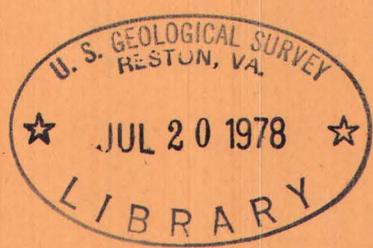


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Synthesis of calcium vanadate minerals and related compounds

By Richard Marvin



Trace Elements Investigations Report 616

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Geology and Mineralogy

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Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

SYNTHESIS OF CALCIUM VANADATE MINERALS AND RELATED COMPOUNDS*

By

Richard Marvin

June 1956

Trace Elements Investigations Report 616

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SYNTHESIS OF CALCIUM VANADATE MINERALS AND RELATED COMPOUNDS

By Richard Marvin

ABSTRACT

Synthesis of natural vanadates shows that most of them are stable in an acid environment. Phase studies of a portion of the system $\text{CaO-V}_2\text{O}_5\text{-H}_2\text{O}$ indicate that calcium vanadates are an indicator of environmental pH conditions. Some minerals, such as pascoite, indicate rapid evaporation of vanadate solutions; other minerals, such as hewettite, show that slow evaporation took place. cursory examination of systems $\text{K}_2\text{O-UO}_2(\text{NO}_3)_2\text{-V}_2\text{O}_5$ and $\text{CaO-UO}_2(\text{NO}_3)_2\text{-V}_2\text{O}_5$, both in aqueous solution, has yielded information on the relationships among carnotite, tyuyamunite, and rauvite.

INTRODUCTION

The weathering of primary vanadium and uranium minerals leads to the formation of many secondary minerals, some containing both uranium and vanadium. Synthesis of some of the secondary minerals was undertaken to obtain knowledge of the environment of formation. The synthesis of vanadium minerals containing only fully oxidized vanadium (V) was first undertaken. Then uranium (VI) was added to solutions to obtain uranium-containing vanadates. In this way, the pH range, temperature, and saturation conditions under which some of these minerals can be synthesized are now known.

As these minerals presumably result from the attack of ground water and air on primary uranium and vanadium minerals, resulting in their

oxidation and solution, synthesis was attempted from aqueous solutions containing the desired ions at temperatures between 20° and 90° C. The pH of a solution was varied by adding either acetic or nitric acid. The solid phases were identified by X-ray diffraction patterns and, when possible, by optical methods. The fine-grained habit of some precipitates made optical identification unreliable.

CALCIUM VANADATES

One- to two-liter stock solutions containing calcium and vanadate ions were prepared from dry reagents, CaO and V₂O₅ (containing a small amount of V₂O₄), in the following way. The V₂O₅ was powdered and stirred into 1 liter of water containing 100 ml of 30 percent H₂O₂ which increased the solubility of V₂O₅ and oxidized any V(IV) to V(V). The powdered CaO was then added. The mixture was agitated and slowly heated to boiling to rid the solution of excess H₂O₂. Care was taken in boiling the solution as the release of O₂ from the H₂O₂ was very rapid and the solution violently agitated. The ratio of V₂O₅ to CaO should not be smaller than 3:1 by weight unless the solution is very dilute, as a fairly insoluble hydrated pyrovanadate will precipitate when the solution is heated. After the excess H₂O₂ was destroyed, the solution was cooled, filtered, and analyzed. A useful stock solution has a concentration of 0.04M CaO and 0.08M V₂O₅. More concentrated solutions are saturated at room temperature.

After the stock solution was prepared and analyzed, an aliquot was taken (generally not less than 20 ml). The pH was adjusted to the desired value by adding dilute (1+9) nitric acid dropwise (dilute acetic acid was sometimes used). The solution was then placed in an oven set at the

desired temperature and evaporated until a solid phase or phases separated out. Table 1 illustrates the actual handling of two aliquots.

As can be seen from the samples in table 1, the pH of a solution varies with time. Solutions having pH values over 6.2 tend to drift toward this value. Very basic solutions absorb atmospheric CO_2 which lowers the pH and forms calcite crystals. Solutions in the pH range 4.8 to 6.2, generally reveal a pH drift toward 6.2. Between pH 2.3 and 4.8, the drift is towards the latter value; below 2.3 it is towards 0 pH.

As stock solutions with a pH greater than 8 necessarily have a very low concentration of V_2O_5 and CaO to prevent precipitation during preparation, large aliquots must be taken to provide sufficient solid phase for proper identification. To facilitate matters an aliquot of a more concentrated stock solution (pH less than 7.5) was placed in a beaker and diluted sufficiently with H_2O to prevent immediate precipitation of a solid phase at the basic pH which was to be explored. The electrodes of the pH meter were then placed in the diluted aliquot and the pH raised to the desired value by adding freshly prepared $\text{Ca}(\text{OH})_2$ solution or 100 to 200 mg of powdered CaO . In the latter case, the solution was vigorously stirred until the pH rose to the desired value; the solution was then filtered to remove excess solid CaO and then evaporated at the desired temperature.

The addition of CaO or $\text{Ca}(\text{OH})_2$ changed the known $\text{V}_2\text{O}_5/\text{CaO}$ ratio. Since it was impractical to analyze each solution prepared in the above manner, the approximate ratio was determined as a function of the pH. From the analyses of stock solutions and their pH values, a graph of pH plotted against $\text{V}_2\text{O}_5/\text{CaO}$ ratio was constructed. Then the approximate ratio of a solution can be determined from its pH by using this graph. Knowledge of the exact ratio is not necessary as it has been found that the phase

Table 1.--The preparation and handling of two runs used in construction of parts of
CaO-V₂O₅-H₂O phase diagram.

	<u>Run no. Ca-17-18</u>	<u>Run no. Ca-17-19</u>	<u>Remarks</u>
CaO-V ₂ O ₅ solution			
CaO 0.0084 g/ml	20 ml	20 ml	Dilute HNO ₃ added to each run
V ₂ O ₅ 0.0279 g/ml			
pH of runs on 1st day	5.15	4.0	Beakers were covered with watch-glasses and placed in oven at 56° C.
pH on 3d day	5.0	3.9	Hewettite forming in each beaker.
pH on 5th day	4.95	3.9	Hewettite recovered from solution Ca-17-19.
pH on 7th day	4.85	--	Hewettite plus a few pascoite crystals recovered from solution Ca-17-18.
			Phases were separated from the mother liquor in a Buchner funnel, washed with water, acetone or alcohol, and air-dried.

boundaries are not sensitive to this variable.

