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Crystal chemistry of the natural vanadium bronzes

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ABSTRACT

The crystal chemistry of the natural vandium bronze minerals is reviewed on the basis of published information and new studies (mainly by X-ray powder-diffraction methods), using type material wherever possible. The known V bronze minerals are divided into three categories: (1) the hewettite group with layer structures analogous to synthetic $Li_3V_6O_{16}$, including hewettite, metahewettite, barnesite, hendersonite, and grantsite, (2) the straczekite group with layer structures analogous to synthetic $Ag_{5.44}V_8O_{20}$, including straczekite, corvusite, fernandinite, bokite, and bariandite, (3) other structure types including navajoite, schubnelite, fervanite, shcherbinaite, bannermanite, and melanovanadite. All known structures associated with the fibrous V bronzes (fiber spacing 3.6 Å) can be considered as various lateral linkages (into sheets or networks) of only two types of polyvanadate chains: (1) a divanadate chain $(V_2O_6)_n$ consisting of alternating square pyramids, and (2) a tetravanadate chain $(V_4O_{12})_n$ consisting of four highly condensed single octahedral chains.

INTRODUCTION

Vanadium occurs in a very distinctive and complex group of minerals. Its geochemical behavior depends radically on its oxidation state, which can vary continuously from 3+ to 5+, and (in aqueous environment) on the ambient acidity (pH). Evans and White (1987) have cataloged all the V mineral species known up to 1987, which are 119 altogether, and have described briefly how their geochemistry and crystal chemistry vary with oxidation potential and acidity. Evans and Garrels (1958) have analyzed these relationships in detail using available thermodynamic data and showed how V minerals in a weathering process alter from one species to another as oxidation potential increases and acidity changes. Evans and White recognized a particular group of vanadate minerals lying in the acid stability range of pH 2 to 5 and having mixed valence between 4+ and 5+. These species are characteristically fibrous with high luster and dark colors, are often chemically nonstoichiometric, and generally have a variable water content. Such minerals as hewettite and corvusite are representative of a class of compounds referred to by solid state chemists as V bronzes. The vanadium bronzes constitute a large group of V-rich oxide compounds whose synthetic members have been studied extensively for many years. The group of minerals we consider and review in this paper have these chemical and physical characteristics and constitute the natural V bronzes.

Many of the minerals considered here are listed in review papers by A. D. Weeks (Weeks and Thompson, 1954; Weeks, 1961), in which the physical and chemical properties and geochemical relationships of the minerals of the Colorado Plateau of the western United States are described. Here we are concerned with the structural chemistry of the natural V bronzes and their crystal-chemical relationships.

VANADIUM BRONZES

Hagenmuller (1971, 1973, 1975) has reviewed the studies of the synthetic systems M_xO-V_2O_4-V_2O_5, where M is Li, Na, K, Cu, or Ag. Each system contains a series of compounds with discrete crystal structures, but most of the compounds span a considerable composition range (Fig. 1). Hagenmuller describes six structure types, four of which we find correspond to certain mineral species. In a parallel study, which included systems with Cs, several other structure types were described by Waltersson (1976), but only one of these has been found thus far to occur in nature as an analogous structure type.

Nearly all of the structures referred to by these authors are based on chains of VO_6 octahedra linked by opposite corners, which impart to these compounds their fibrous character. The fiber period is commonly about 3.6 Å, the distance between opposite vertices of the VO_6 octahedron. The $(VO_5)_n$ chains are generally joined laterally, either by sharing lateral corners, or by sharing inclined octahedral edges so that adjacent chains are displaced along the fiber direction by ½ the 3.6 Å period. The octahedra are always highly distorted, with V-O distances varying from 1.55 Å to over 2.3 Å. Sometimes the long bond is so extended (2.7 Å or more) that the coordination can be considered as a fivefold square pyramid. Through this lateral linkage of chains, sheet structures may be formed, or even three-dimensional networks. In all cases

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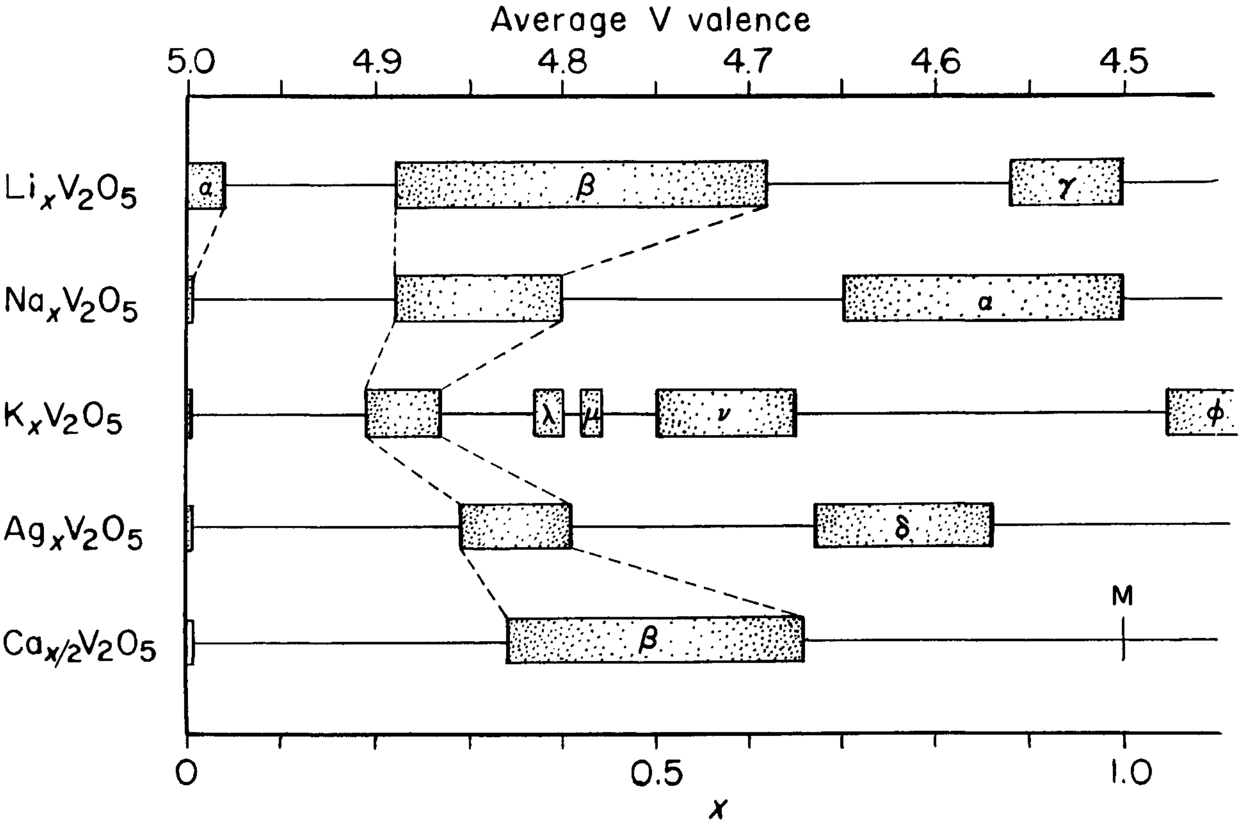

Fig. 1. Scheme showing composition ranges of various synthetic V bronzes of the type $M_xV_2O_5$ at about 600 °C (after Hagenmuller, 1971, 1973). The position of melanovanadite is indicated by M.

open channels are left between the sheets or in the networks, and these channels are occupied by various cations and water molecules. The V may be entirely in the pentavalent state or partially reduced by varying degrees. The cation content in the channels will depend on the charge developed in the V-oxide framework, thus leading to substantial compositional homogeneity ranges and nonstoichiometry.

