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DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
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November 19, 1956

AEC-193/7

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-622, "The crystal chemistry and mineralogy of vanadium," by Howard T. Evans, Jr.

We are asking Mr. Hosted to approve our plan to publish this report as a chapter of a Geological Survey professional paper on mineralogy and geochemistry of the ores of the Colorado Plateau. Acknowledgment of AEC sponsorship will be made in the introductory chapter.

Sincerely yours,

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

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Geology and Mineralogy

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UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

THE CRYSTAL CHEMISTRY AND MINERALOGY OF VANADIUM*

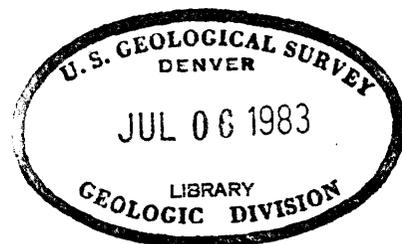
By

Howard T. Evans, Jr.

June 1956

Trace Elements Investigations Report 622

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THE CRYSTAL CHEMISTRY AND MINERALOGY OF VANADIUM

By Howard T. Evans, Jr.

ABSTRACT

Many recent crystal structure investigations on vanadium oxides and compounds are reviewed in terms of the over-all chemistry and mineralogy of the element. The structure studies are compared with the oxidation potential-pH phase diagram which is constructed from the best available thermodynamic data for the element. From these correlative studies, an alteration sequence is derived for the weathering process of the vanadium ores of the Colorado Plateau. Accordingly, montroseite $[\text{VO}(\text{OH})]$ is treated as the primary vanadium mineral. During weathering, montroseite is converted to various insoluble tetravalent and quinquevalent oxide minerals, including paramontroseite and "corvusite." Final oxidation of "corvusite" yields soluble polyvanadate complexes from which crystallize pascoite, hummerite, hewettite, and other quinquevalent vanadate minerals. Under more alkaline environments, duttonite $[\text{VO}(\text{OH})_2]$ is formed, from which may be derived simplotite, melanovanadite, and rossite. If uranium is present these are converted to rauvite, tyuyamunite, and carnotite. Generally speaking, in its lower valence states vanadium is similar to manganese in behavior, but in the higher states of oxidation it resembles phosphorus (in strongly alkaline media) and molybdenum and tungsten (in acid media).

INTRODUCTION

Until recently, vanadium has played a minor role in mineralogy. Lately, interest in vanadium mineralogy has been increased because vanadium plays a key role in the paragenetic relationships in the sandstone-type uranium deposits, such as those of the Colorado Plateau. Recent geologic studies have raised many questions concerning the time, mechanism, and mode of deposition of the uranium and vanadium ores in the sandstones, shales, and conglomerates, and their subsequent weathering and transport. Extensive recent studies on the chemistry and crystallography of vanadium compounds and minerals in various laboratories have led to a greater understanding of the behavior of vanadium under varying conditions of oxidation potential and pH, which give promise to provide valuable clues to the solution of these problems.

An important vanadium ore mineral (at Globe, Arizona, for example) is vanadinite, a member of the apatite group of minerals. A second important type is vanadium silicate, as mica, as clay minerals, and as chlorites. Vanadium forms a host of other minerals, many of which are as yet undescribed or poorly characterized. They are listed in a miscellaneous group in Dana's System of mineralogy (Palache, Berman, and Frondel, 1951, p. 1042) and also in a U. S. Geological Survey publication by Weeks and Thompson (1954). Phases involving oxygen are very complex and numerous, mainly because of the variability of the valence state of vanadium.

A fair amount of information concerning the chemical and mineralogical behavior of vanadium is available in a widely dispersed and somewhat conflicting literature. In addition, recent work in X-ray crystallography by members of the U. S. Geological Survey has revealed new and significant

structural relationships among vanadium compounds and those of other elements. It is the purpose of this report to review briefly present knowledge of the behavior of vanadium in the solid state.

The emphasis in this paper will be on the structure and nature of the known minerals as they are found in nature, in relation to each other and to artificial solid compounds, and to the solution studies of Garrels (1953), Ducret (1951), Jander and Jahr (1933), and others. While the methods of electrometric and pH titration have proved to be the most informative in the study of the solution phases, the most powerful approach to the problem of the constitution of the solids has been through the medium of X-ray diffraction and crystal structure analysis. As the body of structural information increases, it is often possible to infer the nature of the solution components through various interrelationships and characteristic physical properties of the solids.

The ideas and information presented in this paper have resulted from the concerted efforts of many workers at the U. S. Geological Survey, some of whom have been mentioned in the text, as well as numerous other independent workers outside the Survey. Especial thanks are due to R. M. Garrels of the Survey, who has continuously urged and encouraged the compilation of this report on vanadium chemistry and mineralogy and who has contributed in no small way directly to its makeup. Finally, the author wishes to express his gratitude to W. H. Barnes and his colleagues of the National Research Council of Canada who have provided much valuable information in personal discussions from time to time.

THE ELECTROCHEMISTRY OF VANADIUM

Before entering upon a discussion of the various minerals containing vanadium, let us review briefly the equilibrium behavior of vanadium under various conditions of pH and oxidation potential as it has been revealed in studies by Souchet and Carpeni (1946), Ducret (1951), Garrels (1953), and others. The best thermodynamic information available to us is summarized in figure 1, in the manner described by Pourbaix (1949). The tabulated data of Latimer (1952) have been used in the construction of the diagram.

In figure 1, all conditions of pH (hydrogen ion concentration) and Eh (oxidation potential) are represented. The diagram is divided into regions which are labelled with the species that predominates in that region. Two sloping dashed lines are shown: the lower one represents the limit below which hydrogen ion is reduced to hydrogen, a condition which ordinarily does not occur in nature; the upper line is the limit above which water or hydroxyl ion is oxidized to oxygen, and toward which all systems below the line trend under terrestrial weathering conditions.

The areas between the heavy lines represent the four valence states of vanadium. They correspond roughly to the regions of stability of $V(OH)_3$, $VO(OH)_2$ and $V_2O_5 \cdot nH_2O$ as determined by Garrels (1953). The slope of these heavy lines is determined by the way in which H^+ ions are involved in the oxidation reaction. Thus, the oxidation potential required to convert V^{+2} to V^{+3} is independent of pH as no H^+ ions are involved in the oxidation reaction; but when V^{+2} is converted to V_2O_3 , H^+ is liberated in the reaction, and the potential boundary falls with increasing pH. When no oxidation or reduction takes place, changes in pH will effect

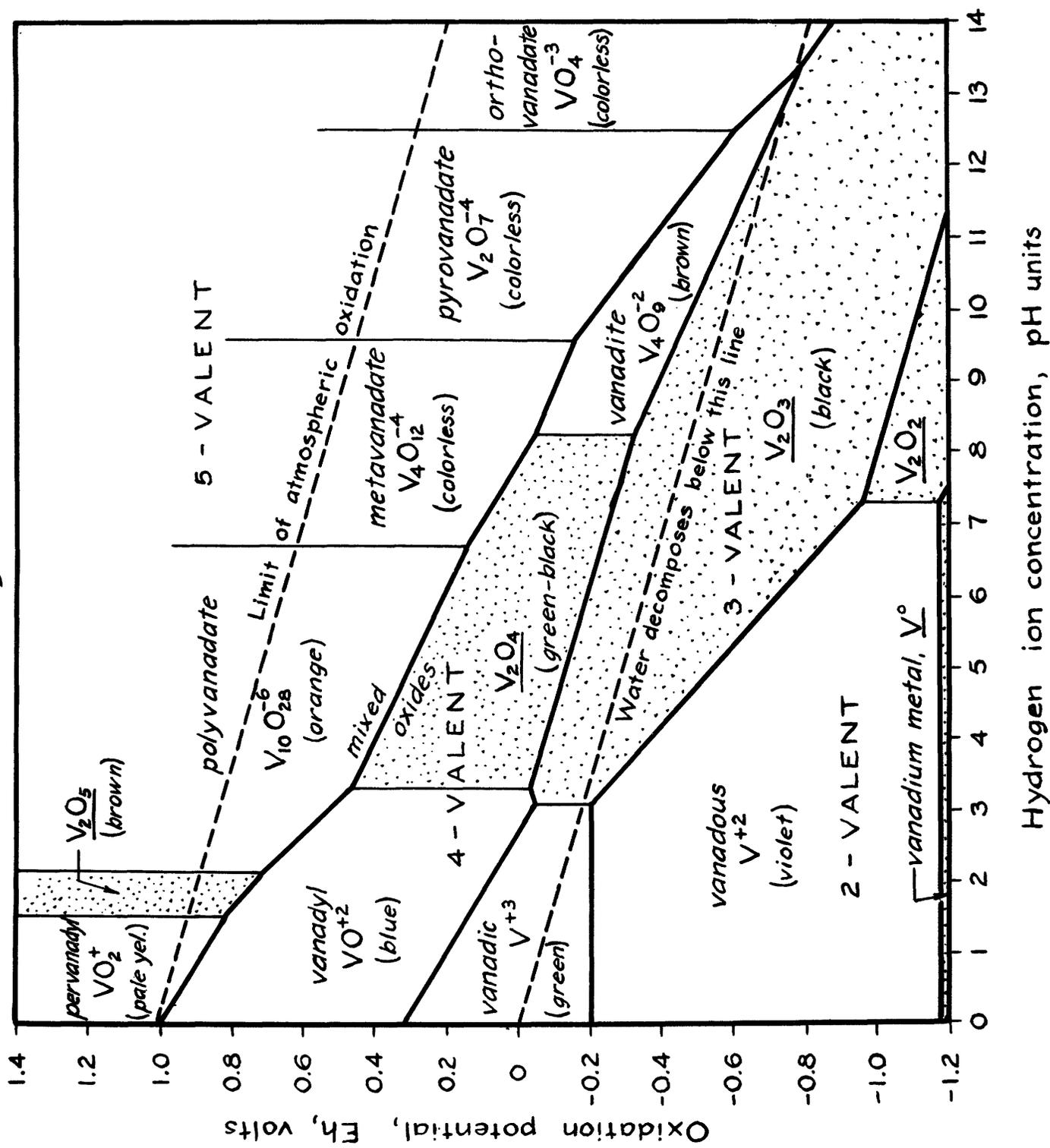


Figure 1.--Oxidation potential-pH phase diagram for vanadium in aqueous solution. Stippled fields represent solids (solubility of V < 0.01 mol/liter). Phases may be hydrated or hydrogenated to an unknown degree.

profound changes in the constitution of the vanadium-bearing ion or solid; these changes are marked by vertical lines on the diagram. The formula species indicated may actually be replaced by hydrates, without changing the phase boundaries significantly. The presence of hydrogenated ions such as $HV_2O_7^{-3}$ may affect the boundary distributions to a small degree.

In the following discussion, reference will be made to figure 1 to clarify relationships among minerals and artificial compounds under consideration. Thus, the diagram will serve as a "road map" in our survey of the mineralogy and chemistry of vanadium.

VANADIUM (II), VANADIUM (III), AND VANADIUM (IV)

Vanadium (II)

Bivalent vanadium is unstable and releases hydrogen from water. This behavior is consistent with the diagram of figure 1, which shows that the conditions under which V^{+2} ions are stable are well below the limit below which water decomposes. The artificial compound VO is known; like MnO, it has the rock salt structure. Thermodynamic considerations have shown that bivalent vanadium probably does not occur in nature (Garrels, 1953, p. 1263).