Figure 1 shows sections of the CaO-V₂O₅-H₂O system with pH plotted on the vertical axis. The pH, temperature, and rate of evaporation all determine the solid phase which is formed.

The concentration of CaO or V₂O₅ seems to be unimportant. In each section, an area has been enclosed by dashed lines. This area represents the pH range of CaO-V₂O₅ stock solutions. The pH is dependent on dilution and V₂O₅/CaO ratio. The more dilute a solution is the closer its pH value will approach 7. The V₂O₅/CaO ratio starts at 0 with a high pH value. As V₂O₅ is added, the pH gradually decreases; solutions change from basic to acid.

Suppose a very dilute solution having a certain V₂O₅/CaO ratio and an initial pH value near 7 is evaporated. The pH will gradually move either up or down, toward the area between the dashed lines. When the pH value falls within this area, the appearance of a solid phase is imminent.

To explore the system at lower pH values than could be obtained with dissolved CaO-V₂O₅ alone, HNO₃ was added to solutions as described above. Likewise, exploration at higher pH values could have been accomplished by adding a soluble base but not without adding an anion which might form new solid phases, further complicating the phase diagram. It seems reasonable to assume that the phase boundaries would remain the same if extended to the right.

The phase diagram shown in figure 2 is constructed from the pH readings obtained on first noticing a phase present in an evaporating solution.

Hydrated orthovanadates and pyrovanadates are the stable phases under basic conditions. None of these solids has been established as minerals

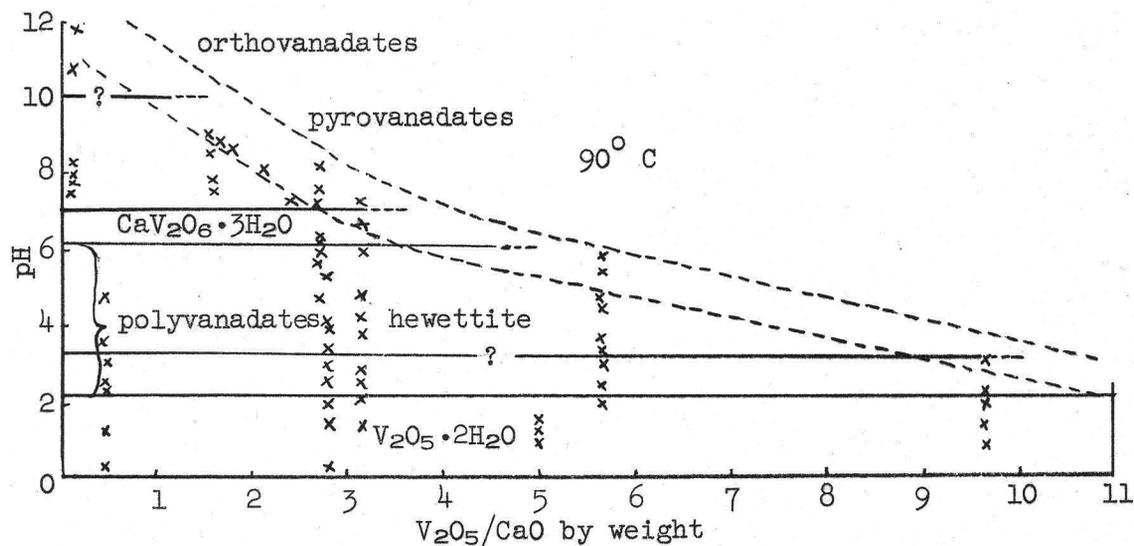
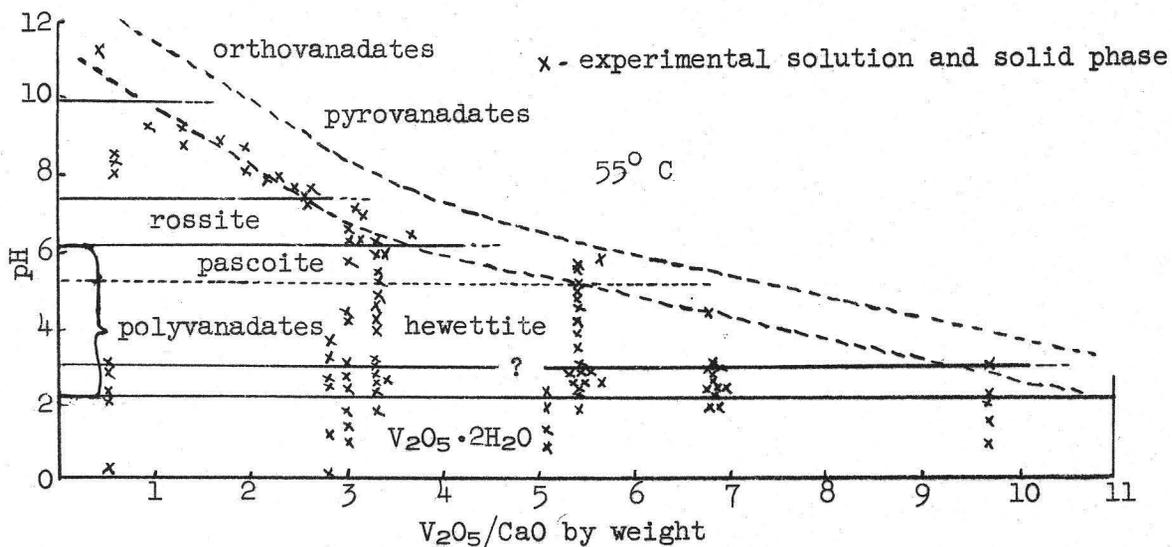
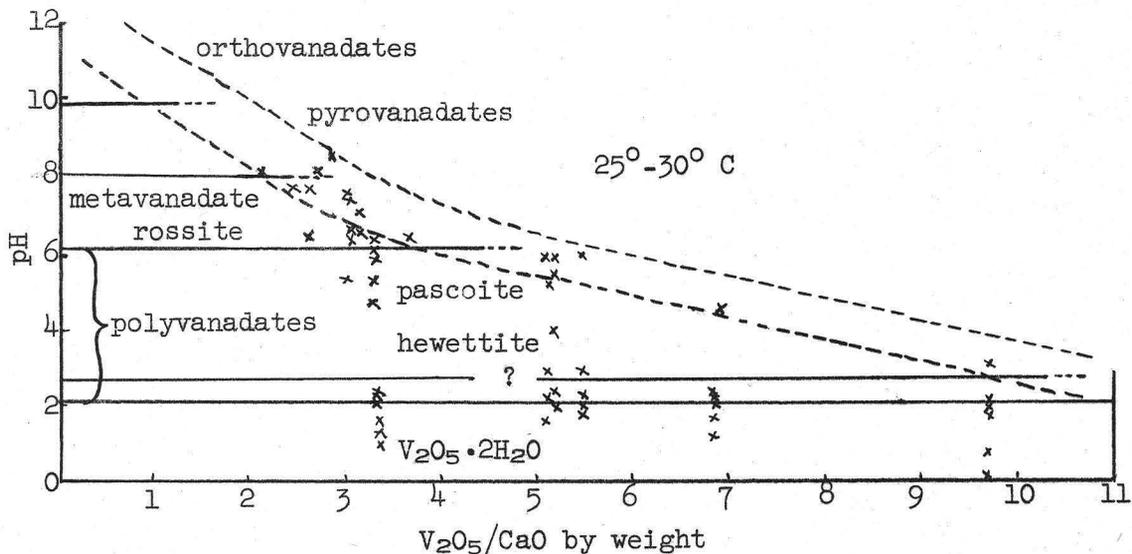