Water is excluded in all the synthetic bronzes (which are prepared at high temperatures) but plays a major role as channel occupant in the mineral bronzes. The V bronzes are always highly colored and lustrous, red in the fully oxidized phases and dark green or black in the reduced (V^{4+}-V^{5+}) phases. Figure 1 illustrates the complexity of the V bronze systems and the broad composition ranges of the various phases.

Five structure types are now known to occur as minerals, corresponding to certain synthetic phases. Four of the five, and many of the synthetic ones, may be considered as assemblages of only two types of complex chains. One consists of two single chains joined laterally by sharing inclined octahedral edges, forming a zigzag double chain. One external oxygen atom is removed or remote from each VO_6 octahedron so that the chain is actually a double square-pyramid $(V_2O_6)_n$ chain (Fig. 2a). The second complex chain is quadruple, consisting of four single octahedral chains joined laterally by sharing inclined edges, forming a highly condensed fourfold $(V_4O_{12})_n$ fiber (Fig. 2b). These two types of chain are found as separate structural entities in two compounds (Fig. 3): the divanadate $(V_2O_6)_n$ chain, which occurs in munirite, $NaVO_3 \cdot 1.9H_2O$ (Butt and Mahmood, 1983; Evans, 1988), and the tetravanadate $(V_4O_{12})_n$ chain, which occurs in synthetic $Ag_3V_4O_{12}$ (Drozdov et al., 1974). The isolated divanadate chain also occurs in rossite, $Ca(VO_3)_2 \cdot 4H_2O$ (Ahmed and Barnes, 1963) and metarossite, $Ca(VO_3)_2 \cdot H_2O$ (Kelsey and Barnes, 1960). These minerals and munirite are colorless, white or pale yellow, and are not normally classed as bronzes. The manner in which these two complex chain elements are joined to form the different types of mineral bronzes is described in the following paragraphs (Greek-letter designations are those of Hagenmuller, 1973).

θ-$Li_3V_6O_{16}$ phase. Wadsley (1957) determined the structure of this compound (which he referred to as γ-$Li_{1+x}V_3O_8$, with $x = 0.5$), but few other synthetic analogues of this structure type have been described, and no other full structure determinations are reported. Wadsley's structure has been refined by Evans (1989) using Wadsley's data. According to Wadsley the $(V_6O_{16})_n$ sheets in one crystallographic unit are formed by alternately joining tetravanadate chains and divanadate chains lat-

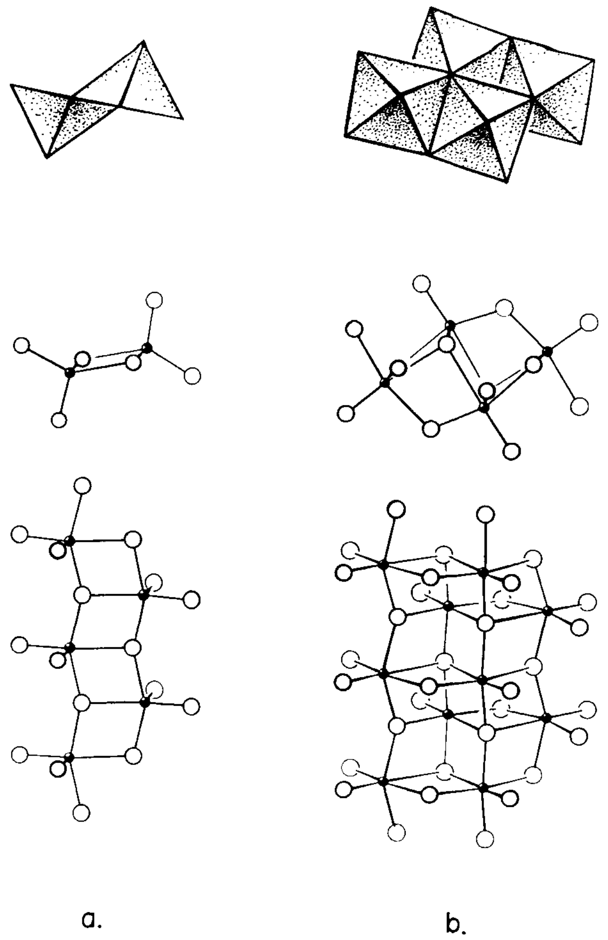

Fig. 2. Divanadate chain (**a**) and tetravanadate chain (**b**), components of the fibrous vanadium bronzes. Bond structures (middle and bottom) and polyhedral representations (top) are shown. The bottom views are oblique with the 3.6-Å fiber axes vertical; the top and middle views are projected along the fiber axes.

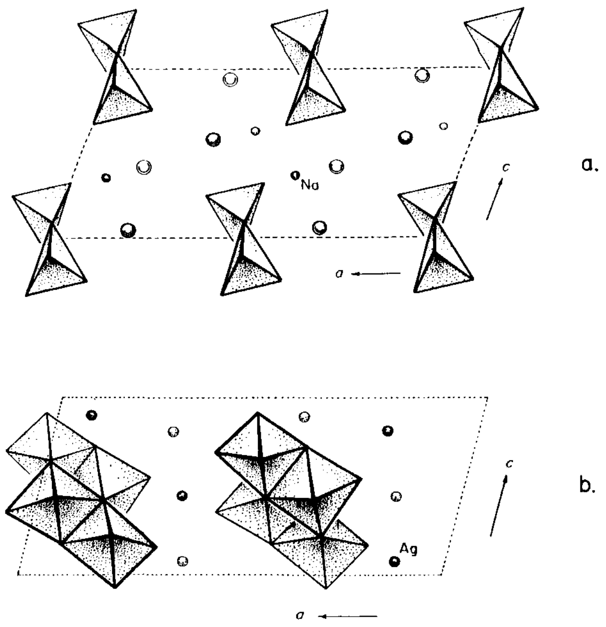

Fig. 3. Structures of (**a**) munirite, $NaVO_3 \cdot 1.9H_2O$ (Björnberg and Hedman, 1977), and (**b**) synthetic $Ag_3V_4O_{12}$ (Drozdov et al., 1974). In these and following figures the projections are along the monoclinic *b* (fiber) axis.

erally by sharing corners (Fig. 4). The V-O bonds in the distorted octahedra and square pyramids range in length from 1.59 Å to 2.36 Å; the V atoms in the latter also approach a sixth O atom in an adjacent chain at a distance of 2.86 Å, forming a very weak bond. The sheets are arranged to form a monoclinic layer structure with space-group symmetry $P2_1/m$ and characteristic dimensions within the layer of $a = 12.0$ Å and $b = 3.60$ Å (fiber axis). The third dimension and β angle will depend primarily on the nature and amount of interlayer cations and water molecules. Bachmann (1962) first recognized the analogy between this structure and that of hewettite, noting that hewettite is a natural vanadium bronze.

