydrated by heating to higher and higher temperatures is shown on the next slide (pl. 4). The increase in the angle of the basal reflection with decreasing water content is clearly evident. Measurements on these films show that the removal of water causes a contraction of the interlayer spacing from 9.9 to 6.1 angstrom units. The last pattern on the right hand side of the slide is that of the dehydrated specimen placed in an atmosphere saturated with water vapor. The mineral regained its original water content and expanded back to its original dimension.

A similar reversible expansion and contraction of the interlayer spacing in response to the entrance and exit of water has been studied in another platy mineral, the clay mineral montmorillonite, by a number of workers including Hofmann and Bilke (5) and Hendricks, Nelson, and Alexander (6). Further striking similarities with the clay minerals of the montmorillonite group are found in the base exchange properties of these uranyl vanadates.

Plate 4


20°c 52° 110° 200° Rehydrated

DEHYDRATION OF TYUYAMUNITE

BASE EXCHANGE PROPERTIES

The base exchange properties of tyuyamunite and carnotite were first investigated by Hillebrand (2) (7), who found that although the calcium mineral is readily converted to the potassium one, the reverse exchange takes place very slowly. The results of our preliminary study of the uranyl vanadates of calcium, strontium, barium, and potassium are presented diagrammatically on the next slide (pl. 5).

As a standard test, 0.3 gram of each compound was treated on the steambath with four 30-cc portions of one-normal solutions of the desired base. The final product was washed free of excess salts, and examined both spectrographically and by means of the X-ray diffraction technique.

In analogy to the situation in montmorillonite, we picture the exchangeable bases as being situated between uranyl vanadate layers along with the water molecules.

In general, the results show that an exchange leading to a lower state of hydration and a smaller interlayer spacing takes place far more readily than one leading to a higher state of hydration and a larger spacing. Thus, it is easiest to convert other compounds to the potassium mineral carnotite, and most difficult to change them to the calcium mineral tyuyamunite.

In one experiment, not shown on the slide, an unsuccessful attempt was made to exhange potassium out of carnotite with a molar solution of ammonium nitrate. The ammonium ion would also form a

Plate 5

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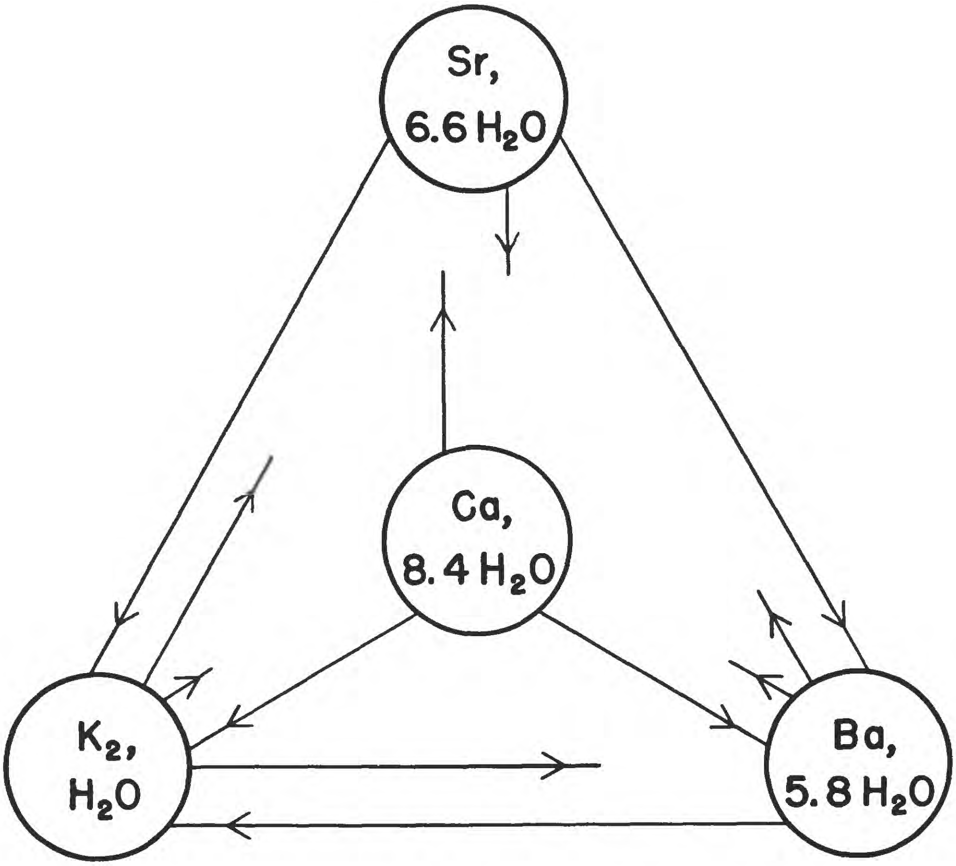