Figure 1.--Sections of the CaO-V₂O₅-H₂O system.

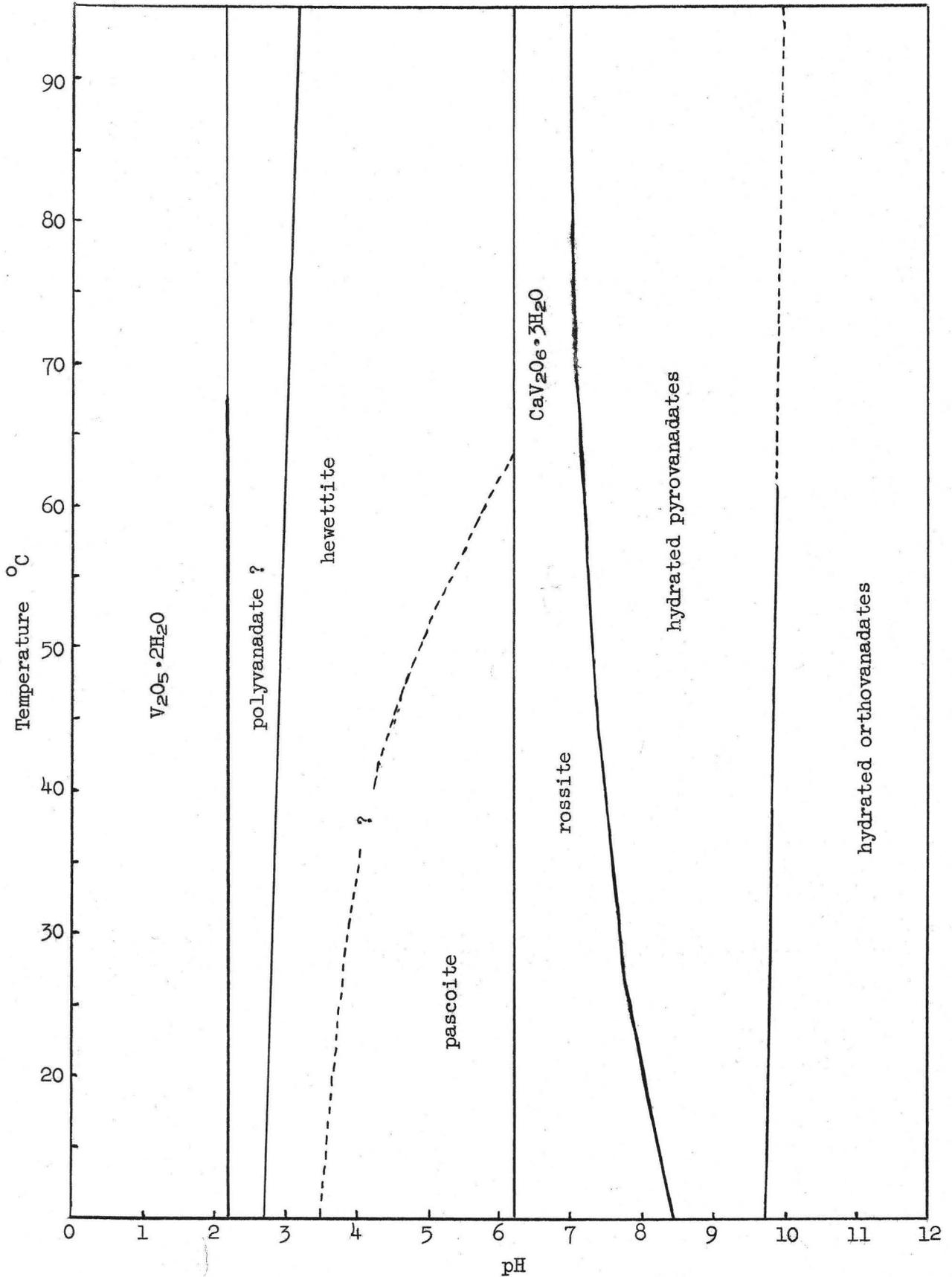


Figure 2.--Diagram showing the relationship of calcium vanadates to pH and temperature.

although Hess and Schaller (1914) reported a mineral which they called pintadoite, $(Ca_2V_2O_7 \cdot 9H_2O)$, a hydrated pyrovanadate. None of the synthetic pyrovanadates now known agrees with the description of pintadoite.

The hydrated metavanadate, $CaV_2O_6 \cdot 4H_2O$, corresponding to the mineral rossite, straddles the neutral region throughout the temperature range. At temperatures around $55^\circ C$ and above, the metavanadate $CaV_2O_6 \cdot 3H_2O$ is also present. This phase is not known to occur in nature. The relationship between the two metavanadates is not clear.