δ-$Ag_xV_2O_5$ phase. The structure of this compound with $x = 0.64$ (referred to by Andersson as δ-$Ag_{1-x}V_2O_5$ with $x = 0.32$) was found by Andersson (1965) (see also Drozdov et al., 1973) to consist of tetravanadate chains joined laterally directly to each other by sharing octahedral edges normal to the fiber direction (Fig. 5). These layers also form a monoclinic structure, but in space group $C2/m$, with characteristic dimensions $a = 11.7$ Å and $b = 3.67$ Å. Again, the c and β angle dimensions depend on the interlayer material. Evans et al. (1984) first recognized this structure type in the mineral straczekite, $(Ca,K,Ba)_{1.11}V_8O_{20} \cdot 3H_2O$. The structure of a synthetic anhydrous analogue of straczekite, $Ca_{1.2}V_4O_{10}$, has been determined with high accuracy by Kutoglu (1983).

β-$Na_xV_2O_5$ phase. Wadsley (1955) first defined this structure type (with $x = 0.33$), which consists of tetravanadate chains joined laterally into sheets by sharing octahedral corners, but in this case the sheets are cross-linked by divanadate chains to form a three-dimensional network (Fig. 6). The structure is monoclinic with space group $A2/m$ and unit cell dimensions $a = 10.08$ Å, $b = 3.61$ Å, $c = 15.44$ Å, and $\beta = 109.6°$. Because of the cross-layer linkage these cell dimensions will change only slightly with varying channel content; also, there is little room for water in the structure. Hughes and Finger (1983a) found that the volcanic fumerole mineral bannermanite is the mineral analogue to this compound, and refined its crystal structure.

α-$Na_xV_2O_5$ phase. When $x = 0$ this compound is the oxide V_2O_5. This form of the α phase has a structure determined by Byström et al. (1950) and recently refined by Enjalbert and Galy (1986). The sheet structure consists of divanadate chains linked laterally by sharing corners, which stack together in an orthorhombic arrangement (Fig. 7). Na can be introduced to a maximum of $x = 0.02$, but

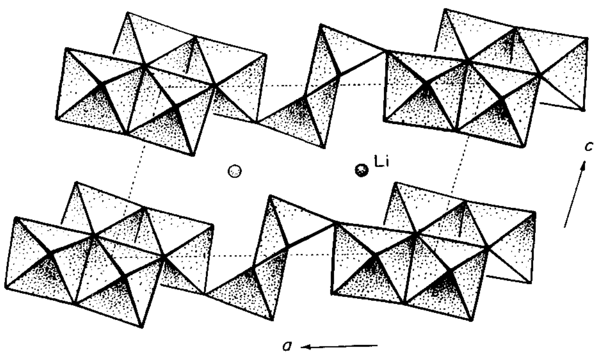

Fig. 4. Structure of $Li_xV_3O_8$ (Wadsley, 1957).

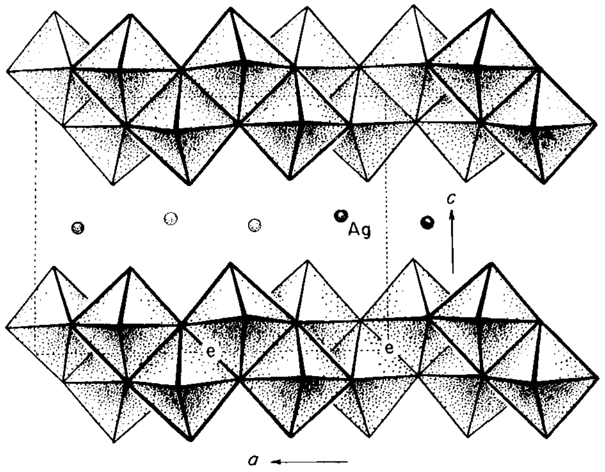

Fig. 5. Structure of δ-$Ag_xV_2O_5$ (Andersson, 1965). Symbol *e* indicates an octahedral edge shared by adjacent tetravanadate chains.

the structure appears again with small modification when $x = 0.7$ to 1.0. The β form (β-$Na_xV_2O_5$, see above) is stable at an intermediate Na content of $x = 0.22$ to 0.40. The volcanic mineral shcherbinaite corresponds to pure V_2O_5 (Borisenko et al., 1970; Hughes and Finger, 1983b).

Other synthetic bronze phases. CsV_2O_5 is a mixed-valance layer structure (Mumme and Watts, 1971) but, unlike the bronzes described above, is not based on laterally linked divanadate or tetravanadate chains. It consists of VO_4 tetrahedra and V_2O_8 double-pyramid groups corner-linked into a sheet arrangement. The mineral melanovanadite ($CaV_4O_{10} \cdot 10H_2O$) has recently been found to be based on this type of structure (Konnert and Evans, 1987).

Several other structure types are known in this group of V compounds, although none has so far been recognized among minerals. It is worthy of note, however, that all the known fibrous bronzes are composed of various linkages of the two basic chain types shown in Figure 2. For example, the synthetic compound $Cu_{1.8}V_4O_{10}$ (Galy and Lavaud, 1971) contains corner-linked tetravanadate chains as in $Na_xV_2O_5$, but without the cross-linking divanadate chains. The θ-LiV_2O_5 phase has a structure composed entirely of divanadate chains linked into sheets, but in a manner different from that in V_2O_5 (Galy and Hardy, 1965).

Besides the CsV_2O_5 phase referred to above, two other Cs vanadium bronzes have been described: $Cs_xV_2O_5$ (Waltersson and Forslund, 1977a) and $Cs_xV_3O_7$ (Waltersson and Forslund, 1977b). In these alkali bronzes only divanadate chains are present, linked laterally to form two kinds of hexagonal networks.

EXPERIMENTAL DIFFERENTIATION OF THE VANADIUM BRONZE STRUCTURE TYPES

Two methods have proved effective in identifying the type of structure exhibited by a fibrous V bronze mineral: electron diffraction and X-ray fiber diagrams. Crystals of the natural V bronzes usually contain variable amounts of water, which can change with conditions of humidity. The resulting shifts in structure severely degrade the quality of the crystals, so that good single-crystal diffraction patterns can rarely be obtained. The crystals are also very soft and always severely distorted and twisted. Nevertheless, intense X-ray fiber patterns can often be registered, whereas electron diffraction yields sharp patterns of layer lattices.

The method of electron diffraction was described in detail by Ross (1959) in his crystallographic study of various V minerals. In this case the lathlike crystals tend strongly to lie on the plane of the sheet structure so that the *a* and *b* dimensions of the sheet can be measured. The presence of primitive or centered lattices in such patterns clearly differentiates the $Li_3V_6O_{16}$ (hewettite) and $Ag_xV_2O_5$ (straczekite) structure types, but generally, complete unit cells cannot be measured. The study of Ross (1959) has provided much useful information for the mineral interpretations offered in this paper.