Vanadium (III) and vanadium (IV): the montroseite group

Trivalent vanadium is also relatively unstable and has a short life in the presence of air. Unlike the bivalent ion, V^{+3} is stable in oxygen-free acid water solution, from which, characteristically, vanadium alums may be crystallized [e.g., $CsV(SO_4)_2 \cdot 12H_2O$]. V_2O_3 has the corundum type of structure, but is not yet known in nature. $VO(OH)$ is the mineral

montroseite (Weeks, Cisney, and Sherwood, 1953), which occurs as steel-black prismatic lath-shaped crystals, or as a brittle, crystalline, jet-black mass. Paramontroseite, V_2O_4 , is a common alteration product resulting from the atmospheric alteration of montroseite. Another distinct oxide species (Weeks and Thompson, 1954, p. 54), now designated doloresite (Stern, Stieff, Evans, and Mrose, manuscript in preparation), which is closely associated with paramontroseite, forms dark-brown, nonmetallic crystalline masses when pure and is probably a quadrivalent hydrous oxide. Still another quadrivalent oxide species, duttonite, has been identified recently, occurring as pale-brown flaky crystals, but it is found in more alkaline environments. The oxide minerals have proved to be difficult to separate and characterize by the usual chemical and mineralogical methods, but their interrelationships and essential constitution have been revealed by the methods of X-ray diffraction and crystal structure analysis.

Montroseite and paramontroseite both have the diasporite ($Al_2O_3 \cdot H_2O$) structure. The details of these structures have been given by Evans and Block (1953), and Evans and Mrose (1954). The structure contains double chains of VO_6 octahedra sharing edges, the chains being linked to each other by sharing octahedron corners. (See the pictorial view in fig. 2.) Evans and Mrose found that single crystals of montroseite give multiple diffraction patterns showing the presence of two intimately mixed phases, but whose crystal structures are similar and are in parallel position throughout the crystal mass. By means of separate Fourier analyses of the electron-density distribution in each of the two phases, they were able to show conclusively that hydrogen is present in one and absent in the other.

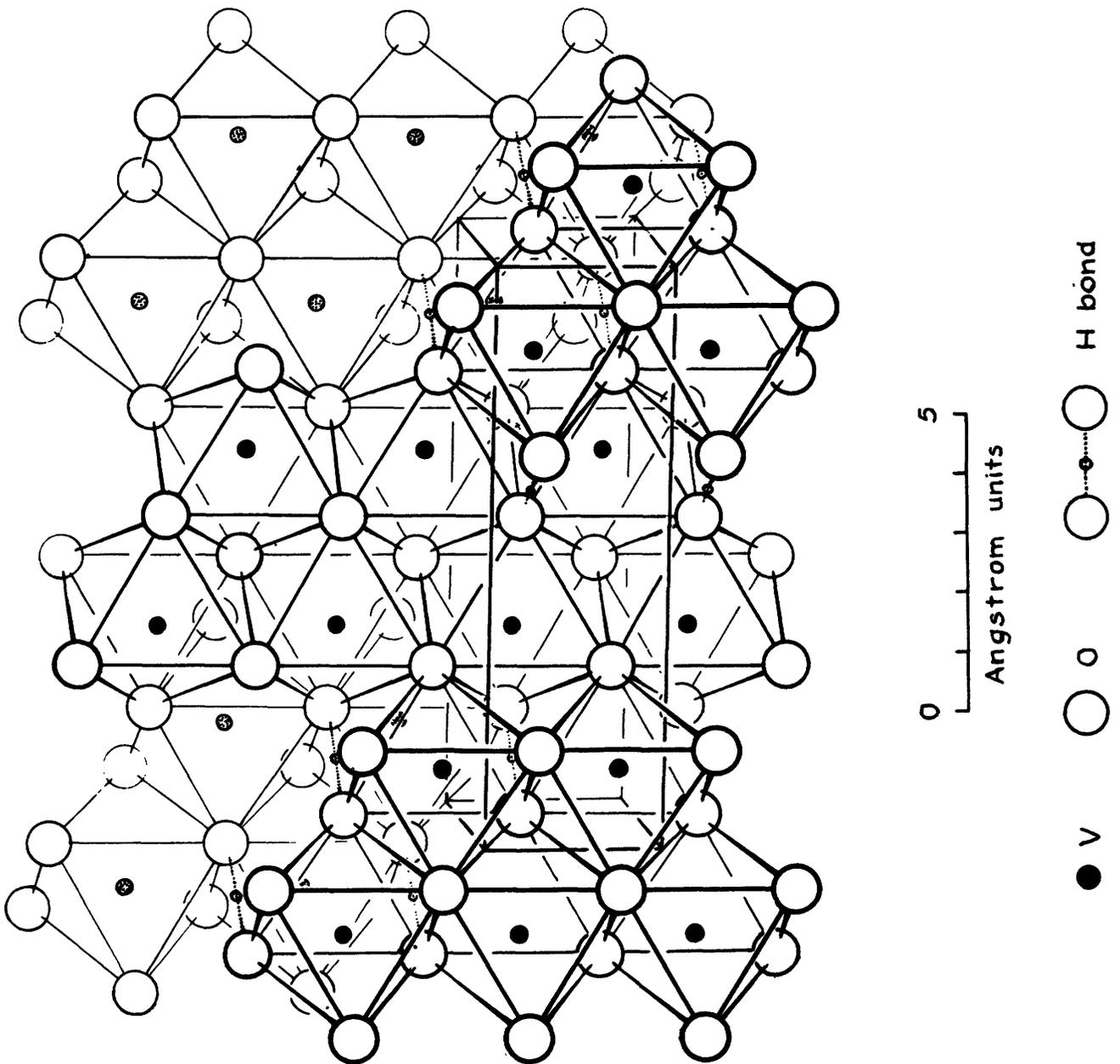


Figure 2.--Pictorial view of montroseite structure (diaspore type).

These two structures, which are montroseite and paramontroseite, respectively, are illustrated in figure 3, projected along the chain axis. The chains are visible in end view in both drawings. Comparison of the two structures leads unequivocally to the conclusion that the original host mineral is montroseite $[\text{VO}(\text{OH})]$ and that the paramontroseite (V_2O_4 or VO_2) has originated by the solid-state oxidation of montroseite. The oxidation process has taken place by the diffusion of hydrogen out of the structure without breaking the vanadium-oxygen bonds or disrupting the hexagonal close-packed oxygen framework.

Artificial vanadium tetroxide, V_2O_4 , has a slightly distorted rutile type of structure (Andersson, 1953). This structure is characterized by straight octahedron chains as shown in the pictorial view of figure 4. It is very probable that the diasporite-like form of VO_2 , paramontroseite, is entirely metastable and can only be formed through the low-temperature alteration mechanism just described, controlled by the original montroseite structure. Similar alteration mechanisms have been observed for certain of the iron oxides (Evans and Mrose, 1954). Montroseite is a highly insoluble stable mineral under reduced conditions, but by its conversion to the metastable paramontroseite, it becomes readily decomposable and subject to further oxidation.

Paramontroseite (pseudomorph after montroseite) is sometimes intimately mixed with another vanadium oxide mineral doloresite. Petrographic studies (Coleman, oral communication) indicate that doloresite replaces montroseite or paramontroseite. Since any remnant montroseite is oxidized to paramontroseite on atmospheric exposure, the mixture probably represents a close association of stable and a metastable form of the tetravalent

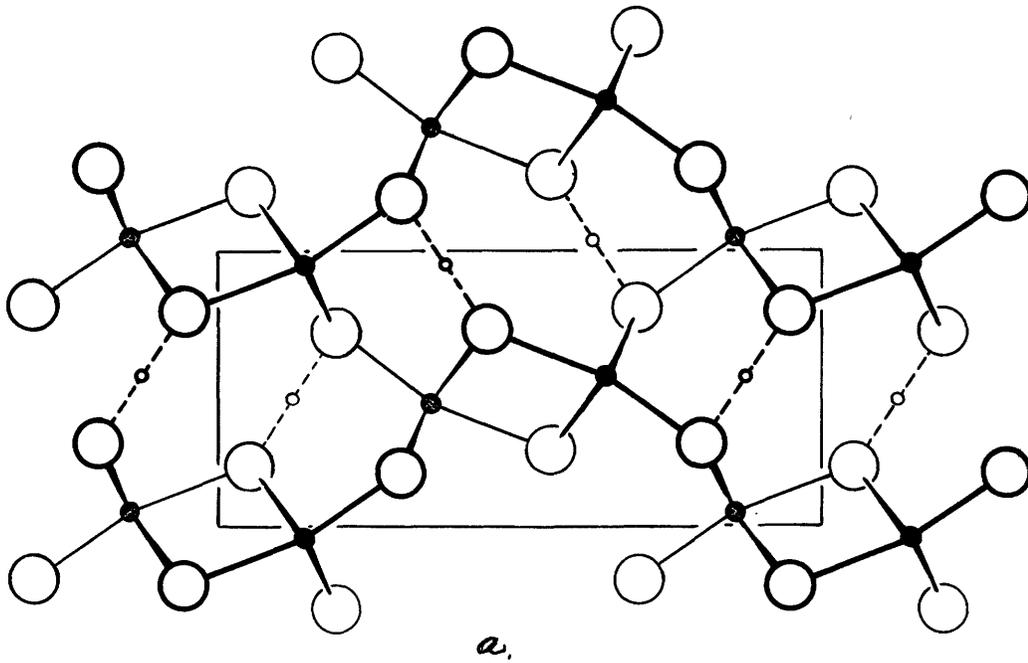
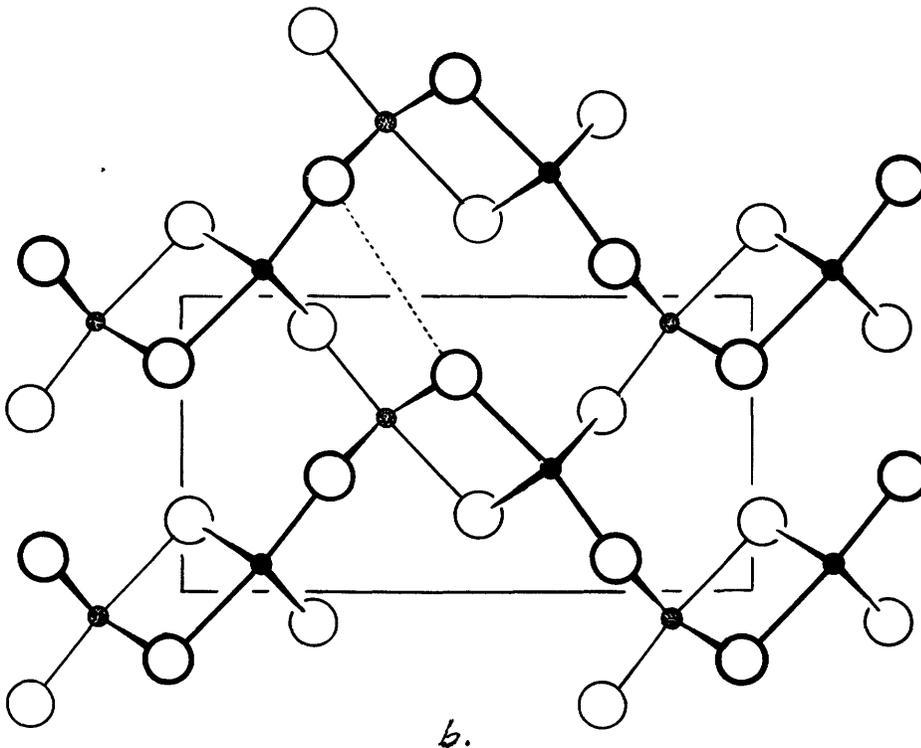


Figure 3.--Projections along the c-axis of the crystal structure of (a) montroseite and (b) paramontroseite. Large circles are oxygen atoms, dark circles vanadium, small open circles hydrogen. Note absence of hydrogen bond in paramontroseite.