EXTENT OF BASE EXCHANGE

WITH 4 PORTIONS OF ONE-NORMAL SOLUTION

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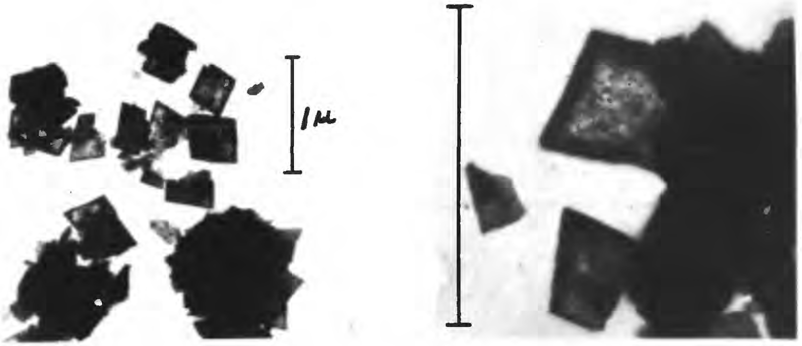
monohydrated compound. Apparently, one molecule of water per formula weight does not cause the interlayer spacing to be wide enough for ready movement of both the incoming and outgoing ions. The conversion of carnotite to compounds of the alkaline-earths thus must take place through a simultaneous invasion by alkaline-earth ions and water molecules.

These preliminary results merely indicate general trends, and in order to predict whether a given exchange would occur in nature more data on the equilibrium ratios of the bases involved must be obtained at different concentration levels and temperatures.

According to the work of Page and Baver (8), the clay mineral beidellite of the montmorillonite group shows preferential retention or "fixation" of potassium and barium if the samples are dried prior to base exchange treatment. The ionic diameters of potassium and barium are nearly the same, and it is believed that they are of just the right size to fit into sites in the atomic structure of beidellite that are identical to sites occupied by potassium in mica. These considerations of structure add special interest to the observation that the uranyl vanadates also preferential retention of potassium and barium. The effect is very much more marked with the uranyl vanadates because the hydration of these minerals and their interlayer spacing are more closely related to the nature of the base present between the layers.

Except for expansion or contraction in the direction normal to the plates, the conversion of one uranyl vanadate into another through base exchange does not alter the dimensions of the crystals. Our observations are not sufficiently precise to exclude minute changes in the angles of the rhombs. When viewed in the direction normal to the rhombic plates, the exchanged products, therefore, seem to be pseudomorphs of the original compounds. The (010) face that is normally found only in tyuyamunite is preserved in carnotite made from tyuyamunite through base exchange.

A very striking example of this pseudomorphous relationship has been found in a sample of carnotite that was only partly converted to the barium compound during a base exchange experiment. Electron micrographs of the crystals are shown in the next slide (pl. 6). An X-ray powder pattern of this material indicates the presence of both phases. These crystals differ radically from those of any of the pure compounds in showing contrasting outer and inner zones, and it seems reasonable to assume that we have interrupted a pseudomorphous conversion of carnotite into the barium compound. Because the ratio of the interlayer spacing of the barium compound to that of carnotite is 5:4, the outer zone would be that much thicker than the core. We have not, as yet, seen any evidence for appreciable solid solution between compounds of markedly different hydration.



Carnotite Partially
Replaced by Barium

PHOTOSENSITIVITY

The photosensitivity of some of these uranyl vanadate compounds is another property of considerable interest. When natural tyuyamunite is exposed to direct sunlight, its color changes surficially from canary yellow to dark green in about 20 minutes. This solarization was first noted by Chirvinsky (9) in the mineral from the type locality in Turkestan. W. T. Schaller has observed the same color change in a sample from Colorado, and he has further shown that the irradiated mineral slowly recovers its original color when kept in the dark. Simply heating the mineral does not induce this color change.

Among the synthetic compounds, those of potassium and ammonium do not solarize, and the calcium compound always does. When the calcium compound is converted to the potassium one through base exchange, the power of solarization is lost. Most (but not all) preparations of the remaining compounds solarize. There is some subtle difference between the solarizing and non-solarizing samples of this last group that has so far escaped detection.

The dark green color of the solarized compounds is quickly changed back to the original yellow color by treatment with dilute acids, but not with dilute alkalies. A dilute solution of sodium peroxide, however, is effective in restoring the yellow color, but an alkaline hydroquinone reducing solution is not. The presence of some kind of a reduced substance in the solarized compounds is suggested by these experiments.

We do not know enough yet to describe the exact mechanism of solarization. However, a temporary change in the valence of uranium or vanadium or of both is undoubtedly involved. The absence of solarization in calcium uranyl phosphate and arsenate of the uranite group suggests that uranium is not the element that undergoes a change in valence.

The next slide (pl. 7) gives reflectance measurements on synthetic carnotite, tyuyamunite, and solarized tyuyamunite, kindly made for us by Mr. H. J. Keegan of the U. S. Bureau of Standards. The reflectance curves for carnotite and tyuyamunite are typical of a yellow substance. The curve for the green solarized tyuyamunite discloses a general darkening or greater absorption beginning in the green region of the spectrum and extending to longer wavelengths.