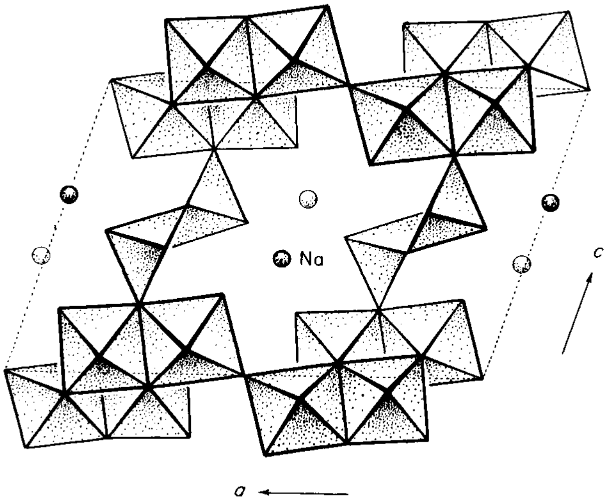

Fig. 6. Structure of bannermanite, β-$Na_xV_6O_{15}$ (Wadsley, 1955).

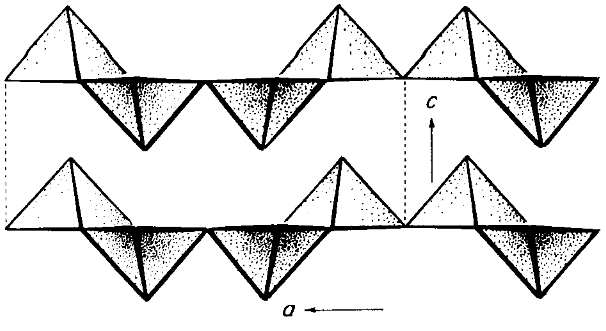

Fig. 7. Structure of shcherbinaite, V_2O_5 (Enjalbert and Galy, 1986).

X-ray fiber patterns can usually be obtained in a rotation camera or Debye-Scherrer camera. Such patterns are generally characteristic of a particular structure type. It is often possible to index such patterns to find the *a*, *c*, and *β* parameters of a preliminary monoclinic unit cell. This technique was first applied to V minerals by Lindberg et al. (1962) in their description of the mineral hendersonite. It was also used in the description of grantsite by Weeks et al. (1964) and of straczekite by Evans et al. (1984).

Other points of distinction of the fibrous bronzes are the following:

1. The monoclinic crystal lattice is primitive for the hewettite group, and the *a* and *b* axes are close to 12.3 and 3.60 Å, respectively, whereas for the straczekite group the lattice is *C*-centered with *a* and *b* axes close to 11.7 and 3.65 Å, respectively. This information is readily obtained from electron-diffraction measurements, as shown by Ross (1959).

2. Certain powder X-ray reflections can be readily recognized for the fibrous bronzes. The interlayer spacing along *c* leads to an intense 001 reflection at a low Bragg angle. If there are two such lines, the sample is probably a mixture of two bronzes (possibly two hydrates). In these structures all the atoms are close to mirror planes at $y = 0$ and ½ along the fiber axis (monoclinic *b* axis); thus, the 020 reflection at about 1.8 Å will be at maximum amplitude and will appear as a relatively strong and sharp line. For the same reason the *h*2*l* reflections will mirror the *h*0*l* reflections, and the 021 reflection will appear as a weak line just on the high-θ side of 020.

3. In the interpretation of chemical analyses, when V is set to 6 for the hewettite-group minerals, the oxygen count will be close to 16 (V/O = 3/8), and for the straczekite-group minerals the oxygen count for 8 V will be close to 20 (V/O = 2/5). It is sometimes uncertain what cations to include as interlayer material (Al,U?), but in any case the chemical composition may or may not be stoichiometric. If Fe is present it may be uncertain whether it lies in the layer substituting for V, or in the interlayer region, or both. These problems may make the O count unreliable as an indicator.

Table 1. The natural vanadium bronzes

Mineral	Generalized formula	Avg. V valence
I. Fibrous bronzes		
Hewettite group		
Hewettite	$CaV_6O_{16}\cdot 9H_2O$	4.95
Metahewettite	$CaV_6O_{16}\cdot 3H_2O$	5.00
Barnesite	$(Na,Ca)V_6O_{16}\cdot 3H_2O$	5.00
Hendersonite	$Ca_{1.3}V_6O_{16}\cdot 6H_2O$	4.88
Grantsite	$(Na,Ca)V_6O_{16}\cdot 4H_2O$	4.87
Straczekite group		
Straczekite	$(Ca,K,Ba)_2V_8O_{20}\cdot 6H_2O$	4.80
Corvusite	$(Na,K,Ca,Mg)_2V_8O_{20}\cdot 6\text{-}10H_2O$	4.86
Fernandinite	$Ca_{0.6}V_8O_{20}\cdot 10H_2O$	4.84
Bariandite	$Al_{0.6}V_8O_{20}\cdot 18H_2O$	4.80
Bokite	$(Al,Fe)_{1.4}(V,Fe)_8O_{20}\cdot 7.4H_2O$	4.77
II. Other bronze types		
Navajoite	$Ca_{0.05}(V,Fe)_{10}O_{24}\cdot 12H_2O$	4.95
Schubnelite	$Fe_{2-x}V_2O_4(OH)_4$	4.66
Fervanite	$Fe_4V_4O_{12}\cdot 5H_2O$	5.00
Shcherbinaite	V_2O_5	5.00
Bannermanite	$Na_{0.7}V_6O_{15}$	4.88
Melanovanadite	$CaV_4O_{10}\cdot 10H_2O$	4.50

4. If the unit cell is known, the (sub)cell content will have 6 V atoms per layer in the hewettite-group minerals, and 8 V atoms per layer in the straczekite-group minerals. These V counts will establish the unit cell formula, which can be checked with a density measurement. Also, the unit-cell volume should be consistent with the volume of the layer (275 Å^3 for a hewettite V_6O_{16} layer, 360 Å^3 for a straczekite V_8O_{20} layer), plus interlayer material (23 Å^3 for H_2O, 10 Å^3 for Ca, etc.). These molecular volumes can thus be used to estimate the amount of water in a particular crystal.

New X-ray power-diffraction data are reported here for many V bronze species using material (often type) obtained from the Smithsonian Institution in Washington, D.C. The best patterns were made with the Gandolfi camera using Cr*Kα* radiation. The specimens were prepared by rolling a few grains into a ball with cement, with the radius of the ball being 0.1 to 0.3 mm. This technique made it possible to obtain the sharpest patterns at the highest resolution, with the least amount of material and least preferred orientation (Hildebrand, 1953). Wherever possible, indexing was assisted by information derived from a fiber pattern. Least-squares analysis has provided the best unit-cell parameters in each case (Appleman and Evans, 1973). Intensities were measured from microdensitometer traces of the patterns by comparison with a linearly exposed, stepped film strip.