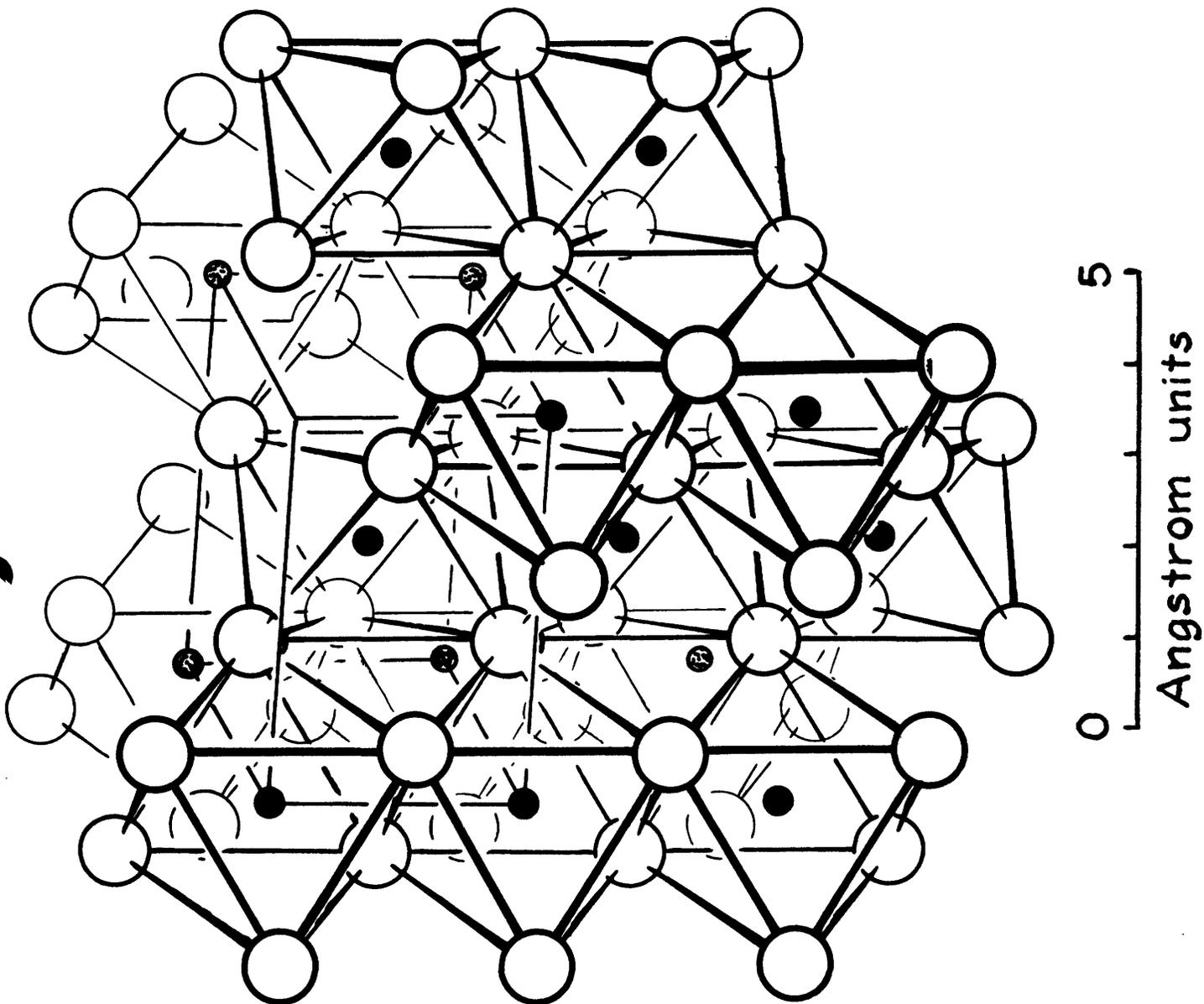


Figure 4.--Pictorial view of artificial V_2O_4 structure (distorted rutile type). Large circles are oxygen atoms, small circles vanadium.

oxide. Crystalline fragments of doloresite give exceedingly poor single-crystal diffraction patterns, but it has been possible to index them on an orthorhombic lattice which is obviously related to montroseite and artificial V_2O_4 . These oxides all share a fibre axis spacing of 3.0 Å, which is characteristic of the octahedron chain.

All evidence indicates that montroseite is probably the chief primary vanadium mineral, aside from the vanadium silicates, of the Colorado Plateau sandstone deposits. The conditions of formation are not known, but possibly they are hydrothermal in type. Figure 1 shows that a portion of the V_2O_3 field extends above the water decomposition line at pH values higher than 3. While the room-temperature conditions represented by the diagram will be altered somewhat at elevated temperatures, montroseite may be considered to have formed somewhere in this region.

Recently, the new mineral duttonite (Thompson, Roach, and Meyrowitz, 1956b) has been found at the Peanut mine, Bull Canyon, Montrose County, Colorado, where more alkaline conditions prevail. Crystal structure studies have shown that it is the tetroxide hydrate, $V_2O_4 \cdot 2H_2O$. The structure consists of strings of VO_6 octahedra linked vertically by their apices to form sheets, which are then tied together with hydrogen bonds (fig. 5). An unusual feature of the structure is the close approach of the vanadium atom to the apical oxygen atom to form a strong V-O bond, corresponding to a VO^{+2} ion. As this ion is well known from chemical studies, its appearance in the solid is not surprising. In fact, it is probably present in the artificial V_2O_4 structure, in which the ideal tetragonal cell is doubled in volume and reduced to monoclinic symmetry. If the octahedron chains (vertically arranged in fig. 4) contain the VO^{+2} bond pointing in

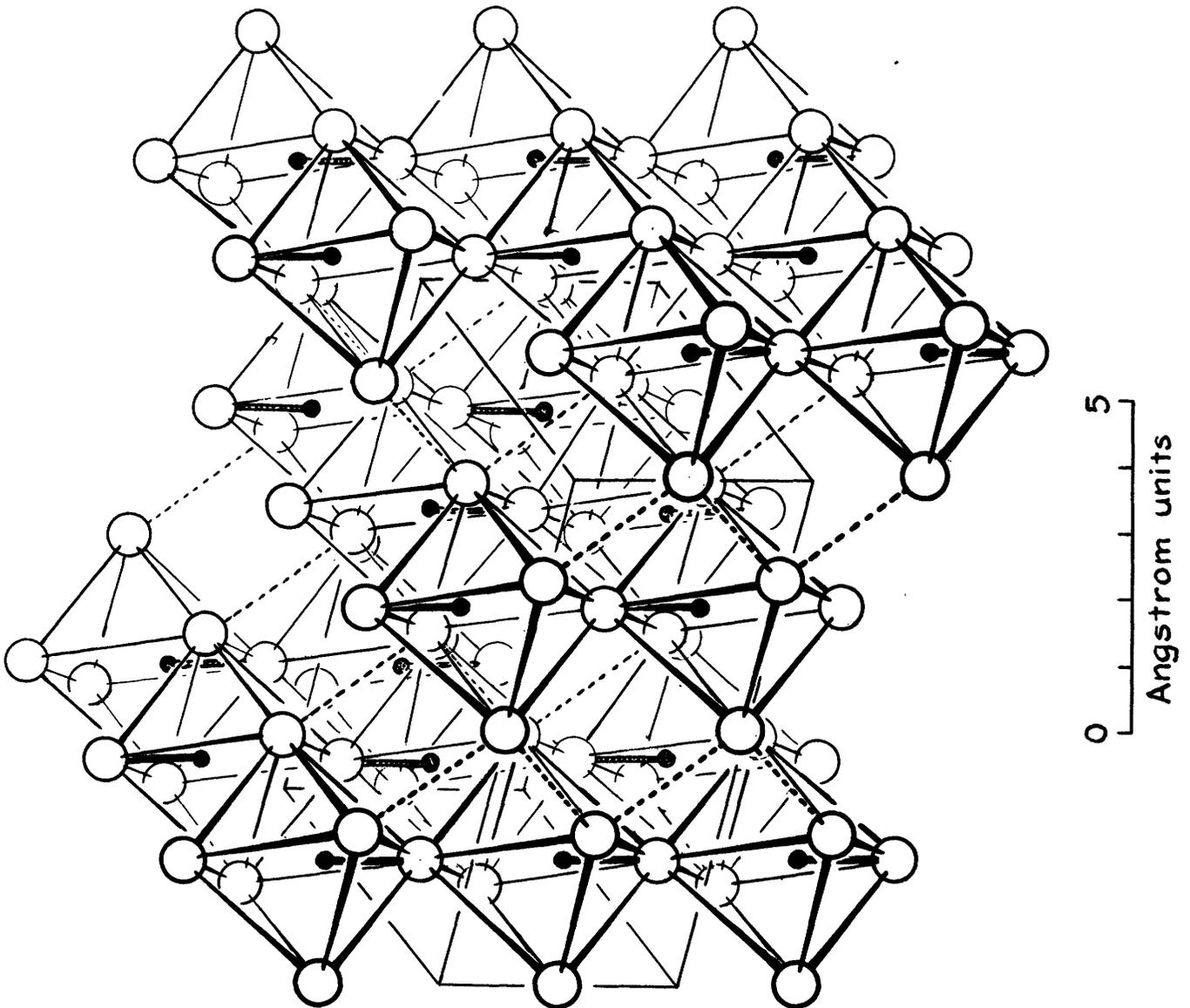


Figure 5.--Pictorial view of duttonite. Large circles are oxygen atoms, small circles vanadium, and dashed lines are hydrogen bonds.

alternate directions as in duttonite, such a distortion would readily be accounted for.

In its valence states three and four, vanadium is similar to manganese in its behavior. Single- and double- and even triple-octahedron chains have been found in several manganese oxide minerals (e.g., pyrolusite, coronadite, hollandite, psilomelane; Wilson, 1949, 1950). Indeed, groutite, $Mn_2O_3 \cdot H_2O$, and ramsdellite, Mn_2O_4 (Wilson, 1949), are completely analogous to montroseite and paramontroseite, respectively. Unfortunately, very little work has been done on the phase relations of manganese oxide minerals in the natural environment, so that we are not at present able to compare any similarities there may be to vanadium systems. On the other hand, the tendency of vanadium to form asymmetric oxygen bonds in its coordination environment when it attains the quadrivalent or higher state is in contrast to manganese.

VANADIUM (V)

Oxidation of tetravalent vanadium

Weathering action ultimately raises vanadium oxide minerals to the highest oxidation state, i.e., +5. This oxidation process is evident from the sequence of minerals in the Colorado Plateau region and is also predicted by the thermodynamic studies which are summarized in figure 1. The oxidation process is very complex and passes through numerous intermediate stages. Many take place in the solid state, like the conversion of montroseite to paramontroseite described in the previous section. When vanadium passes above the tetravalent state, its oxides are still relatively insoluble (above pH 3), but the oxide structures are completely reconstituted.