Below pH 6.2, the hydrated polyvanadates, $Ca_3V_{10}O_{28} \cdot 16H_2O$ and $CaV_6O_{16} \cdot 9H_2O$, crystallize, corresponding respectively to pascoite and hewettite. Their formation is dependent on pH, temperature, and rate of evaporation. A calcium vanadate solution at $40^\circ C$ with a pH value between 2.8 and 5.5 produces pascoite if rapidly evaporated and hewettite if very slowly evaporated. Increasing the temperature of the solution favors the crystallization of hewettite. Sometimes hewettite will start crystallizing, then pascoite crystals will also appear, and the two will grow simultaneously.

Potassium polyvanadates, like the calcium polyvanadates, are dependent on temperature and rate of evaporation between pH 5 and 6.7. Various evaporation rates at temperatures below $40^\circ C$ cause polyvanadates of composition $K_2V_4O_{11} \cdot 7H_2O$, $K_6V_{10}O_{28} \cdot 10H_2O$, and $K_6V_{10}O_{28} \cdot 8H_2O$ to crystallize. Preventing further evaporation will cause any existing polyvanadate to redissolve and the stable phase $K_2V_6O_{16}$ to crystallize. By analogy, pascoite, $Ca_3V_{10}O_{28} \cdot 16H_2O$, is considered the metastable phase and hewettite, $CaV_6O_{16} \cdot 9H_2O$, the stable phase, although pascoite cannot be redissolved and hewettite crystallized in its place merely by stoppering the solution as is possible with potassium vanadate solutions.

Solutions with a pH value slightly above 2.2 precipitate a brownish, very fine grained material which is probably a polyvanadate or mixture of a polyvanadate and hydrated V_2O_5 . Below pH 2.2, calcium vanadates do not form as solid phases; instead, dull-green or black $V_2O_5 \cdot 2H_2O$ precipitates. $V_2O_5 \cdot 3H_2O$, corresponding to the mineral navajoite, has not been produced in these studies.

Synthetic rossite and pascoite are identical to the natural minerals in physical properties and appearance, but the synthetic materials are better crystallized. Synthetic hewettite is like the natural hewettite in fibrous habit, silky luster, and hardness but differs in color. Natural hewettite is a vivid deep red; synthetic hewettite is a light- to dark-brown color. Like their natural counterparts, synthetic rossite and hewettite dehydrate on exposure to the atmosphere to metarossite and meta-hewettite, respectively.

Below, are the optical properties determined for synthetic rossite and pascoite using phosphorus-sulfur-methylene iodide index liquids with white light.

Rossite ($CaV_2O_6 \cdot 4H_2O$)

$\alpha = 1.720 \pm 0.003$ at $28^\circ C$	triclinic (Weeks and Thompson, 1954)
$\beta = 1.783 \pm 0.003$	biaxial negative
$\gamma = 1.842 \pm 0.003$	$2V = 85^\circ$ (calc.)
	colorless, nonpleochroic
	$r < v$ (?) dispersion, faint

Chemical analysis, in percent, of synthetic rossite by George B. Magin, Jr., U. S. Geological Survey.

	CaO	V_2O_5	H_2O	Total
Found	18.58	58.43	22.89	99.90
Calc.	18.09	58.67	23.24	100.00

Pascoite ($\text{Ca}_3\text{V}_{10}\text{O}_{28}\cdot 16\text{H}_2\text{O}$)

$$\begin{aligned}\alpha &= 1.771 \pm 0.003 \text{ at } 27^\circ \text{ C} \\ \beta &= 1.824 \pm 0.003 \\ \gamma &= 1.826 \pm 0.003\end{aligned}$$

monoclinic (Evans et al., 1954)
 biaxial negative
 $2V = 30^\circ$ (calc.)
 pleochroic
 X = light cadmium yellow
 Y = orange
 Z = cadmium yellow
 absorption $X < Z < Y$
 $r > v$ dispersion, very strong

Chemical analysis, in percent, of synthetic pascoite by George B. Magin, Jr., U. S. Geological Survey.

	CaO	V ₂ O ₅	H ₂ O	Total
Found	12.56	65.23	22.23	100.02
Calc.	12.32	66.58	21.10	100.00

Pascoite has been heretofore listed as $\text{Ca}_2\text{V}_8\text{O}_{17}\cdot 11\text{H}_2\text{O}$ (Hillebrand, Merwin, and Wright, 1914; Palache, Berman, and Frondel, 1951), but crystallographic and density studies (Evans, Mrose, and Marvin, 1954) on synthetic pascoite plus chemical analyses show that its formula should be $\text{Ca}_3\text{V}_{10}\text{O}_{28}\cdot 16\text{-}17\text{H}_2\text{O}$. The formula as determined from the chemical analysis alone requires 17 molecules of water, but 16 molecules of water to agree best with density measurements (Evans, Mrose, and Marvin, 1954). The exact amount of water will not be known until the crystal structure has been determined. The extra water revealed by chemical analysis may be due to included water in rapidly formed crystals.

Synthetic hewettite was not identified optically because of its fine fibrous habit, its high indices of refraction (above 2.0), and its reaction with high-index oils which changed the color of the fibers from a yellow or red to a dark green or black. Nonreacting index oils show that the fibers have a yellow to red color, parallel extinction, and are nonpleochroic. Identification was made by X-ray powder diffraction films.

The $V_2O_5 \cdot 2H_2O$ phase is usually very fine grained, occasionally fibrous. It has a dark reddish brown color in the mother liquor but changes on washing and drying to a dull brown or green. Solutions with pH values less than 1 sometimes produce a black hydrated vanadium pentoxide. The $V_2O_5 \cdot 2H_2O$ is soft with a dull, sometimes velvetlike, luster. Examination with a petrographic microscope reveals an anisotropic, yellowish-green material with indices of refraction greater than 1.9; high-index oils react with the material. Identification is made by X-ray powder diffraction patterns and chemical analyses.

The solubilities of synthetic rossite, pascoite, hewettite, and $V_2O_5 \cdot 2H_2O$ as determined in doubly distilled water at 30° C are as follows:

Rossite - 4.55 g/liter, pH of solution 6.8

Pascoite - more than 20 g/liter, pH of solution 6.1

Hewettite - 0.03 g/liter, pH of solution 4.5

$V_2O_5 \cdot 2H_2O$ - 0.03 g/liter, pH of solution 4.1

The solubility figure of the pascoite is approximate. Hewettite crystallized within a short time from the nearly saturated or saturated pascoite solution and changed the ratio and concentration of dissolved $CaO-V_2O_5$.