CLASSIFICATION AND CHARACTERIZATION OF THE NATURAL VANADIUM BRONZES

Evans and White (1987) listed 14 mineral V bronze species. These may now be divided into subgroups according to their basic structure types. Table 1 shows this grouping and displays generalized formulas and average V valencies for these minerals. Five such groups can be assigned, but three so far contain only one species each. Other structure types and subgroups may be found in the

Table 2. Crystallographic data for members of the hewettite group

Phase	*a* (Å)	*b* (Å)	*c* (Å)	*β* (deg.)	V (Å³)	Reference
Synthetic $Li_3V_6O_{16}$	12.03	3.60	6.68	107.83	275.4	Wadsley (1957)
Hewettite $CaV_6O_{16} \cdot 9H_2O$	12.56	3.615	11.47	97.0	517	Qurashi (1961)
Intermediate hewettite $CaV_6O_{16} \cdot 6H_2O$	12.5	3.61	11.1	113	447	Qurashi (1961)
Dehydrated hewettite $CaV_6O_{16} \cdot 3H_2O$	12.3	3.61	9.45(×2)	118.5	368(×2)	Qurashi (1961)
Reconstituted hewettite $CaV_6O_{16} \cdot 9H_2O$	12.250	3.497	11.174	97.25	478	Bayliss (1982)
Dehydrated hewettite $CaV_6O_{16} \cdot 3H_2O$	12.15	3.607	9.22(×2)	118.03	356(×2)	Bayliss and Warne (1979)
Hewettite $CaV_6O_{16} \cdot 9H_2O$ (AW-220-54)	12.290	3.590	11.174	97.24	489	Evans (1989)
Sodian hewettite $NaCa_{0.5}V_6O_{16} \cdot 2H_2O$	12.26	3.58	8.11	92.5	355	Bachmann and Barnes (1962)
Sodian hewettite $NaCa_{0.5}V_6O_{16}$	12.28	3.60	8.00	96.25	351	Bachmann and Barnes (1962)
Barnesite $Na_2V_6O_{16} \cdot 3H_2O$	12.17	3.602	7.78	95.03	342	Weeks et al. (1963)
Hendersonite* $Ca_{1.5}V_6O_{16} \cdot 6H_2O$	12.40	3.59(×3)	9.46(×2)	—	421(×6)	Lindberg et al. (1962)
Grantsite* $Na_2Ca_{0.75}V_6O_{16} \cdot 4H_2O$	12.429	3.604	8.771(×2)	95.33	391	Weeks et al. (1964)

* Unit-cell axis labels redefined to show similarity to other members of the group.

future. At present the most important groups are what are here designated the hewettite (θ-$Li_3V_6O_{16}$-type) group, and the straczekite (δ-$Ag_xV_2O_5$-type) group.

Hewettite group

Crystallographic data that have been recorded for this group are collected in Table 2. All of the lattices (sublattices in the cases of dehydrated hewettite, hendersonite, and grantsite) are primitive, space group $P2_1/m$, with characteristic dimensions $a = 12.2 \pm 0.2$ Å and $b = 3.60 \pm 0.01$ Å (Ross, 1959). The family resemblance of the X-ray fiber patterns for these minerals, which is a function of the basic (V_6O_{16}) layer structure, gives further confirmation of the common structural basis of this group of bronzes.

Hewettite, metahewettite. In their original description of these minerals, Hillebrand et al. (1914) distinguished two types of the new mineral, both of which they formulated as $CaV_6O_{16} \cdot 9H_2O$. On the basis of subtle differences in their physical properties, especially the dehydration behavior on heating, they labeled the material from Minasragra, Peru as "hewettite" (after D. Foster Hewett, who reported on the mineralogy of that locality) and that from Utah and Colorado (Thompson's district and Paradox Valley, respectively) as "metahewettite," considering them to be dimorphous. Barnes (1955) studied eight specimens labeled "hewettite" and "metahewettite" and found a confused mineralogical situation. Some of the specimens he found to contain Na either partly or wholly replacing Ca; these seemed to be less hydrated and not affected by atmospheric humidity (see barnesite, below). The calcium hewettites, as Hillebrand et al. (1914) had found, proved to be very sensitive to humidity changes. Barnes (1955) found that specimens dried over P_2O_5 consistently reached the unique phase $CaV_6O_{16} \cdot 3H_2O$, but higher hydrates or rehydrated samples gave similar but slightly varying X-ray powder-diffraction patterns. The details of the hydration process were worked out from Weissenberg photographs by Qurashi (1961), who measured unit cells for the nine-, six-, and three-hydrates (Table 2). Recently, Bayliss (1982) reported new diffractometer powder-diffraction data for hewettite reconstituted from air-dried material from Monument Valley, Arizona, by soaking in a saturated humid atmosphere for one year at room temperature. His unit cell is enlarged from that of the dehydrated material (Table 2) but differs from that of Qurashi (1961). Bayliss and Warne (1979) gave new data for the dehydrated material and found a unit cell close to that of Qurashi for the trihydrate. Bayliss and Warne, following Strunz (1977), referred to the dehydrated sample as metahewettite. Although the definitions of hewettite and metahewettite in Dana's System of Mineralogy (Palache et al., 1951) followed the description of Hillebrand et al. (1914), Alice Weeks (in Ross, 1959) suggested that the term "metahewettite" be transferred to the trihydrate, conforming with other high- and low-hydrate mineral phases, such as torbernite-metatorbernite. Fleischer still wrote the formula for metahewettite with $9H_2O$ in the fourth edition of his Glossary of Mineral Species, but in the fifth edition (Fleischer, 1987) it is changed to $3H_2O$. The existence of the dehydrated mineral, hewettite, $CaV_6O_{16} \cdot 3H_2O$, is thus established as a discrete phase, but the higher hydrates are evidently variable and not reproducible from specimen to specimen. In this paper we use the nomenclature of Strunz (1977) and Fleischer (1987).

Wadsley's crystal structure analysis of $Li_3V_6O_{16}$ serves as the model for this group of bronzes and is the only

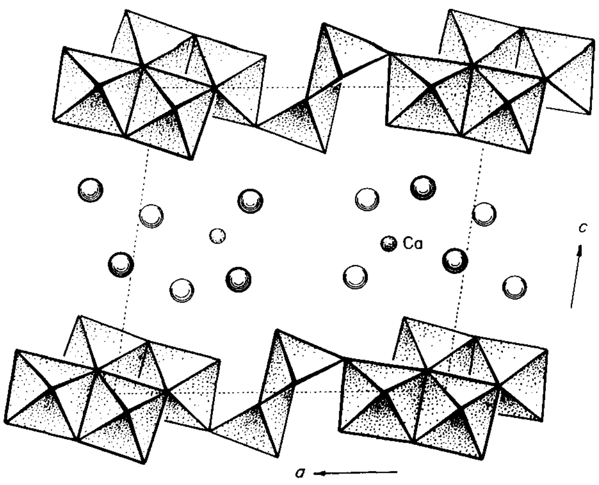

Fig. 8. Structure of hewettite, $CaV_6O_{16}\cdot 9H_2O$ (Evans, 1989).

well-determined structure of this type. Evans (1988) was able to refine Wadsley's structure by least-squares analysis using Wadsley's data, to $R = 0.070$. Evans (1989) also studied the structure of hewettite using unusually good crystals from the Colorado Plateau, although the intensity data were limited in number and of poor quality. He established a layer structure (Fig. 8) entirely consistent with that of $Li_3V_6O_{16}$ and concluded that this layer is quite rigid and maintains its integrity in all structures of the hewettite group. In this matter Evans called into question the structures proposed earlier by Bachmann and Barnes (1962), which contain grossly distorted versions of the layer defined by Wadsley. These structures were based on data of very poor quality taken from oscillation photographs. It is also noteworthy that the unit-cell dimensions they report for the hydrated and dehydrated phases are quite inconsistent with the assumed compositions; both have cell volumes close to that of the three-hydrate (barnesite, Table 3).