A number of phases, changing one into another, probably exist between $V_2O_4 \cdot nH_2O$ and $V_2O_5 \cdot nH_2O$. These phases are the principal constituents of the so-called blue-black ore. None of these phases has been isolated and uniquely characterized as yet. "Corvusite" is a name associated with a fibrous vanadium oxide hydrate which yields a blue-black powder on scratching or crushing. Its essential constitution and nature are unknown (it may be a mixture), and "corvusite" cannot yet be regarded as a well-established species. Other oxide phases in this range have a green streak and all are commonly coated with an almost iridescent blue tarnish.

During oxidation the pH of the environment tends to drop, especially if much pyrite is present. The vanadium then becomes relatively soluble and is leached out of the oxide bodies as VO^{+2} and $V_{10}O_{28}^{-6}$ ions as would be expected by reference to figure 1. As soon as the solutions reach the surrounding rock, they become diluted and react with the calcium carbonate cement. The pH is thus raised sharply again, causing the remaining VO^{+2} ions to be completely oxidized by atmospheric action.

Complete oxidation of vanadium to vanadium (V) is marked by a distinct color change from the blue-black associated with the vanadium (IV)-(V) complexes to brown, red, or orange shades associated with derivatives of V_2O_5 . The presence of uranium introduces yellow and yellow-green phases in this oxidized zone.

The pH dispersion of vanadium (V) complexes in solution

Vanadium pentoxide is strongly amphoteric, dissolving readily to form cations in strong acid solutions and anions in weakly acid and alkaline solutions. In these solutions, vanadium forms a great variety of oxygen

ion complexes. The relative concentrations of the various complexes depend critically upon the acidity and concentration of the solution, the presence of other complexing ions (e.g., UO_2^{+2} or PO_4^{-3}), and because of the slow rate of many of the reactions, the history of the solution. Some insight into the constitution of V_2O_5 solutions as a function of pH has been gained by Jander and Jahr (1933) by means of diffusion-rate studies. In figure 6 is shown their plot of diffusion rate of vanadium in solution (corrected for viscosity) against pH. The presence of plateaus in this curve suggests that at certain critical pH values the ions present in the solution react to form other more complex ions (with decreasing pH), but that between these critical values, the solutions are relatively stable. Assuming very approximately that ion molecular weight is proportional to the square of the diffusion rate, Jander and Jahr suggested that above pH 12.6 only VO_4^{-3} ions are present; in the range pH 9.6 to 12.6, $V_2O_7^{-4}$ ions are present; in the range pH 6.7 to 9.6 ions like $V_4O_{13}^{-6}$ exist; and between pH 6 and the oxide precipitation point at pH 2.2, ions similar to $V_5O_{18}^{-7}$ predominate. A study of solutions in the system $K_2O-V_2O_5-H_2O$ by R. Marvin (written communication, 1954), of the U. S. Geological Survey has produced a large number of crystallized products. Crystal structure studies of these products suggest that the constitution of all solutions of pH below 12 are somewhat more complex than is suggested by Jander and Jahr's diffusion studies.

Similar plateaus are also observed on titration curves of pH versus added acid. Such a curve is shown in the upper half of figure 6 as measured by Ducret (1951). The breaks in such curves between plateaus correspond to the vertical boundaries in the quinquevalent field at the top of figure 1.

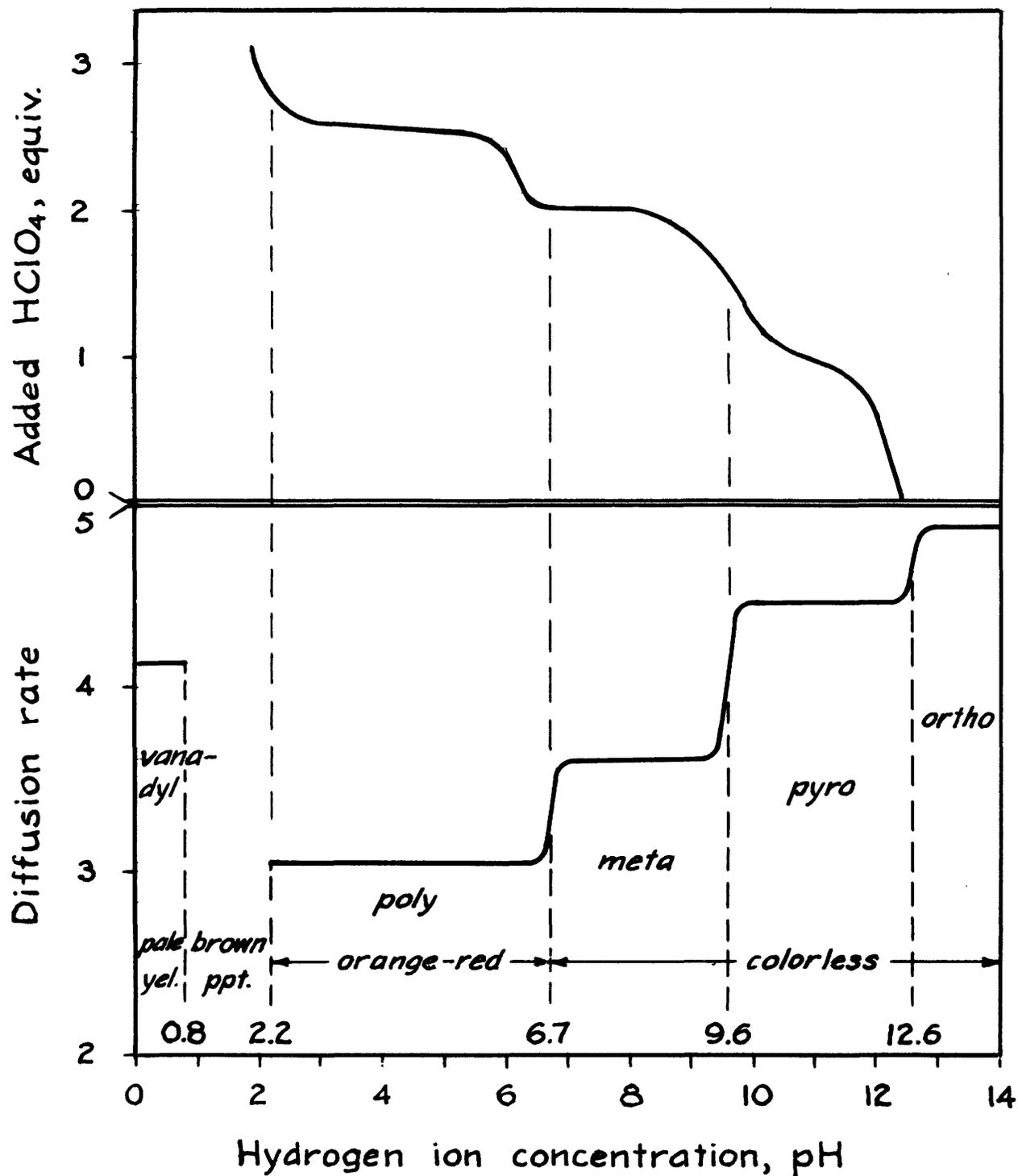
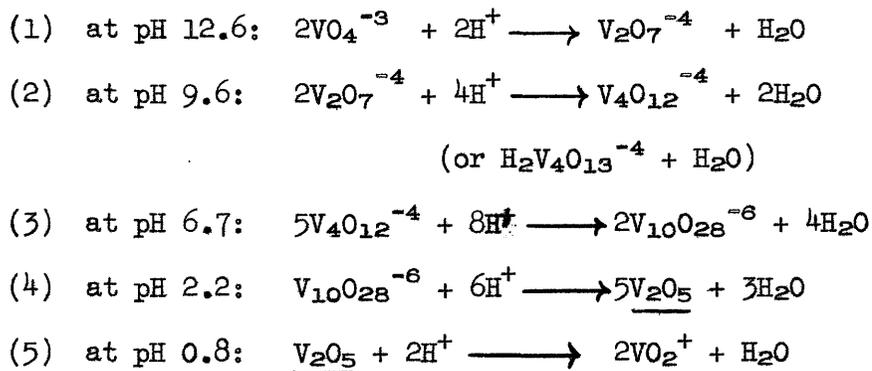


Figure 6.--Dispersion of vanadate phases with pH. Upper diagram, titration curve for sodium vanadate solution after Ducret (1951). Lower diagram, diffusion rate curve for sodium vanadate solution after Jander and Jahr (1935).

Souchet and Carpeni (1946) and previous workers have associated the indicated stability fields with complexes similar to those proposed by Jander and Jahr, but Ducret, basing his conclusions on the shape of the titration curves in the vicinity of the breaks, repudiates the idea of successive condensation to higher molecular weight groups. Only in the orange "polyvanadate" region does he postulate the existence of a $\text{H}_3\text{V}_2\text{O}_7^-$ ion; in the "meta-" and "pyro-" regions the ions H_2VO_4^- and $\text{HVO}_4^{=2}$, respectively, are supposed to predominate. Nevertheless, all the structures that have been worked out related to this system show that there is a powerful tendency for the orthovanadate ion to condense into complex groups, and it seems very likely that such complexes are important constituents of the solutions.

In view of all the evidence that is now available, we may propose the following reactions as taking place over the whole pH range:



All of the vanadium groups written in these equations may be more or less hydrated. Some of the ions may also form hydrogenated ions like $\text{HV}_2\text{O}_7^{-3}$ or $\text{H}_2\text{V}_2\text{O}_7^{-2}$.

These reactions are based primarily on the concept of condensation, that is, the linking together of small coordination groups to form larger ones, by splitting out H_2O . The behavior of quinquevalent vanadium with

respect to the stepwise formation of more condensed complexes, with increasing coordination as pH decreases, greatly resembles that of molybdenum and tungsten.

The ortho- and pyrovanadates

At pH levels above 12.6, the tetrahedral orthovanadate ion VO_4^{-3} seems to be stable in solution. Although no crystal structures of orthovanadates prepared from such solutions have been studied in detail, a number of highly soluble, deliquescent salts have been obtained which are clearly isostructural with the corresponding phosphates and arsenates. Thus, H. Baker (1885) demonstrated by crystallographic and optical means the following isomorphous groups:

$\text{Na}_3\text{VO}_4 \cdot 12\text{H}_2\text{O}$	hexagonal
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	
$\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$	
$\text{Na}_3\text{VO}_4 \cdot 10\text{H}_2\text{O}$	cubic
$\text{Na}_3\text{PO}_4 \cdot 10\text{H}_2\text{O}$	
$\text{Na}_3\text{AsO}_4 \cdot 10\text{H}_2\text{O}$	
$\text{Na}_3\text{VO}_4 \cdot 8\text{H}_2\text{O}$	orthorhombic
$\text{Na}_3\text{PO}_4 \cdot 8\text{H}_2\text{O}$	
$\text{Na}_3\text{AsO}_4 \cdot 8\text{H}_2\text{O}$	
$2\text{Na}_3\text{VO}_4 \cdot \text{NaF} \cdot 12\text{H}_2\text{O}$	cubic
$2\text{Na}_3\text{PO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$	
$2\text{Na}_3\text{AsO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$	

This strong evidence by analogy for the prevalence of the VO_4^{-3} ion in solution is in direct contradiction to Ducret's conclusion (1951) that this ion cannot exist in the presence of water.