To apply the information of the phase diagram to field conditions, one must understand what happens during the attack by air and ground water on the primary mineral assemblage. Thus, the breakdown of sulfides, predominantly pyrite, produces acid conditions. The acid conditions and available oxygen facilitate the solution and oxidation of vanadium. The pH of such a solution is affected by the solution of vanadium minerals and associated calcite, dilution by other ground waters which may be slightly basic, and movement through the sediments. When the solution is saturated,

rossite will crystallize if the pH is above 6.2. (It is doubtful if the pH ever rises much above 8 as no indisputable evidence of natural pyrovanadates has been found.) Hewettite will develop if the pH is less than 6.2 and concentration is very slow. The necessity of very slow concentration in the formation of hewettite is shown by the fact that it does not form as an efflorescence on mine walls or surface exposure where evaporation is rapid, as does pascoite. Hewettite is found in porous or fractured sediments where evaporation is greatly retarded.

If the ground water is quite acid, below pH 2.2, hydrated vanadium pentoxide will form. It is possible that if only a very minor amount of calcium ions or other cations were present in the ground water, hydrated V_2O_5 would also form at higher pH values, since hydrated V_2O_5 has formed at pH values as high as 4 in the laboratory.

URANIUM-CONTAINING VANADATES

In an attempt to learn about the formation of carnotite, $K_2(UO_2)_2(VO_4)_2 \cdot 1-3H_2O$, and tyuyamunite, $Ca(UO)_2(VO_4)_2 \cdot 7-10.5H_2O$, exploration of the systems $K_2O-UO_3-V_2O_5-H_2O$ and $CaO-UO_3-V_2O_5-H_2O$ was started.

The method of exploration was much the same as in the $CaO-V_2O_5-H_2O$ system. Thus, in the $K_2O-UO_3-V_2O_5-H_2O$ system, stock solutions were prepared from the dry reagents, KOH, V_2O_5 (containing some V_2O_4), and $UO_2(NO_3)_2 \cdot 6H_2O$. Since KOH and $UO_2(NO_3)_2 \cdot 6H_2O$ are readily soluble in water, stock solutions of 5.5M KOH and 0.127M $UO_2(NO_3)_2$ were easily prepared. A colloidal solution of V_2O_5 (0.0015M) was prepared by dissolving V_2O_5 in water containing H_2O_2 , then boiling to rid the solution of excess H_2O_2 . A KOH- V_2O_5 stock solution was prepared by dissolving KOH in 1 liter of H_2O ,

adding powdered V_2O_5 and 50 ml of 30 percent H_2O_2 , and heating to boiling to rid the solution of excess H_2O_2 . The solution was then cooled, filtered, and analyzed. Concentrations ranged from 0.18 to 0.32M KOH and 0.23 to 0.62M V_2O_5 .

Solutions for evaporation are prepared from aliquots of the stock solutions. These aliquots have to be diluted approximately 100 fold to prevent instant precipitation on mixing. The KOH- V_2O_5 aliquot is first diluted, then any additional KOH or V_2O_5 which is needed to obtain the desired ratio is added from the prepared stock solutions. The $UO_2(NO_3)_2$ aliquot is put in another beaker and diluted. The two solutions are then mixed by pouring the uranium nitrate into the KOH- V_2O_5 solution. The reverse procedure results in initially cloudy solutions. The pH is adjusted by adding HNO_3 (1+9). Solutions are evaporated at room temperature (24° to 30° C) or on a hot plate at 80° C. The above description is illustrated by table 2.

The precipitated phases are usually so fine grained that identification is made by X-ray powder diffraction patterns rather than by optical methods.

Figure 3 shows a section containing the KOH axis and midpoint of the opposite side of the triangular phase diagram of the KOH- V_2O_5 - $UO_2(NO_3)_2$ system. This section shows the tentative relationship between carnotite, rauvite, and hydrated vanadium pentoxide. Phase boundaries are dependent on pH and concentration of reacting ions; temperature has no appreciable effect on phase boundaries. The dashed line across the top of the diagram indicates the limits of exploration. No experimental solution had an initial pH above the dashed line. The area below the line was explored by depressing the pH of a solution with HNO_3 .

Table 2.--The preparation and handling of two runs used to obtain data for phase diagram of uranium-containing vanadates in aqueous solution.

	Run no. 2-N-2	Run no. 4-N-2	Remarks
<u>Solution 1</u>	<u>Solution 4</u>	<u>Solution 6</u>	
UO ₂ (NO ₃) ₂ solution 0.127M	2 ml of solution 1 + 100 ml H ₂ O	1 ml of solution 1 + 100 ml H ₂ O	
<u>Solution 2</u>	<u>Solution 5</u>	<u>Solution 7</u>	
KOH-V ₂ O ₅ solution KOH 0.32M V ₂ O ₅ 0.18M	0.26 ml of solution 2 + 100 ml H ₂ O	0.26 ml of solution 2 + 100 ml H ₂ O	
<u>Solution 3</u>		<u>Solution 8</u>	
KOH solution 5.5M	-----	0.08 ml of solution 3	Solution 8 added to solution 7. Solution 4 added to solution 5. Solution 6 added to solution 7.
pH of solution 4 + 5 and solution 6 + 7 + 8	3.55	4.5	Solution transparent.
pH of solution 4 + 5 after 20 minutes	3.45		Solution now cloudy. Runs were covered with watchglasses and digested at 80° C on hot plate.
pH after 22 hours	2.85	4.9	Yellow precipitates were formed.
X-ray diffraction pattern of precipitate	matched pattern for carnotite	matched pattern for carnotite	