Barnesite. Barnesite is the Na end-member of the series $CaV_6O_{16}\cdot 3H_2O$-$Na_2V_6O_{16}\cdot 3H_2O$, first mentioned by Barnes (1955). Qurashi studied the crystallographic properties of the Na mineral from the Cactus Rat mine in Utah and showed that its hydration state is stable with respect to changes in humidity. Bachmann and Barnes (1962) found this to be true also for the mixed Na-Ca crystals that they studied, although they considered those crystals to be a dihydrate (see grantsite, below). The pure Na mineral was described in detail by Weeks et al. (1963) and named after W. H. Barnes, a major contributor to our knowledge of the minerals described in this paper.

Hendersonite. Although vanadium in the hewettite, metahewettite, and barnesite is almost always fully oxidized, or only slightly reduced (Hillebrand et al., 1914), Lindberg et al. (1962) in their description of this new mineral from the J J mine, Paradox Valley, Colorado, reported that the mineral contains an appreciable amount of V^{4+}. On the basis of microanalyses of three samples, they found a composition close to $Ca_2H_{0.1}V_{8.9}O_{24}\cdot 8H_2O$. The dark, greenish black crystals are orthorhombic with unit-cell dimensions (Table 2, transformed) that strongly suggest the presence of a sublattice based on the $Li_3V_6O_{16}$ structure. Ross (1959) found the $a \times b$ net (original $a \times c$ net) to be primitive and the 3.6 Å b axis to be tripled. The X-ray fiber pattern shows a strong similarity to the hewettite-structure type. We therefore place this species in the hewettite group. In Tables 1, 2, and 4 we have written the formula on the basis of 6 V rather than 9 V for consistent comparison with other members of the group. This is the content of the subcell, and the content of the full cell is $Z = 2 \times 3 = 6$ formula units. Our X-ray powder-diffraction data obtained from type material are in close agreement with those reported by Lindberg et al., but the unit-cell parameters given in Table 2 were derived from our data by least-squares analysis.

Grantsite. This mineral, described by Weeks et al. (1964) from several Colorado Plateau localities, also contains a significant amount of V^{4+}. The unit cell (Table 2)

Table 3. Crystallographic data for members of the straczekite group

Phase	a (Å)	b (Å)	c (Å)	β (deg)	V (Å³)	Reference
Straczekite $(Ca,K,Ba)V_8O_{20}\cdot 2.9H_2O$	11.679	3.661	10.636	100.53	447	Evans et al. (1984)
Bokite $(Al,Fe,K)_x(V,Fe)_8O_{20}\cdot 4.75H_2O$	11.85	3.650	11.11	110.6	452	This work (Table 6)
Corvusite (type) $(Na,Ca,K,Fe,Mg)_x(V,Fe)_8O_{20}\cdot 6H_2O$	11.977	3.636	11.263	106.62	470	This work (Table 5)
Fernandinite $Ca_{0.6}V_8O_{20}\cdot 8H_2O$	11.704	3.671	11.021	105.10	457	This work (Table 5)
Bariandite $Al_{0.6}V_8O_{20}\cdot 10H_2O$	11.70	3.63	14.53(×2)	101.5	605(×2)	Cesbron and Vachey (1971)
Synthetic $Ag_{5.44}V_8O_{20}$	11.742	3.667	8.738	90.48	376	Andersson (1965)
Synthetic $(NH_4)_2V_8O_{20}$	11.71	3.666	9.72	101.5	409	Vidonne et al. (1971)
Synthetic $Ag_{2.86}V_8O_{20}$	11.93	3.69	8.81	90.4	397	Drozdov et al. (1973)
Synthetic $Ca_{2.4}V_8O_{20}$	11.805	3.709	9.270	101.87	387	Kutoglu (1983)

TABLE 4. Analytical formulas for hewettite-group and straczekite-group minerals

Mineral	Analytical formula	Ref. (below)
I. Hewettite group		
Hewettite	$(Ca_{1.04}Na_{0.03}Fe_{0.01})_{\Sigma 1.08}(V_{5.99}Fe_{0.01})_{\Sigma 6.00}O_{16}\cdot 9.29H_2O$	1
	$(Ca_{1.00}Na_{0.02}K_{0.01}Mg_{0.01}Fe_{0.01})_{\Sigma 1.05}(V_{5.99}Fe_{0.01})_{\Sigma 6.00}O_{16}\cdot 9.13H_2O$	2
	$(Ca_{1.08}Na_{0.03})_{\Sigma 1.11}(V_{5.96}Fe_{0.02})_{\Sigma 5.98}O_{16}\cdot 9.69H_2O$	3
Barnesite	$Na_{0.98}V_{6.01}O_{16}\cdot 2.85H_2O$	4
Hendersonite	$(Ca,Sr)_{1.20}V_{6.06}O_{16}\cdot 6.06H_2O$	5
	$(Ca_{1.26}Sr_{0.10})_{\Sigma 1.36}V_{6.00}O_{16}\cdot 6.02H_2O$	6
	$(Ca,Sr)_{1.33}V_{6.01}O_{16}\cdot 5.85H_2O$	7
Grantsite	$(Na_{1.91}Ca_{0.38})_{\Sigma 2.29}V_{6.03}O_{16}\cdot 4.59H_2O$	8
	$(Na_{2.05}Ca_{0.27}Sr_{0.04})_{\Sigma 2.35}V_{6.00}O_{16}\cdot 4.02H_2O$	9
	$(Na_{1.90}Ca_{0.46}Sr_{0.01})_{\Sigma 2.37}V_{6.02}O_{16}\cdot 3.94H_2O$	10
II. Straczekite group		
Straczekite	$(Ca_{0.39}Ba_{0.33}K_{0.33}Na_{0.11})_{\Sigma 1.14}(V_{7.90}Fe_{0.10})_{\Sigma 8.00}O_{20}\cdot 2.9H_2O$	11
	$(Ca_{0.58}K_{0.11}Na_{0.06}Fe_{0.04})_{\Sigma 0.79}(V_{7.87}Fe_{0.13})_{\Sigma 8.00}O_{20}\cdot 3.17H_2O$	12
Corvusite	$(Na_{0.40}Ca_{0.32}K_{0.20}Fe_{0.20}Mg_{0.06})_{\Sigma 1.18}(V_{7.56}Fe_{0.44})_{\Sigma 8.00}O_{20}\cdot 5.96H_2O$	13
	$(Ca_{0.30}K_{0.20})_{\Sigma 0.50}V_{8.00}O_{20}\cdot 6.64H_2O$	14
	$(Ca_{0.40}K_{0.24}Fe_{0.24})_{\Sigma 0.88}V_{8.00}O_{20}\cdot 8.74H_2O$	15
Fernandinite	$(Ca_{0.64}K_{0.12}Mg_{0.02})_{\Sigma 0.78}(V_{7.90}Fe_{0.10})_{\Sigma 8.00}O_{20}\cdot 9.50H_2O$	16
Bokite	$(Al_{0.72}Fe_{0.60})_{\Sigma 1.32}(V_{6.80}Fe_{1.20})_{\Sigma 8.00}O_{20}\cdot 7.46H_2O$	17
	$(Al_{0.80}Fe_{0.46}K_{0.26})_{\Sigma 1.32}(V_{6.74}Fe_{1.26})_{\Sigma 8.00}O_{20}\cdot 7.44H_2O$	17
Bariandite	$Al_{0.68}(V_{7.90}Fe_{0.02})_{\Sigma 7.92}O_{20}\cdot 9.14H_2O$	18