Several orthovanadate mineral types are well known, e.g., vanadinite, isostructural with apatite. These minerals are usually characterized by the presence of a complexing amphoteric element such as Pb, Zn, or Bi, and

are formed under hydrothermal conditions. Truly ionic compounds such as the sodium salts mentioned above are not known in nature, as is to be expected from their strong basic character and high solubility. Carnotite, $K_2(UO_2VO_4)_2 \cdot nH_2O$, and tyuyamunite, $Ca(UO_2VO_4)_2 \cdot nH_2O$, are the only orthovanadates present in the Colorado Plateau area, but recent work by R. Marvin of the U. S. Geological Survey has shown that these complex compounds are stable in acid solutions and are decomposed only at pH 2.2. These minerals are discussed below.

The properties of V_2O_5 solutions in the range of pH 9.6 to 12.6 suggest that a pyrovanadate ion, $V_2O_7^{-4}$, may be stable. No crystal structure evidence is available to establish its existence definitely, although colorless crystalline salts such as $Ca_2V_2O_7 \cdot 2H_2O$ are readily formed in this pH range.

The metavanadates

The range from pH 6.7 to pH 9.6 represents a stability field corresponding to the so-called metavanadates. The crystal structures of the colorless compounds KVO_3 (Evans and Block, 1953) and $KVO_3 \cdot H_2O$ (Christ, Clark, and Evans, 1954) which readily crystallize in this range of pH have been worked out. These crystals both have chain structures, which means that the actual ion present in the solution is still unknown. In the pyrovanadate range we see the tendency for the single VO_4^{-3} tetrahedra to condense into coordination complexes, containing several vanadium atoms, as the pH is lowered. In KVO_3 (fig. 7), tetrahedra link into endless zigzag chains of composition $(VO_3)_n^{-n}$, by sharing corners. These chains are very similar to the silicate chains in diopside, $CaMg(SiO_3)_2$; indeed,

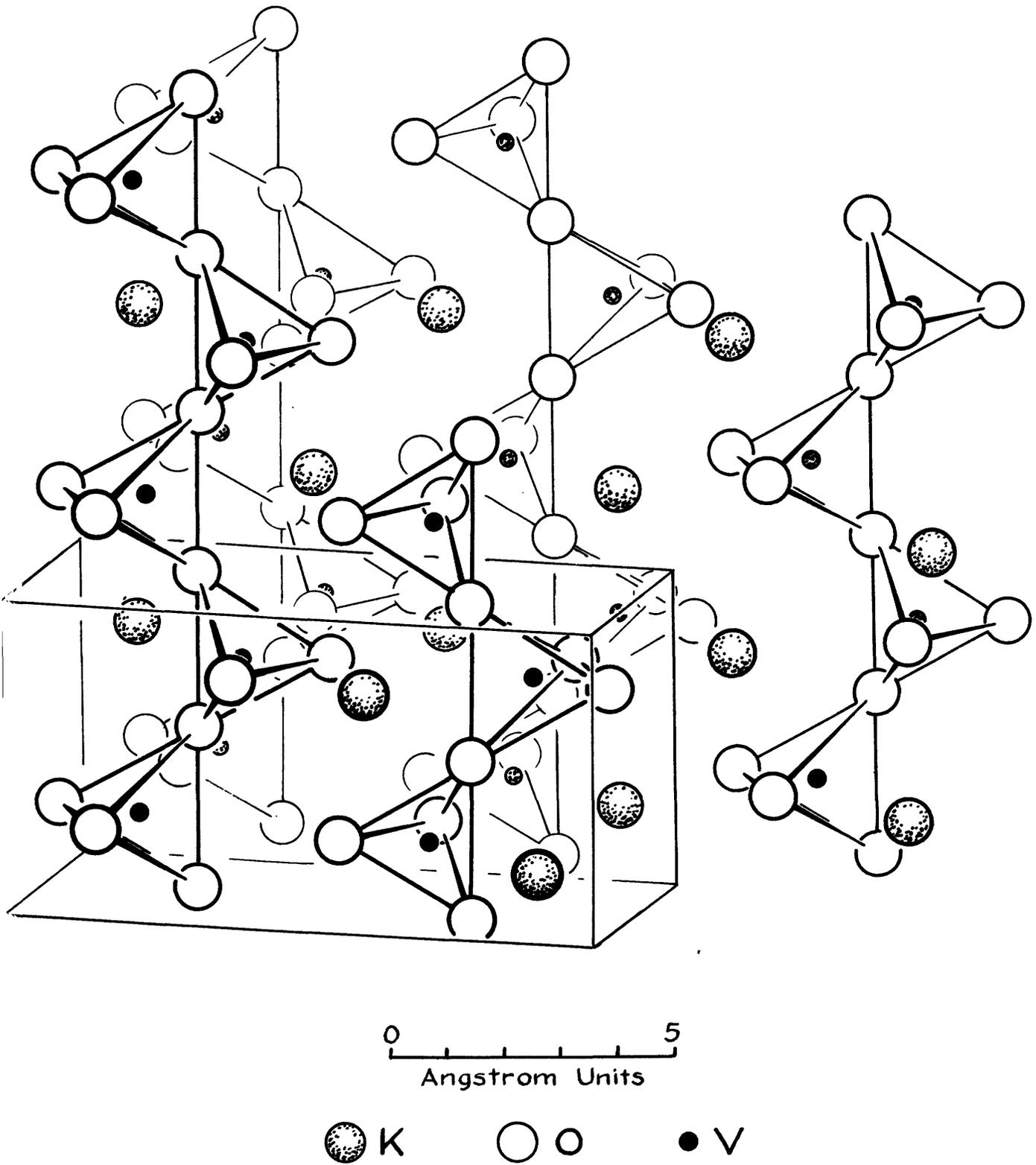


Figure 7.--Pictorial view of the crystal structure of artificial KVO_3 .

the compound NaVO_3 appears to be isostructural with diopside. KVO_3 forms needlelike crystals from hot solutions, and is only slightly soluble in cold water.

At low temperatures, prisms of $\text{KVO}_3 \cdot \text{H}_2\text{O}$ are also formed, and these have an entirely different structure (fig. 8). In the monohydrate, the vanadium is in strict five-fold coordination with oxygen, forming a trigonal bipyramid configuration which links into endless chains of composition $(\text{VO}_3)_n^{-n}$ by sharing edges. A similar type of chain has been confirmed for V_2O_5 by Bystrom, Wilhelmi, Brotzen (1950), but the chains are linked laterally to form sheets, and the vanadium coordination is distorted so that it approaches sixfold. The two structures are compared in figure 9, in which the end view of the chain elements are projected on the (001) planes. In this compound, vanadium shows the tendency to increase its oxygen coordination as the pH is lowered. Although the two types of chain appear to be completely different, it is not hard to imagine that the fivefold chain could be formed by an accordion-like pleating of the fourfold chain along its length, while each vanadium atom picks up an extra oxygen bond from an adjacent tetrahedron (fig. 10). Apparently, little energy is involved in this process, because there is evidence to show that simply grinding the $\text{KVO}_3 \cdot \text{H}_2\text{O}$ will convert it partly to KVO_3 (Christ, Clark, and Evans, 1954).

$\text{KVO}_3 \cdot \text{H}_2\text{O}$ has a prism axis (chain direction) spacing of 3.70 Å. This spacing is the fundamental fivefold chain-link unit length, and is a characteristic feature, often easily recognized as a fibre spacing, of many vanadate compounds and minerals formed in an acid environment of low temperature which is characteristic of present-day Colorado Plateau

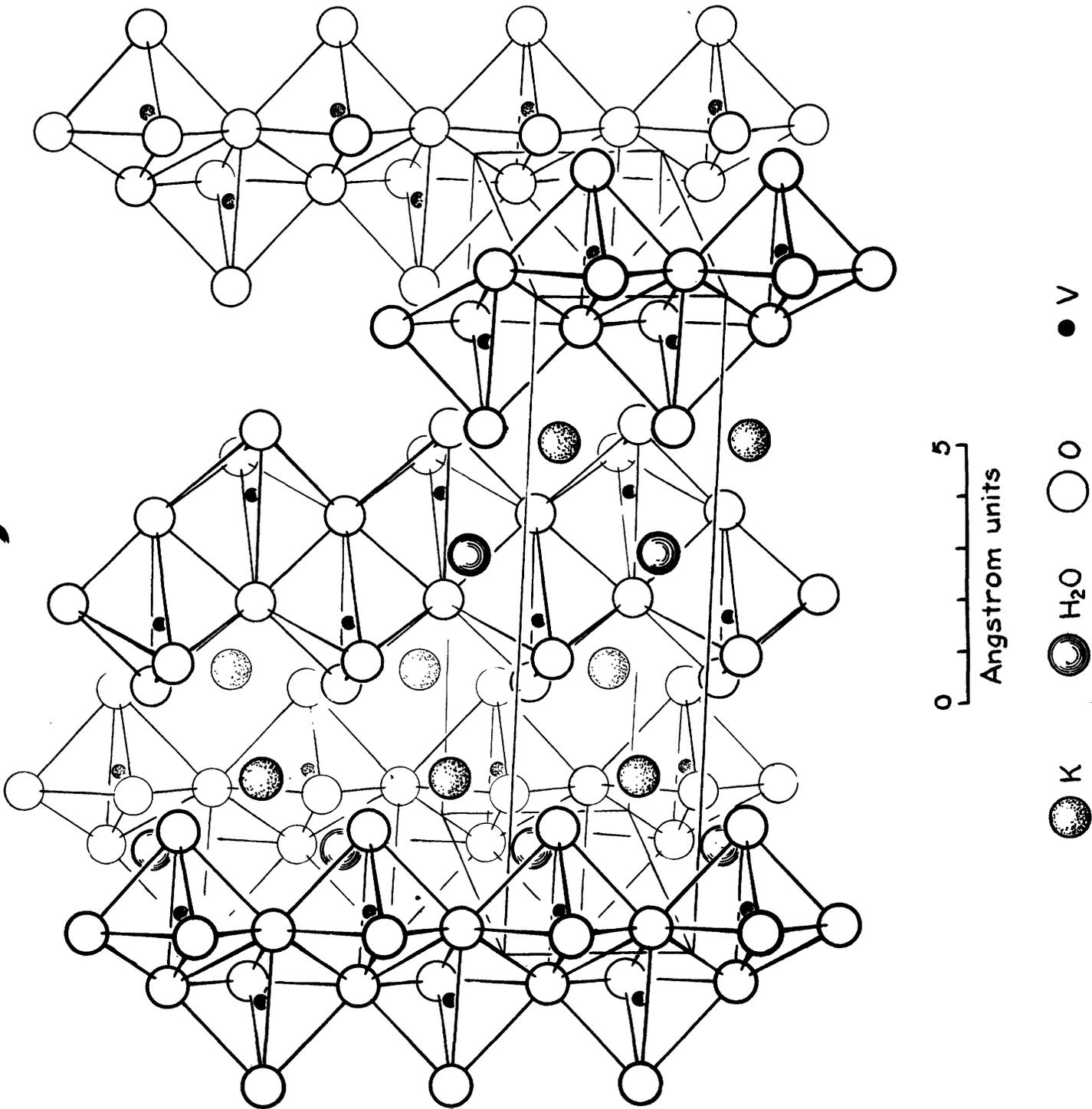


Figure 8.--Pictorial view of the crystal structure of artificial $\text{KVO}_3 \cdot \text{H}_2\text{O}$.