The ratios of reflectances of the original and solarized tyuyamunite for different wavelengths is shown in dashed lines. This curve gives the shape of the new band of absorption that has appeared in the mineral as a result of solarization. The simple, structureless curve is that of a blue substance. As is well known, quadrivalent vanadium is characterized by the blue color of its compounds, and we tentatively conclude that solarization involves a temporary photochemical reduction of vanadium from a valence of +5 to +4.

Plate 7

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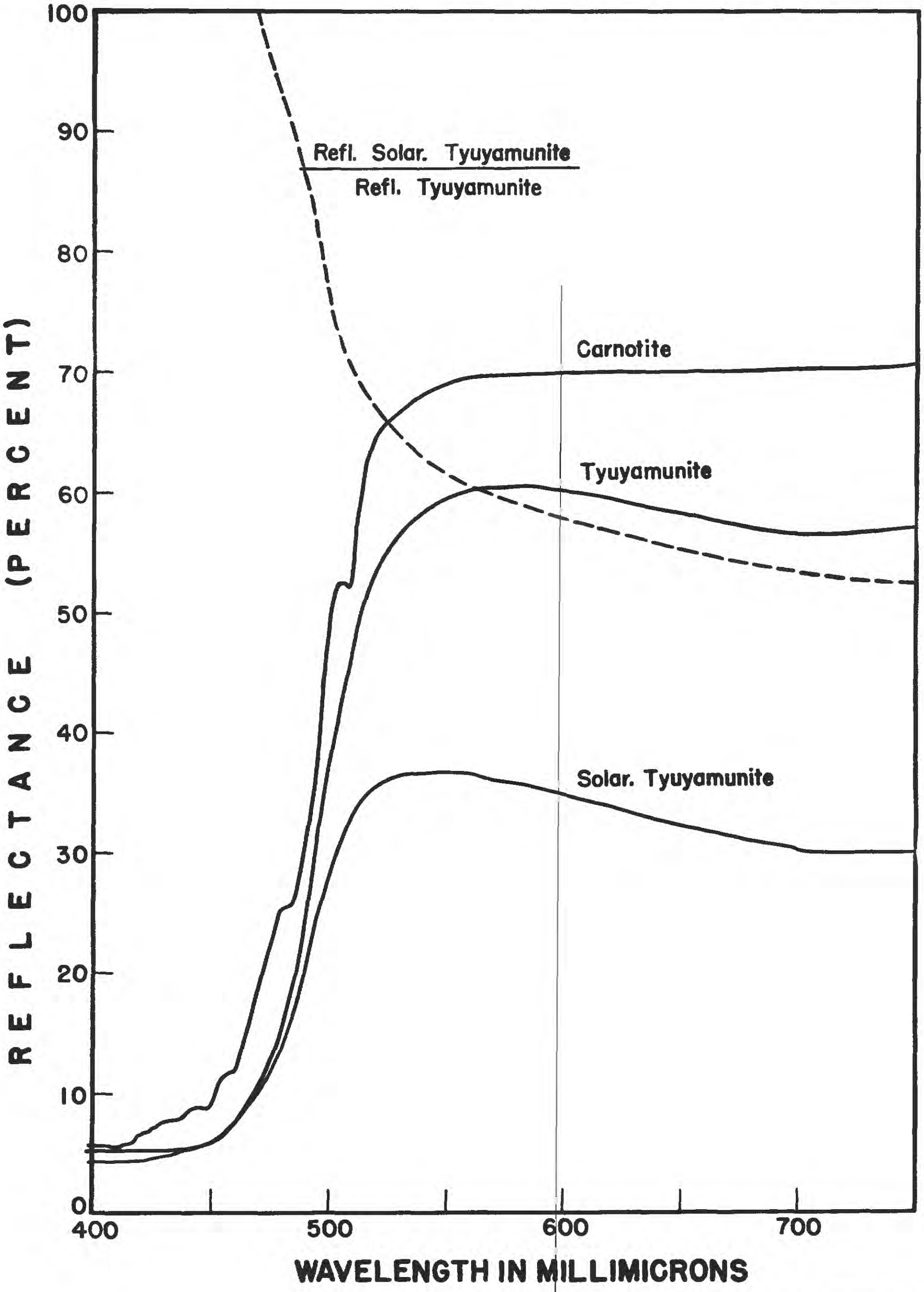

Data by U.S. BUREAU OF STANDARDS

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SUMMARY

In summary, the remarkable similarity should be noted between the uranyl vanadate compounds and the clay minerals of the montmorillonite group with respect to hydration and base exchange properties. This similarity is undoubtedly due to a type of internal structure that is common to both groups of minerals - an interleaving of water and exchangeable ions between sheets of the fundamental structure. Our work has been exploratory in nature, and much remains to be done in order to make our knowledge more complete and precise.

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