Note: UO_3, MoO_3, SiO_2, insoluble residue, where reported, are omitted from these formulations. Fe_2O_3 is apportioned arbitrarily between layer and interlayer components to give best the (V,Fe)/O ratio. O is set equal to 16 or 20. References (samples prefixed AW are from the Alice D. Weeks collection, now residing at the Smithsonian Institution): 1. Hillebrand et al. (1914). Minasragra, Peru. 2. Hillebrand et al. (1914). Near Thompson, Grand County, Utah. Assigned the name "metahewettite." 3. Ankinovich and Ankinovich (1967). Kurumsak area, Kazakhstan, U.S.S.R. 4. Weeks et al. (1963). Thompson, Grand County, Utah. Sample no. AW-202-54. 5. Lindberg et al. (1962). Eastside Carrizo mine, San Juan County, New Mexico. Sample no. AW-15-55. 6. Lindberg et al. (1962). J J mine, Montrose County, Colorado. Sample no. GJM-70-1. 7. Lindberg et al. (1962). J J mine, Montrose County, Colorado. Sample no. GJM-70. 8. Weeks et al. (1964). Golden Cycle mine, Montrose County, Colorado. Sample no. AW-141-56. 9. Weeks et al. (1964). LaSalle mine, Montrose County, Colorado. Sample no. AW-47-57. 10. Weeks et al. (1964). F-33 mine, Valencia County, New Mexico. Sample no. AW-20-57. 11. Evans et al. (1984). Union Carbide vanadium mine, Wilson Springs, Garland County, Arkansas. 12. This work. J. Marinenko, analyst. Monument No. 2 mine, Apache County, Arizona; Harvard Mineralogical Museum specimen no. 105103. 13. Henderson and Hess (1933). Jack claim (Utah), near Gateway, Montrose County, Colorado. Purplish black sample, USNM 96806. 14. Henderson and Hess (1933). Ponto No. 3 claim, San Miguel County, Colorado. Lustrous black sample; Mg, K, Na not determined. 15. Ross (1959). Corvusite-like sample from Monument No. 2 mine, Arizona. 16. Schaller (1915). Analysis by Schaller reported by Ford (1915). Minasragra, Peru. 17. Ankinovich (1963). Kurumsak area, Kazakhstan, U.S.S.R. 18. Cesbron and Vachey (1971). Mounana, Gabon.

is closely in line with those of other members of the hewettite group, but with a doubled interlayer *c* value (*a* axis of Weeks et al., 1964). The space group is $A2/a$ in our setting, but the subcell symmetry is $P2_1/m$. The composition was reported as $Na_4Ca_xV_{12}O_{32}\cdot 8H_2O$ with $x = 0.6$–0.9, but again we list the subcell unit in Tables 1, 2, and 4. Here also our powder-diffraction data are in close agreement with those of Weeks et al. (1964); from the latter we have derived by least-squares analysis the unit-cell parameters given in Table 2. Among the low-hydrate phases, the crystallography of grantsite is most similar to that of barnesite and the sodium-calcium hewettite of Bachmann and Barnes (1962) but is clearly distinct from Qurashi's dehydrated hewettite and from hendersonite. Weeks et al. (1964) used an X-ray fiber pattern to confirm the relationship of grantsite to the hewettite group and emphasized the contrast between these minerals and the corvusite-type minerals. The range of composition of grantsite, as found from three localities, illustrates well the variable nonstoichiometry of this V bronze with changes in average valence of V.

Straczekite group

Evans et al. (1984) have described another fibrous V-oxide mineral, which they named "straczekite." They were unable to fit the chemistry and crystallographic properties of this mineral to a hewettite formulation, but, mainly through single-crystal electron-diffraction techniques, discovered that the structure is analogous instead to the δ-$Ag_xV_2O_5$ structure of Andersson (1965). In the electron-diffraction study of Ross (1959) described above, two types of electron-diffraction patterns were found to be common for the fibrous vanadates: one based on a primitive monoclinic cell and one on a *C*-centered cell. Although Evans et al. did not realize it at the time, several other V-oxide mineral species upon X-ray examination could immediately be associated with the *C*-centered cell, which represents the δ-$Ag_xV_2O_5$-type layer. As mentioned earlier, the unit-cell volume gives an indication of the degree of interlayer hydration, assuming that one V_8O_{20} unit occupies 360 Å³ of space. As with the hewettite-group minerals, much of the H_2O is zeolitic and can be liberated at 105 °C, or at room temperature in vacuum, or by dessication.

The V-oxide bronze minerals that possess the V_8O_{20} layer structure are termed the straczekite-group minerals, after the mineral among them that is best described. These minerals and several synthetic compounds, which have *C*-centering and $a = 11.7$ Å, $b = 3.65$ Å in common, are listed in Table 3.

Straczekite. This mineral was found at the Union Carbide mine at Wilson Springs, Arkansas, as lustrous, greenish black, lathlike crystals. As mentioned above, it was found to belong to the δ-$Ag_xV_2O_5$ structure type, with

TABLE 5. X-ray powder-diffraction data for corvusite and fernandite

		Corvusite, Utah				Fernandinite, Peru			
		Fiber*		Powder**			Powder†		
hkl	d_{cal} (Å)‡	d_{obs} (Å)	I_{rel}	d_{obs} (Å)	I_{rel}	d_{cal} (Å)§	d_{obs} (Å)	I_{rel}	*hkl*
001	10.79	10.81	100	10.82	100	10.64	10.68	100	001
200	5.74	5.73	1	5.75	1	5.65	5.65	3	200
003	3.598	3.594	5	3.590	6	3.547	3.545	4	003
110	3.466			3.464	18	3.491	3.483	26	110
111	3.220			3.255	2	3.241	3.241	3	111
$\bar{1}12$	3.038					3.033	3.032	2	$\bar{1}12$
$\bar{4}01$	2.994					2.926	2.925	3	$\bar{4}01$
$\bar{4}02$	2.900	2.894	4	2.900	2	2.818			$\bar{4}02$
400	2.869					2.825	2.826	7	400
004	2.698	2.699	2	2.698	2	2.660	2.668	3	004
401	2.595			2.595	3	2.569			401
$\bar{3}12$	2.577					2.548	2.549	4	$\bar{3}12$
311	2.451					2.450	2.459	1	311
005	2.159	2.157	4	2.160	2	2.128	2.136	4	005
313	1.951					1.949	1.949	6	313
$\bar{6}03$	1.934	1.937	5	1.934	4	1.878			$\bar{6}03$
020	1.818			1.819	6	1.835	1.836	8	020
021	1.793			1.798	1	1.809	1.813	2	021
				1.512	2		1.629	4	

* Jack claim, La Sal Mountains, Utah; USNM No. 96806. Cr*Kα* radiation.