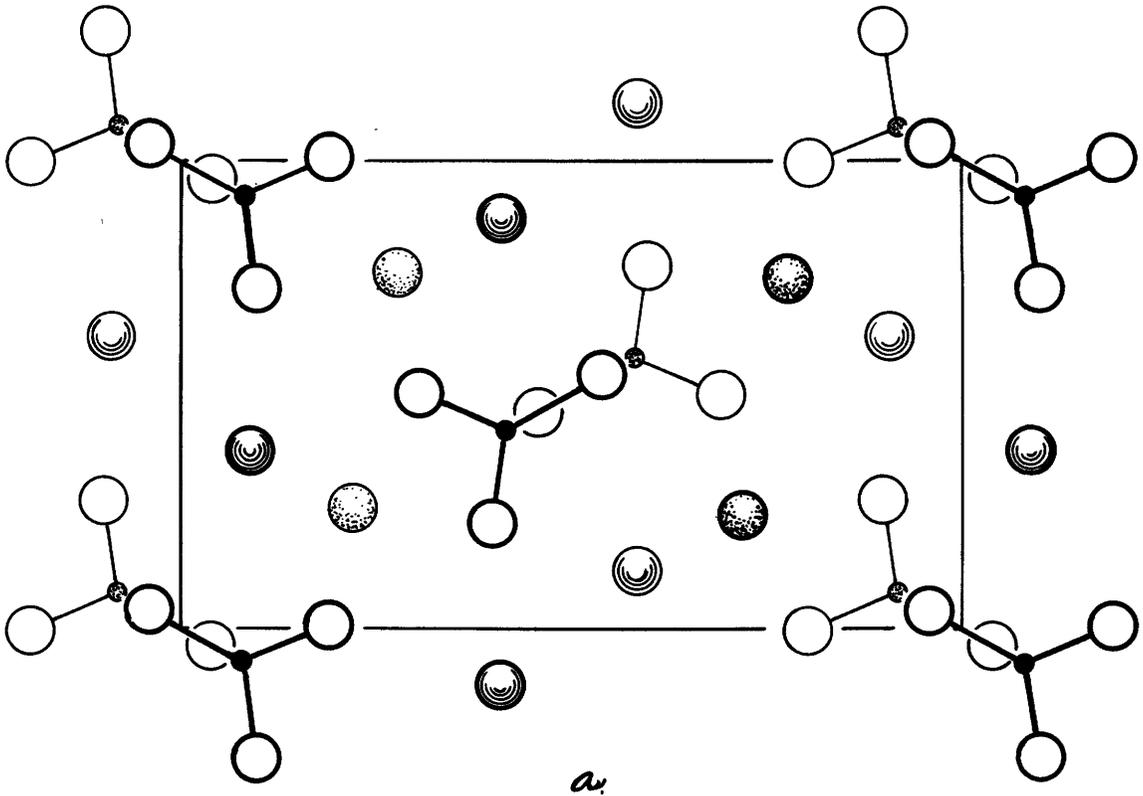
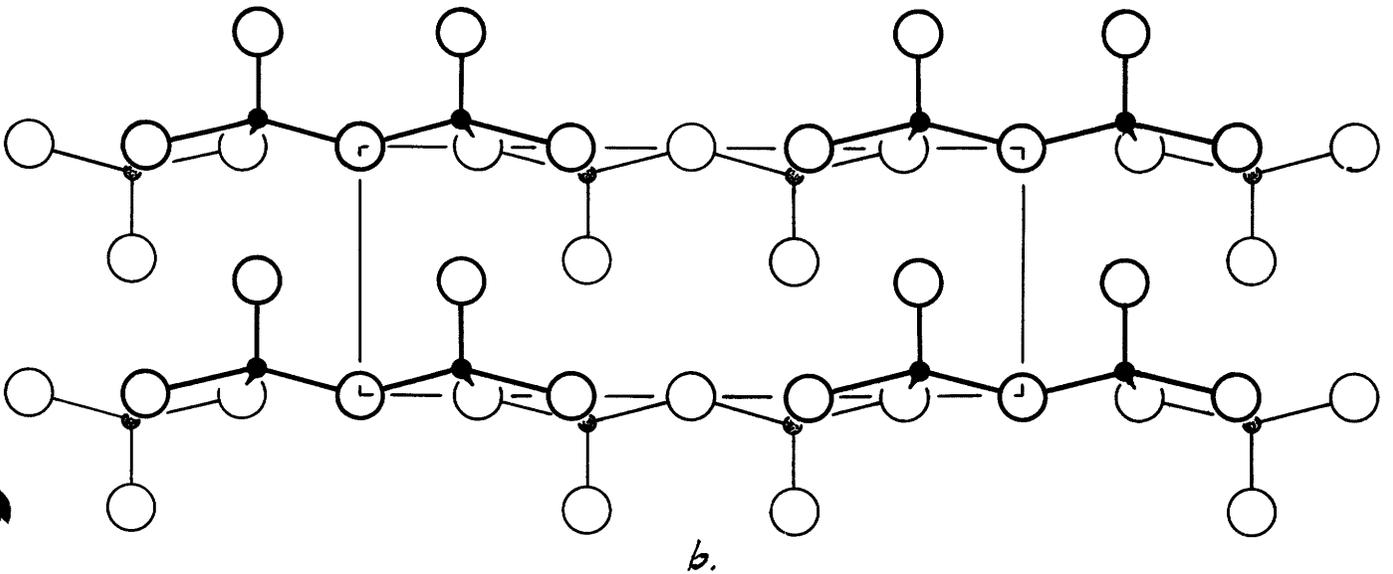


Figure 9.--Projections along the c -axis of the crystal structure of (a) $KVO_3 \cdot H_2O$ and (b) V_2O_5 . Large open circles are oxygen atoms, small dark circles vanadium, large arc-shaped circles H_2O , and large stippled circles K^+ ions.



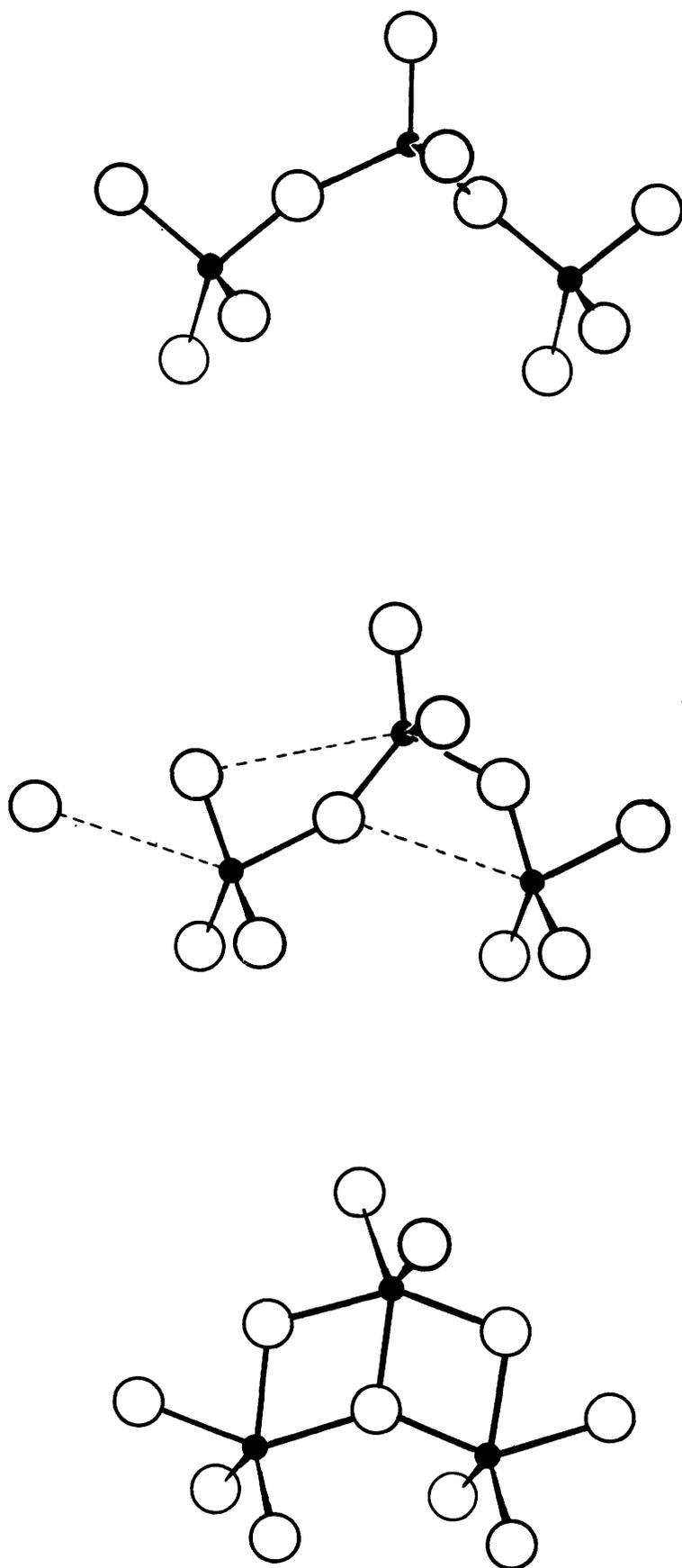


Figure 10.--Possible mechanism for transformation from 5-fold to 4-fold coordinated metavanadate chain. Large circles are oxygen atoms, small circles vanadium.

deposits. Apparently, this fivefold chain in one or another modification is a common fundamental structure motif of such compounds.

Minerals which correspond to the metavanadate range are rare; the only ones likely to belong here are rossite $\text{Ca}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ and metarossite $\text{Ca}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$. Their true character is not certain because their structures are not yet known.

Regarding the nature of the ion which is stable in the metavanadate solutions, it seems reasonable to suppose that it consists of either a trivanadate, $\text{V}_3\text{O}_{10}^{-5}$, or a tetravanadate, $\text{V}_4\text{O}_{13}^{-6}$, or probably both in addition to others. These would be threefold and fourfold links from the KVO_3 chain. Analogous phosphate complexes are known to exist in solution, in equilibrium with the HPO_4^{-2} and H_2PO_4^- ions, but apparently HVO_4^{-2} and H_2VO_4^- ions are much less stable than the corresponding acid phosphate ions.

The polyvanadates; the pascoite group

If a V_2O_5 solution is acidified below pH 6.7, the solution suddenly turns orange, and it enters a new stability field covering the range from pH 6.7 to 2.2, corresponding to the so-called polyvanadates. These solutions yield a variety of different orange and red crystalline products of complex composition. Marvin has prepared, among others, the following compounds, which have been characterized crystallographically (Evans, Mrose, and Marvin, 1955):

- I. $\text{K}_8\text{O}_{10}\text{O}_{28} \cdot 10\text{H}_2\text{O}$, triclinic (pseudomonoclinic).
- II. $\text{K}_8\text{V}_{10}\text{O}_{28} \cdot 9\text{H}_2\text{O}$, monoclinic.
- III. $\text{Ca}_3\text{V}_{10}\text{O}_{28} \cdot 16\text{H}_2\text{O}$ (pascoite), monoclinic.^{1/}
- IV. $\text{K}_2\text{Mg}_2\text{V}_{10}\text{O}_{28} \cdot 16\text{H}_2\text{O}$ (hammerite), triclinic.
- V. KV_3O_8 , monoclinic.