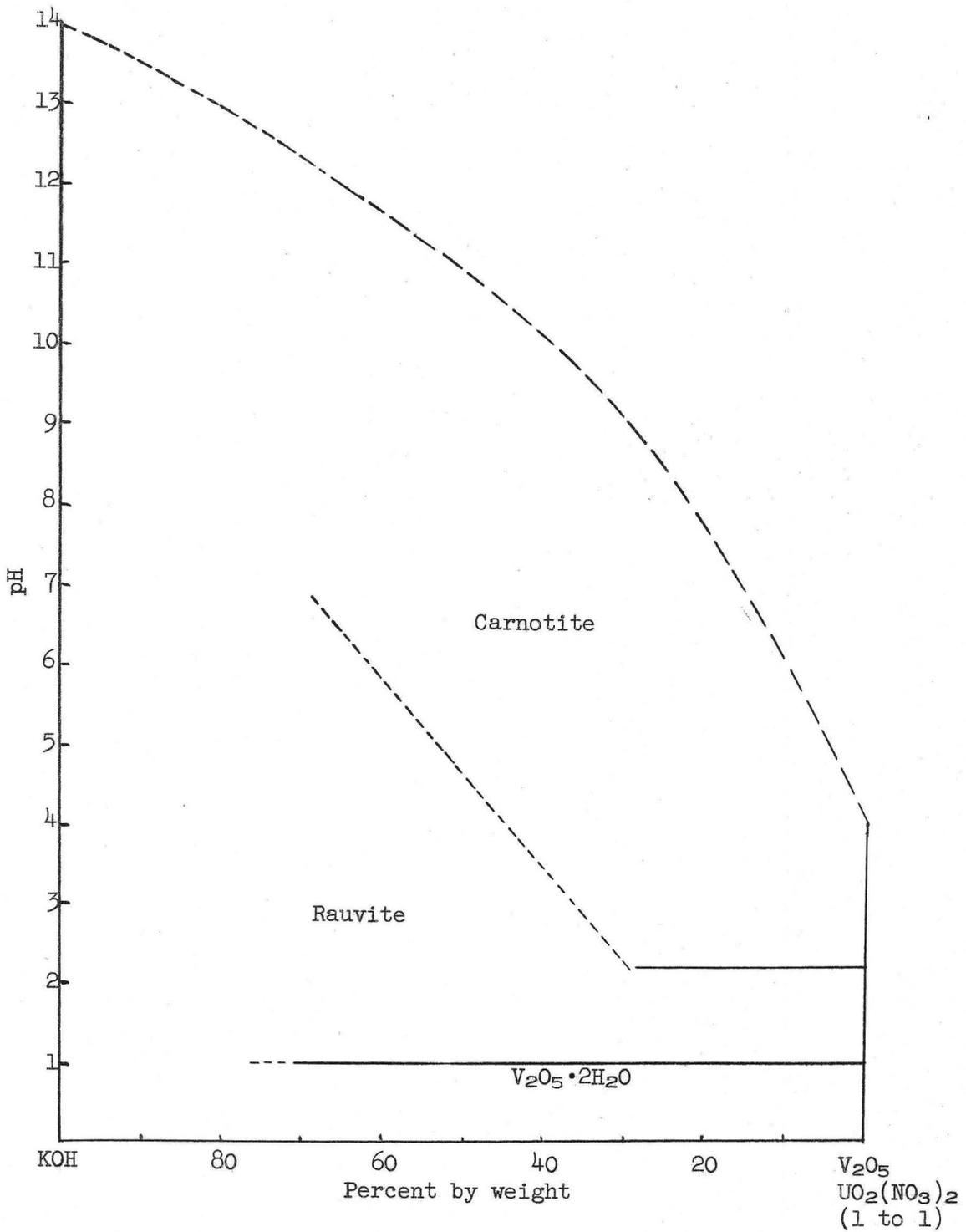


Figure 3.--A section of the $KOH-V_2O_5-UO_2(NO_3)_2$ aqueous solution phase diagram showing the relative positions of the initial phases formed upon evaporation of solutions.

The yellow synthetic carnotite, as identified by X-ray diffraction patterns, has a fairly large area of stability. The only noticeable difference between carnotite formed in the basic environment, as against that formed in an acid environment, is in the degree of crystallinity. The carnotite formed in the basic region is finer grained and gives broad, diffuse X-ray diffraction lines. No chemical analyses are available as yet on these synthetic carnotites. A solubility study on synthetic carnotite has indicated that its solubility is near 0.15 ppm in distilled water and increases to 4 ppm at pH 3.3 (NO_3^- present).

Synthetic rauvite or rauvitelike material forms under acid conditions as a bright-yellow precipitate which dries to a dull yellow, orange, or brown material. The bright-yellow color usually returns when the material is returned to water. The X-ray diffraction pattern of this material is distinctive, but the lines are broad and diffuse, due to very fine grain size and possibly to a disordered structure. Malcolm Ross of the Geological Survey, after examining natural rauvite with the electron microscope, suggests that it has a platy or clay-like character. His examination of synthetic rauvite showed it to consist of very fine, crystalline aggregates.

Although natural rauvite has been listed as $\text{CaO} \cdot 2\text{UO}_3 \cdot 5\text{V}_2\text{O}_5 \cdot 16\text{H}_2\text{O} (?)$ (Weeks and Thompson, 1954), some doubt remains as to its real composition. No analysis on rauvite or rauvitelike material precipitated from solutions containing potassium ion is available. But synthetic rauvite, as identified by X-ray powder diffraction pattern, was precipitated as a bright-yellow material from a solution containing only $\text{UO}_2(\text{NO}_3)_2$ and V_2O_5 , no calcium or potassium ions present. A chemical analysis of this material,

in percent, by George Magin, Jr., U. S. Geological Survey, gave the following composition:

UO ₃	V ₂ O ₅	H ₂ O	Total
47.08	37.72	15.49	100.29

This composition gives the tentative formula, UO₃·V₂O₅·5H₂O.

When a solution is prepared containing relatively high concentrations of uranium and vanadium ions, rauvite is sometimes precipitated in the stability region of carnotite. This action suggests that rauvite may form as a metastable phase and later convert to the stable phase, carnotite.

Results of solubility runs with synthetic rauvite are not available, but its solubility is thought to be comparable to carnotite.

Solutions with pH values less than 1, precipitate dark-brown to black V₂O₅·2H₂O, as identified by X-ray methods. Precipitation of the V₂O₅·2H₂O continues until the vanadium pentoxide in solution is depleted. Then green crystals of UO₂(NO₃)₂·xH₂O crystallize if the solution is at room temperature. At 80° C a fine-grained yellow material forms, tentatively identified by X-ray powder diffraction patterns as a hydrated uranium oxide. The last material to come out of solution is KNO₃, colorless crystals. As the solutions increase in KOH and V₂O₅ concentration, golden crystals of K₂V₆O₁₆ may form after the precipitation of the carnotite or rauvite at 80° C.

Examination of the CaO-UO₂(NO₃)₂-V₂O₅ system in aqueous solution has been started, but not enough data have been collected to delineate phase boundaries. From what data are known, the phase diagram will probably be similar to that of the K₂O-UO₂(NO₃)₂-V₂O₅ system in aqueous solution, with tuyamunite appearing in place of carnotite.

Preparation of stock solutions of $\text{CaO-V}_2\text{O}_5$, V_2O_5 , and $\text{UO}_2(\text{NO}_3)_2$ used in this study has been described above. Small aliquots of $\text{CaO-V}_2\text{O}_5$ and $\text{UO}_2(\text{NO}_3)_2$ stock solutions are placed in separate beakers and diluted with water. The diluted $\text{CaO-V}_2\text{O}_5$ is brought to the desired ratio by adding the necessary milliliters of V_2O_5 stock solution or freshly prepared $\text{Ca}(\text{OH})_2$ solution (approximately 0.015M). Then the diluted $\text{UO}_2(\text{NO}_3)_2$ is poured into the $\text{CaO-V}_2\text{O}_5$ solution. As mentioned before, this method of mixing prevents immediate precipitation. The pH of a solution is adjusted with HNO_3 . Solutions are then evaporated at 30° , 55° , or 90° C in ovens. The actual preparation and handling of two samples is shown by table 3.

The phases so far encountered are tyuyamunite, $\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5-10.5\text{H}_2\text{O}$, rauvite, and $\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$. They are fine grained, and identification is made by X-ray methods. The tyuyamunite phase corresponds to the carnotite phase of the $\text{K}_2\text{O-UO}_3\text{-V}_2\text{O}_5\text{-H}_2\text{O}$ system. The synthetic rauvite and $\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ are similar to previously synthesized phases. However, in one experiment, the rauvite remained quite yellow in color instead of changing to a dull orange or brownish color.

Again pH, concentration of reacting ions, and temperature are factors affecting stability of the solid phase. Thus far, no tyuyamunite has been synthesized below 90° C at the few points explored on the phase diagram. It may be possible that at lower temperatures rauvite forms as a metastable phase that will slowly convert to tyuyamunite. Most of the rauvite was precipitated under conditions similar to its formation shown by the $\text{K}_2\text{O-UO}_3\text{-V}_2\text{O}_5\text{-H}_2\text{O}$ phase diagram. The same also applies to $\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$. Again, as in the above system, the exact relationship of rauvite to tyuyamunite (or carnotite) is not known. Rauvite may be either a metastable

Table 3.--The preparation and handling of two runs used to explore the system $\text{CaO-UO}_2(\text{NO}_3)_2\text{-V}_2\text{O}_5$ in aqueous solution.

	Run no. T-N-2	Run no. T-N-14	Remarks
<u>Solution 1</u> $\text{UO}_2(\text{NO}_3)_2$ solution 0.05 g/ml	<u>Solution 3</u> 1 ml of solution 1 + 100 ml H_2O	<u>Solution 5</u> 1 ml of solution 1 + 600 ml H_2O	
<u>Solution 2</u> $\text{CaO-V}_2\text{O}_5$ solution CaO 0.0041 g/ml V_2O_5 0.0150 g/ml	<u>Solution 4</u> 1 ml of solution 2 + 80 ml H_2O	<u>Solution 6</u> 10 ml of solution 2 + 300 ml H_2O	
			Solution 3 added to solution 4. Solution 5 added to solution 6. B
pH of solution 3 + 4 and solution 5 + 6	3.4	5.5	Initial pH was not adjusted with HNO_3 . A watchglass was put on each beaker and beakers were placed in oven at 90°C to digest. Within an hour solutions became cloudy and precipitates started to form.
pH of solution 3 + 4 and solution 5 + 6 after formation of yellow precipitates.	3.0	5.7	Bright-yellow precipitates were formed.
X-ray diffraction pattern of precipitate	matched pattern for tyuyamunite	matched pattern for rauvite	

or a stable phase, depending on the pH of the environment.

The study of synthetic carnotite and tyuyamunite shows that carnotite and probably also tyuyamunite can be formed under either acid or basic conditions. However, the attack on the primary mineral assemblage, as previously related, presumably took place in an acid environment, oxidizing and dissolving both uranium and vanadium. Since uranium-containing vanadates are quite insoluble at a pH above 3 and precipitate quite readily, they should form in preference to other vanadates if the fully oxidized uranium and vanadium ions came together in solution. Highly acid conditions, pH 1 or below, would prevent the formation of uranium vanadates and redissolve those already formed. Hydrated V_2O_5 would probably be the first phase to appear under such conditions.

MISCELLANEOUS VANADATES

Some of the rarer vanadates found on the Colorado Plateau have been synthesized.

The sodium analog of hewettite, $Na_2V_6O_{16} \cdot 3H_2O$, which has recently been found in nature (A. D. Weeks, personal communication), can be synthesized either by direct precipitation or by base-exchange. At $55^\circ C$, $Na_2V_6O_{16} \cdot 3H_2O$ formed directly from slowly evaporated $NaOH-V_2O_5$ solutions ($0.22M$ $NaOH$, $0.11M$ V_2O_5) with pH values between 3.0 and 6.0, adjusted with glacial acetic acid. $Na_2V_6O_{16} \cdot 3H_2O$ was identified by X-ray diffraction patterns and chemical analyses. It would probably form at $20^\circ C$ if the solution were evaporated very slowly; more rapid evaporation would produce a metastable polyvanadate analogous to $K_6V_{10}O_{28} \cdot 9H_2O$ and $Ca_3V_{10}O_{28} \cdot 16H_2O$ (pascoite). In forming $Na_2V_6O_{16} \cdot 3H_2O$ by base-exchange, hewettite ($CaV_6O_{16} \cdot 9H_2O$) or one of its lower hydrates is placed in a sodium-bearing

solution with a pH between 3.0 and 6.0 for an appropriate length of time. Several grams of synthetic hewettite were converted to the sodium analog in Na_2SO_4 solutions (Na_2SO_4 concentration varied from 0.1N to 0.7N) in three weeks. Identification was made by X-ray diffraction patterns. Natural $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$ could have formed in either way.