^{1/} Pascoite has been incorrectly described as triclinic and having the composition $\text{Ca}_2\text{V}_6\text{O}_{17} \cdot 11\text{H}_2\text{O}$ in Dana's System of mineralogy (Palache, Berman, and Frondel, 1951).

The appearance of the tenfold group $V_{10}O_{28}^{-6}$ in the first four compounds strongly indicates, since the compounds are quite soluble, that such a poly-complex is an important component of the solution. The strong inference from the crystal-structure studies that high molecular weight poly-ions are stable in these solutions supports generally the views of Jander and Jahr (1933), Souchet and Carpeni (1946) and most other chemical workers, but stands opposed to the hypotheses of Ducret (1951) who maintains that the orange solutions contain mostly $H_3V_2O_7^{\equiv}$ ions.

Neither the crystals nor the solutions are stable for any length of time. The crystals tend to dehydrate, falling to a yellow powder after some weeks at ordinary temperatures. The potassium polyvanadate solutions after some weeks at room temperature, or rapidly at higher temperatures, deposit light-orange insoluble crystals of KV_3O_8 while any crystals of $K_6V_{10}O_{28} \cdot 9H_2O$ present in the solution disappear. KV_3O_8 is apparently a stable end product of a series of competitive condensation reactions going on in the solution. In the same way, hewettite, $CaV_6O_{16} \cdot 9H_2O$, is formed from solutions of pascoite.

A recent structure determination of KV_3O_8 (Block, 1954) indicates that it contains chains built of segments of the fivefold chain of $KVO_3 \cdot H_2O$. These bent chains are linked laterally to form sheets of composition $(V_3O_8)_n^{-n}$ which are interleaved with K^+ ions. The interesting thing about this structure is that two out of three vanadium atoms in the sheet have fivefold coordination while the third approaches sixfold. The structure of the decavanadate complex ion is not yet known, but it also probably consists of some linkage based on the fivefold chain and acts as an intermediate step in the formation of the more highly condensed phases such as KV_3O_8 , hewettite, and others which are referred to below.

The minerals hummerite (Weeks and Thompson, 1954) and pascoite (Palache, Berman, and Frondel, 1951) are true representatives of the polyvanadate stability field. When the vanadium oxides reach the highest valence state, the acid ground waters dissolve them as the polyvanadate, in which form the vanadium moves into the surrounding rock. The brilliant orange crusts of pascoite that form on the blue-black vanadium oxide pockets in the Colorado mines make a striking underground display under the miner's lamp.

The hewettite group

When the vanadate solutions are brought to a pH below 3, the vanadium is almost entirely precipitated as brown and red-brown solids. These products have a constitution that has not been revealed in detail, but they undoubtedly correspond to the natural minerals hewettite and navajoite. The complexes containing large cations like hewettite are apparently stable with respect to the decavanadate ion and may be formed at somewhat higher pH than that allowed for the pure oxide (navajoite). These minerals are fibrous, with the fiber axis invariably exhibiting the characteristic 3.7-A spacing. Recent structure studies by Barnes and his coworkers (Barnes and Qurashi, 1952; Barnes, private communication) have revealed the fivefold chains tied together by oxygen links to form sheets of composition $(VO_3)_n^{-n}$. The details of these structures have not yet been described, but apparently the vanadium atoms are more nearly sixfold in coordination than fivefold. The sheets are loosely held together by Ca^{+2} ions (in hewettite), Na^+ ions (in a new undescribed mineral), or H^+ ions (in navajoite), and varying amounts of water. The variety of discrete

phases that readily transform from one to another by base exchange or change in vapor pressure has made the study of this group of minerals and compounds especially involved.

Mixed vanadium (IV) and vanadium (V); the corvusite group

The picture is made even more confusing at lower oxidation potentials. This brings us again to the group of minerals now designated loosely and collectively as corvusite. No distinct species has yet been isolated from these dark-green or blue-black mixtures. Recently, specimens have been found in which a good fibrous development is apparent, and such fibrous samples always show a fiber spacing of 3.7 Å by X-ray diffraction. The close relation between the corvusite and hewettite groups is further emphasized by the existence of specimens showing the fibrous seams of blue-black corvusite partly altered to navajoite, the fibrous structure being maintained from one phase to the other. Artificial compounds which possibly are related to the corvusite group are: $2V_2O_4 \cdot V_2O_5$; $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$; $Na_2O \cdot V_2O_4 \cdot 11V_2O_5$. All these are prismatic or fibrous in habit and have a 3.7-Å fiber spacing. The last two, described by Flood and Sprum (1943), illustrate the way in which a relatively small amount of alkali can play an essential stoichiometric role to balance corresponding amounts of reduced vanadium in V_2O_5 -like structures. Corvusite usually contains small but appreciable amounts of calcium; $2V_2O_4 \cdot V_2O_5$ actually has a V_2O_5 structure with certain oxygen atoms removed (Aebi, 1948). All these observations indicate that the valence range four to five in vanadium is represented in the corvusite group by many structures based on the fivefold chain of $KVO_3 \cdot H_2O$ in more or less condensed lateral linkages, all retaining

the characteristic 3.7-A fiber habit of the chain. The complexity of the group is increased by the incorporation of alkali and alkaline earth ions and water into these structures. These phases grade into the fully oxidized species of the hewettite group. The fact that the transition from vanadium (IV) to vanadium (V) takes place with little change in structure accounts in part for the fact that the natural vanadates frequently contain 1 or 2 percent V_2O_4 . Some specimens of pascoite have been found which are dark green because of a relatively high V_2O_4 content.

Another mixed quadrivalent and quinquevalent oxide is the mineral melanovanadite. Its structural constitution is unknown at present, but it is apparently unrelated to "corvusite." Its mineralogical associations suggest that possibly it represents an intervalent complex phase adjacent to the metavanadate field, analogous to the "corvusite" phase which is adjacent to the polyvanadate field.

Orthovanadate layer complexes: carnotite,
tyuyamunite, and rauvite

The uranyl vanadate complexes carnotite, $K_2(UO_2VO_4)_2 \cdot nH_2O$, and tyuyamunite, $Ca(UO_2VO_4)_2 \cdot nH_2O$, play a special role in the vanadate (quinquevalent) systems into which uranium is introduced. Their structures consist of a complex linkage of VO_4 tetrahedra and linear UO_2 groups forming a very stable layer fabric, which is negatively charged and interleaved with Na^+ , K^+ , or Ca^{+2} ions and water molecules. A tentative structure for anhydrous KUO_2VO_4 proposed by Sundberg and Sillén (1949) on the basis of an X-ray study of artificial crystals is represented in two views in figure 11. The structure is reminiscent of the autunite $[Ca(UO_2PO_4)_2 \cdot 8H_2O]$ structure

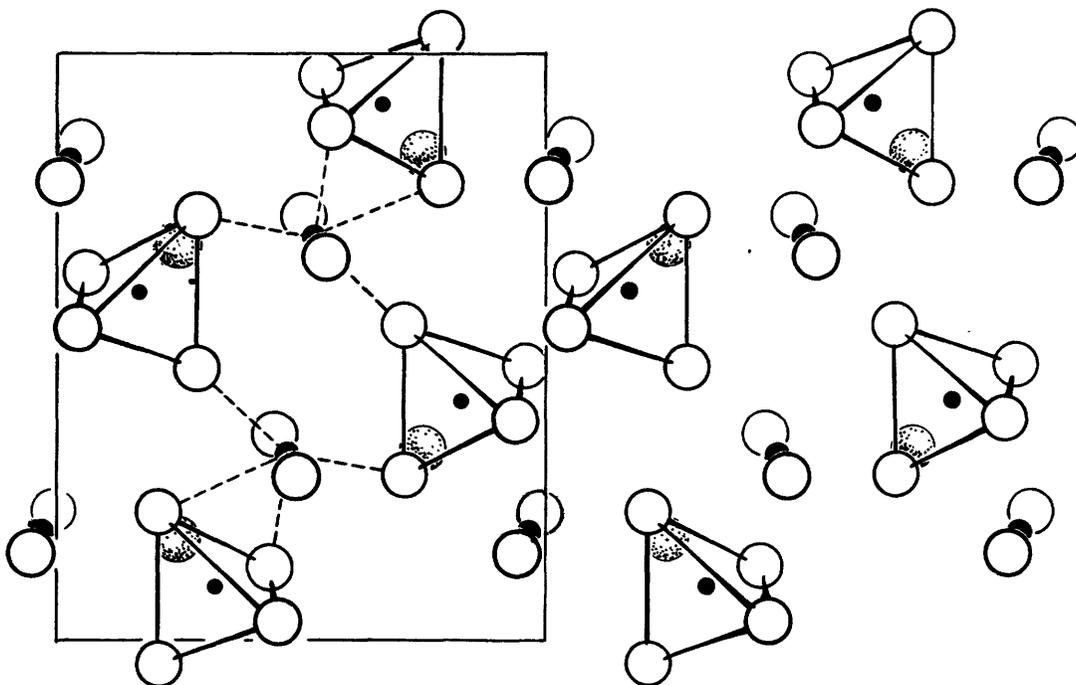
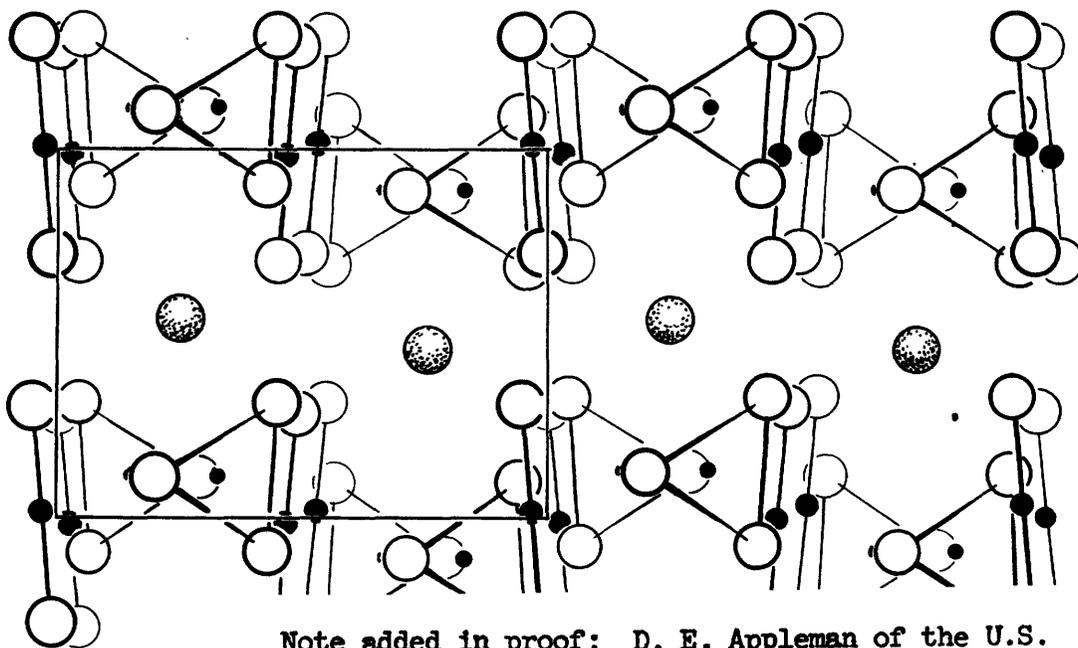


Figure 11.--Projections of the proposed structure for artificial anhydrous carnotite (Sundberg and Sillén, 1949) projected along the c -axis, above (normal to the structural sheets) and along the a -axis, below. Large open circles are oxygen atoms, small circles vanadium, and large shaded circles K^+ ions.