Hummerite, $\text{K}_2\text{Mg}_2\text{V}_{10}\text{O}_{28} \cdot 16\text{H}_2\text{O}$, is easily crystallized from solutions containing stoichiometric amounts of potassium, magnesium, and vanadium at pH 5 by rapid evaporation at room temperatures. Variation in the relative ratios of potassium, magnesium, and vanadium concentrations, if not extreme, does not prohibit hummerite formation. A KOH- V_2O_5 solution (0.00676M KOH, 0.0165M V_2O_5) was made by dissolving dry KOH and V_2O_5 in water. H_2O_2 was used to dissolve the V_2O_5 ; excess H_2O_2 was boiled off. One tenth of a gram of $\text{Mg}(\text{NO}_3)_2$ was then dissolved in 100 ml of KOH- V_2O_5 solution. The pH was raised to the desired pH by adding concentrated KOH solution. The solution was placed in an open shallow evaporating dish, and crystals soon formed. Synthetic hummerite crystals are sensitive to heat and dehydrate readily.

Volborthite, $\text{Cu}_3\text{V}_2\text{O}_8 \cdot 3\text{H}_2\text{O}$, will crystallize slowly out of a solution having a pH between 2.0 and 4.7. Above pH 4.7, it becomes very insoluble and precipitates as a flocculent material which will crystallize if the solution is boiled for a few minutes. In synthesizing volborthite, 20 ml of 0.0855M NH_4VO_3 solution were added to 200 ml of H_2O . The pH was adjusted to 2 with concentrated HNO_3 to prevent an immediate precipitation from forming on addition of 2 ml of 2.5M $\text{Cu}(\text{NO}_3)_2$. The solution was stirred and NH_4OH (1+9) added to raise the pH to the desired value. Heating the solution before the addition of the NH_4OH increases the grain size of volborthite if precipitated at a pH value above 4.7. Identification of the volborthite was made by X-ray diffraction pattern and chemical analysis.

Several attempts were made to synthesize calciovolborthite, $(\text{Cu,Ca})_2\text{VO}_4\text{OH}$, by adding various amounts of 2.5N $\text{Cu}(\text{NO}_3)_2$ to 40-ml portions of $\text{CaO-V}_2\text{O}_5$ solution (0.0365M CaO , 0.0412M V_2O_5). HNO_3 (1+50) was added to the $\text{CaO-V}_2\text{O}_5$ solutions before the $\text{Cu}(\text{NO}_3)_2$ to lower the pH to 5, then again after the addition of the $\text{Cu}(\text{NO}_3)_2$ to give a pH value between 4.5 and 4.0. No calciovolborthite was formed; dark-brown crystalline aggregates of volborthite appeared.

To determine if calciovolborthite was stable at high pH values, the $\text{Cu}(\text{NO}_3)_2$ solution was diluted to approximately 0.005M and then made ammoniacal with NH_4OH . This solution was added to 100 ml of $\text{CaO-V}_2\text{O}_5$ (approximately 0.00035M CaO , 0.0005M V_2O_5) solution and placed in an oven at 90°C . A light-green fine-grained precipitate formed which gave the same X-ray powder diffraction pattern as turanite, $\text{Cu}_5(\text{VO}_4)_2(\text{OH})_4$ (Palache, Berman, and Frondel, 1951). The chemical analysis, in percent, of the precipitate, by George Magin, Jr., U. S. Geological Survey, follows:

CuO	CaO	V_2O_5	H_2O	Total
36.0	8.1	43.7	12.5	100.3

This analysis gives the tentative formula, $6\text{CuO}\cdot 2\text{CaO}\cdot 3\text{V}_2\text{O}_5\cdot 10\text{H}_2\text{O}$. The calcium is believed to be an essential part of the material as solutions with the same pH and ion concentration except for the presence of Ca^{+2} ions did not produce any turanite. It formed at a pH between 8.5 and 10. Volborthite was present as a precipitate in solutions with pH values as much as 8.5.

Several attempts have been made to synthesize fervanite, $\text{Fe}_4(\text{VO}_4)_5\cdot 5\text{H}_2\text{O}$ and steigerite, $\text{Al}_2(\text{VO}_4)_2\cdot 6.5\text{H}_2\text{O}$. The procedure is similar to the synthesis of volborthite except $\text{Fe}(\text{NO}_3)_3$ or $\text{Al}(\text{NO}_3)_3$ were substituted for

$\text{Cu}(\text{NO}_3)_2$. A very insoluble brown flocculent iron vanadate precipitated near pH 1.6; an insoluble yellow flocculent aluminum vanadate precipitated near pH 4. Even though the flocculent materials were boiled for several minutes or precipitated from near-boiling solutions or precipitated by very slowly increasing the pH of the solution (urea, $\text{CO}(\text{NH}_2)_2$, was added; then the solution was heated to cause decomposition of urea and formation of NH_4OH), no indication of crystallinity was detected by X-ray powder diffraction. Chemical analyses by Robert Meyrowitz, U. S. Geological Survey, gave the following empirical formulas: $\text{Fe}_2(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}$ and $\text{Al}_2(\text{VO}_4)_2 \cdot 7.5\text{H}_2\text{O}$.

CONCLUSIONS

Synthesis of many of the vanadates found on the Colorado Plateau, study of the system $\text{CaO-V}_2\text{O}_5\text{-H}_2\text{O}$, and cursory examination of systems $\text{K}_2\text{O-UO}_2(\text{NO}_3)_2\text{-V}_2\text{O}_5$ and $\text{CaO-UO}_2(\text{NO}_3)_2\text{-V}_2\text{O}_5\text{-H}_2\text{O}$, both in aqueous solution, show that the natural vanadates can form over a wide range of pH conditions. The best pH indicators are the calcium vanadates; rossite forms above pH 6.2, pascoite and hewettite crystallize between pH 2.7 and 6.2. Carnotite indicates pH values above 2.2; rauvite and navajoite indicate acid conditions. Although it has not been possible to duplicate actual natural conditions, especially the presence of other ions and their influence on vanadium (V) concentration and precipitation, the presence of pascoite seems to indicate rapid evaporation of ground water carrying vanadate ions; hewettite and probably Na-hewettite seem to indicate slow evaporation.

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