Note added in proof: D. E. Appleman of the U.S. Geological Survey has found that this structure of Sundberg and Sillén is incorrect, and that it actually consists of a complex sheet linkage of UO_2^{+2} groups and $V_2O_8^{-6}$ groups, related to the metavanadate system.

proposed by Beintema (1938) but departs considerably in detail from it. While uranium has regular octahedral coordination in autunite, this configuration is highly distorted in carnotite. The strong layer structure is common to the autunite and carnotite groups and accounts for their outstanding hydration-dehydration and base-exchange properties. As mentioned earlier, it has been found that carnotite is formed in solutions of potassium vanadate to which uranyl ion is added even when the pH is as low as 2.2. The solubility of the carnotite is very low and removes practically all vanadium or uranium (whichever is less) from the solution. It is, nevertheless, a little surprising to find it stable at such low pH values, where the concentration of $\text{VO}_4^{=3}$ ions is extremely low. It is likely that the carnotite sheet complex is formed through some intermediate stages involving the successive build-up of uranyl vanadate complex elements. The exact nature of these complexes is not known.

Related to the problem of the formation of carnotite is the rauvite problem. Rauvite is a red to reddish-brown resinous mineral of variable composition which may be represented by the formula $\underline{x}\text{UO}_3 \cdot \underline{y}\text{V}_2\text{O}_5 \cdot \underline{n}\text{H}_2\text{O}$, with y usually somewhat greater than x. While calcium is frequently present in natural rauvite, it is apparently not an essential constituent. It gives a characteristic X-ray diffraction powder pattern, but instead of sharp lines, the patterns consist of a number of bands. These bands are characteristic of partial crystalline order, such as would be found for a layer structure in which the stacking and orientation of the layers is completely random. Mineralogic associations suggest that the complex elements, which may be regarded as precursors of the carnotite complex, are formed under certain conditions and precipitate in a finely divided and poorly crystallized

state as rauvite. Rauvite is formed artificially from acid potassium vanadate solutions when the relative potassium ion concentration is low. Much work needs to be done to determine the relation between rauvite and carnotite and the mechanism of their formation.

The special characteristics of these layer structures has been further emphasized by the recent new green calcium vanadite mineral, simplotite (Thompson, Roach, and Meyrowitz, 1956a). Preliminary single-crystal work on this species has brought out an unusual crystal-chemical relationship among the following series of minerals:

Mineral	Formula	V valence
Meta-autunite	$\text{CaU}_2\text{P}_2\text{O}_{12} \cdot 4\text{H}_2\text{O}$	--
Metatyuyamunite	$\text{CaU}_2\text{V}_2\text{O}_{12} \cdot 3-4\text{H}_2\text{O}$	5
Sincosite (Peru)	$\text{CaV}_2\text{P}_2\text{O}_{10} \cdot 5\text{H}_2\text{O}$	4
Simplotite	$\text{CaV}_2\text{V}_2\text{O}_9 \cdot 5\text{H}_2\text{O}$	4

These minerals all have the basic layer structure referred to above and form yellow or green plates with a micaceous cleavage and a pseudotetragonal aspect. Apparently, in addition to its similarity to phosphorus, vanadium can also play a role similar to that of uranium in these layer complexes. The implied relationship between the VO^{+2} and UO_2^{+2} ions will be clearer when detailed crystal structure analyses of these minerals become available.

General characteristics of vanadium (V)

In retrospect, we see that the behavior of vanadium (V) varies markedly with conditions of acidity. In basic media, it resembles phosphorus and forms phosphate-like structures (e.g., vanadinite, isostructural with apatite). In acid media, vanadium (V) increases its oxygen coordination to five, tending toward six, and the vanadate groups show a strong tendency to polymerize. In this respect, vanadium is very similar to molybdenum and

tungsten. Vanadium is most soluble in the pH ranges 2.2 to 6.7 and below 0.8 (where the vanadyl ion VO_2^+ is formed), with a gap near the isoelectric point near pH 1.5 where V_2O_5 hydrates precipitate even from moderately dilute solutions.

The presence of powerful complexing agents will greatly alter the limits of the various stability fields. Thus, while vanadium is tetrahedrally coordinated in the carnotite structure, the complexing action of uranium (VI) (as UO_2^{+2} ion) extends the stability range of this phase well into the acid field, in spite of the fact that VO_4^{-3} ions are stable normally only above pH 12.

Since the lower valence vanadium minerals are generally insoluble, we may conclude that vanadium is transported during weathering in the Colorado sandstones only in the fully oxidized polyvanadate or metavanadate form under acid or weakly alkaline conditions. Some vanadium (IV) may also be released by the acid waters, but this will be quickly oxidized by atmospheric action. If uranium and vanadium are oxidized in the same environment, carnotite or tyuyamunite will be precipitated until the uranium or vanadium is used. (No uranium-vanadium complexes are known at lower valence states; apparently, these elements only interact in the fully oxidized state.) Excess vanadium in the form of polyvanadate may be temporarily deposited as pascoite-type or hewettite-type minerals, or be taken up in a silicate hydromica or clay structure, or be washed away altogether.

SUMMARY AND CONCLUSION

Referring once more to figure 1, it is useful to indicate on the Eh-pH diagram the regions in which the various minerals which have been discussed are stable. This has been done in figure 12, in which the direction of alteration is also suggested by means of arrows. The focal point is montroseite, the most reduced state of vanadium oxide minerals. The alteration under weathering then moves upward on the diagram, with excursions to higher or lower pH conditions, depending upon mineral associations and environment. In the region of complete oxidation, the presence of uranium causes the various complex fields above the shaded boundary to be completely replaced by carnotite.

Broadly speaking, the following generalizations may be made in conclusion:

1. Trivalent vanadium is represented by the primary mineral montroseite $[\text{VO}(\text{OH})]$ and is readily oxidized by the atmosphere to the quadrivalent form. Vanadium is similar in its crystal chemistry to manganese in the three- and four-valent state.
2. Mixed vanadium (IV) and (V) oxides comprise the blue-black ores, and probably are derived to a considerable extent from oxidation of montroseite.
3. Vanadium (V) oxide and its derivatives form the final stage of oxidation. In alkaline media, vanadates behave structurally like phosphates; in acid media, vanadates condense successively to form colorless and orange-red soluble complexes, and finally slightly soluble red or brown fibrous hewettite-type compounds. Vanadium (V) is similar to molybdenum and tungsten in behavior with regard to the tendency to polymerize with decreasing pH.

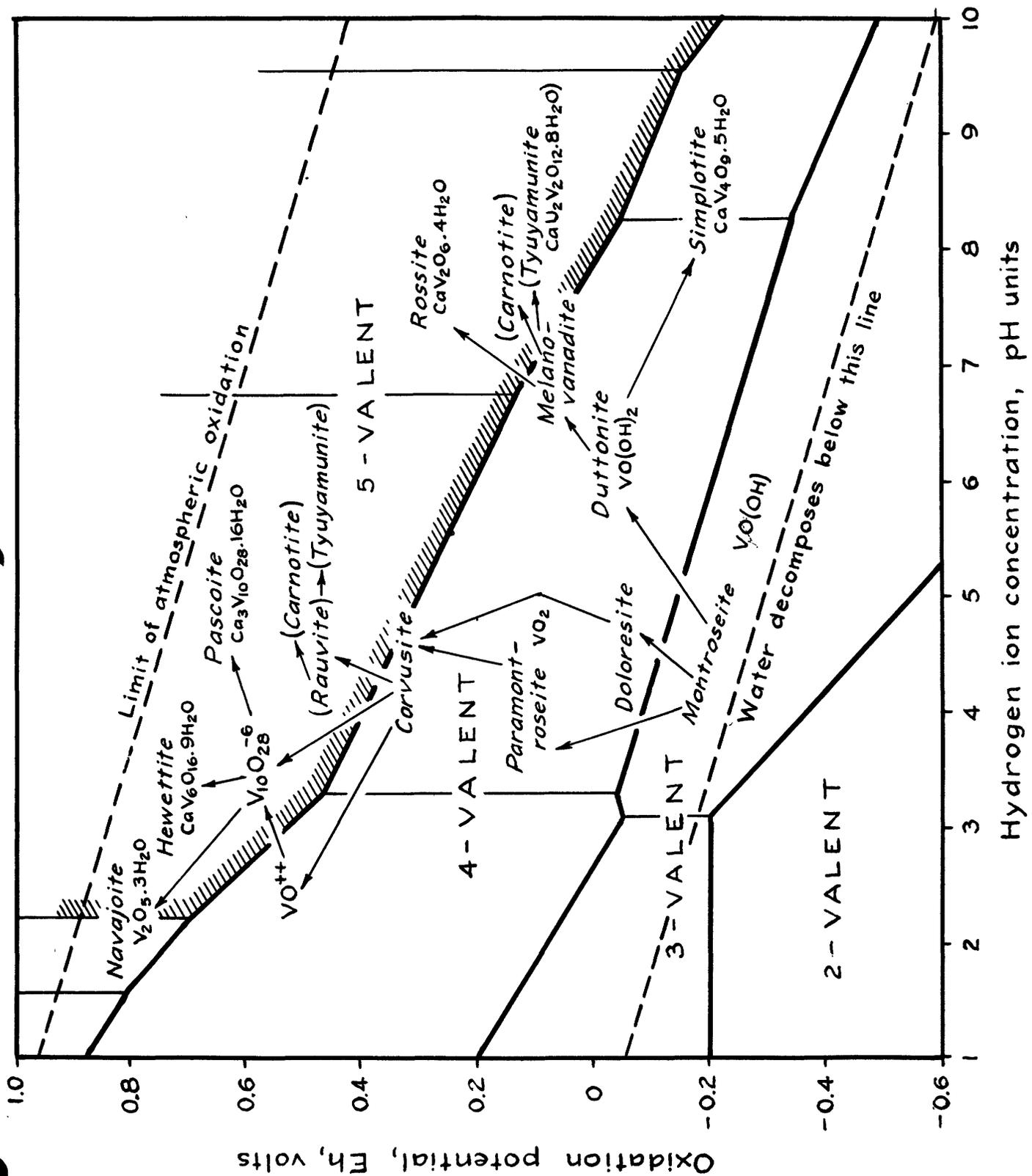


Figure 12.--Portion of the oxidation potential-pH phase diagram of figure 1, showing positions of various vanadium mineral species and probable alteration sequences.

4. An important structural property of quinquevalent vanadium is the formation of the five-coordinated chain which appears between pH 2 and 8. This structure motif appears to play an important role in the formation of the mixed vanadium (IV) and vanadium (V) oxides and hydrates.

5. Carnotite covers a wide pH range of stability for vanadium (V). Quinquevalent vanadium will precipitate any uranium present as carnotite or tyuyamunite. Excess vanadium may be temporarily deposited as hewettite or pascoite or bound up in a silicate mica or clay.

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