** USNM No. 98608; Debye-Scherrer method, Cr*Kα* radiation.

† Minasragra, Peru; USNM No. 87661. Debye-Scherrer method, Cr*Kα* radiation.

‡ Calculated from data for USNM No. 98608, with refined unit-cell parameters $a = 11.977(6)$ Å, $b = 3.636(2)$ Å, $c = 11.263(7)$ Å, $\beta = 106.62(7)°$, $\sigma(2\theta) = 0.048°$.

§ Calculated from data for USNM No. 87661, with refined unit-cell parameters $a = 11.704(6)$ Å, $b = 3.671(1)$ Å, $c = 11.021(11)$ Å, $\beta = 105.10(7)°$, $\sigma(2\theta) = 0.039°$.

Ca, K, Ba, and H_2O in the interlayer region (Evans et al., 1984).

A Ca-rich speciman of straczekite from the Monument No. 2 mine (Apache County, Arizona; Harvard Mineralogical Museum specimen no. 105103, originally labeled "corvusite and navajoite") was found to have the composition shown in Table 4. Gandolfi photographs of this phase in air and in vacuo showed that under vacuum the unit cell contracted about 30 Å^3, corresponding to a loss of about 1.5 H_2O. The refined *a* and *b* parameters do not change by more than 0.02 Å on dehydration, but *c* contracts by 0.68 Å under vacuum. Concomitantly, *hk*0 reflections are unaffected by dehydration, in contrast to the reduction in *d* values for *hkl* reflections under vacuum.

Corvusite. Corvusite, first described by Henderson and Hess (1933), is one of the more common Colorado Plateau V minerals, yet its chemistry and structure have resisted rational interpretation up to this time. The problem with many of the naturally occurring V bronzes was well summarized by the original authors, who noted that despite its relative abundance in the Colorado Plateau region, corvusite specimens suitable for analysis are rare. The tentative formula $V_2O_4 \cdot 6V_2O_5 \cdot nH_2O$ was proposed and has persisted to the present (Fleischer, 1987) despite the fact that greater than 5 wt% of other cation oxides were not explained by the formula. Table 4 shows the original chemical analyses of Henderson and Hess recast with $(V + Fe) = 8$ and shows Na to be the dominant interlayer cation in type corvusite (Utah).

The work of Ross (1959) included electron-diffraction studies of both type corvusite (Peru, Utah) and corvusite-like material from Monument No. 2 mine, Apache County, Arizona. His studies confirm the *C* centering and *a* and *c* lattice parameters typical of the straczekite group minerals. Our fiber patterns of type material (purplish black fibrous sample from Utah, 10 miles east of Gateway, Colorado; USNM No. 96806) clearly show the close relationship of corvusite to the straczekite-type bronzes. The four analyses represented in Table 4 show well how much the cation content can vary among corvusite-like minerals. As a result, this qualified term has frequently been used for material that is lustrous, blue-black or purplish black, and fibrous in texture. Very thin fragments transmit dark, olive-green light and are birefringent. The one chemical constant that seems to prevail, as Henderson and Hess (1933) noted, is the V^{4+}/V^{5+} ratio, which is always close to 1/6. By comparing the indexed powder data for straczekite, we have been able to index the Debye-Scherrer pattern we obtained for the lustrous, blue-black corvusite from Utah (USNM No. 96809) and determine its unit-cell parameters by least-squares analysis (Table 3). In Table 5 are listed our powder-diffraction data for type corvusite. The only other powder-diffraction data reported for corvusite are those of Ankinovich (1963), but her data do not correspond to ours for type material, and the true nature of her sample from Kazakhstan is unknown. The formula unit with 6 H_2O (Table 4) and unit-cell volume 470 Å^3 gives a density of 3.27 g/cm^3, somewhat higher than that measured by Henderson and Hess (1933), but this difference may result from changes in zeolitic water content. The lustrous black masses of the Utah specimen show deep shrinkage cracks, apparently because of loss of water.

Henderson and Hess also applied the name "corvusite" to a dull brown, fine-grained mineral from Gypsum Valley, San Miguel County, Colorado (USNM No. 96807), which had a similar vanadium oxide composition. Ross (1959), in his examination of this material, found small flakes that gave the typical *C*-centered electron-diffraction pattern of corvusite, but the X-ray pattern we obtain contains many lines in addition to those of corvusite. The strongest additional lines are 4.51, 3.35, and 2.60 Å. These, together with a very strong line at 10.7 Å, are characteristic of a vanadium mica, analogous to roscoelite. Both Henderson and Schaller (Henderson and Hess, 1933) found that the dull material contained 24.8 wt% of insolubles and soluble silica, while the lustrous, fibrous material contains only 1.4 wt%. Evidently, the massive, dull brown corvusite is a mixture of the blue-black phase (which we presume to be true corvusite) and a roscoelite-type vanadium mica.

Fernandinite. This mineral was first described by Schaller (1915), and studied by electron diffraction by Ross (1959). The latter study demonstrated extinctions consistent with *C*-centering and $a = 11.69$ Å, $b = 3.674$ Å. Chemical analyses reported in that study show that the dominant interlayer cation in fernandinite is Ca (Table 4). The mineral is fine-grained, greenish black, and soft; bruised surfaces appear almost metallic. Like corvusite, very thin flakes are dark olive-green in transmitted light and birefringent. The fibrous habit is lacking, but the electron-diffraction (Ross, 1959) and X-ray–diffraction patterns and chemical composition are corvusite-like, and the distinction of this species from corvusite has been in doubt.

The X-ray powder-diffraction pattern of type fernandinite from Minasragra, Peru (USNM No. 87661), closely resembles that of corvusite, but is somewhat sharper. We have indexed the powder-diffraction pattern on a unit cell analogous to that of corvusite, and refined the cell parameters by least-squares analysis, as shown in Table 3. The composition reported by Schaller (Ford, 1915) contains 18.07 wt% H_2O. This amount requires 9.5 H_2O in the unit cell, whereas the cell we found has room for only 4 H_2O. We heated 83 mg of the type material in air at 160 °C overnight and found 7.6% loss in weight, corresponding to 4.5 H_2O. Evidently in this case as in others, the original, fresh material contained more water than it does today. The powder-diffraction data for fernandinite are given in Table 5 and compared with those of corvusite. Compositions reported for corvusite-like material generally show varying amounts of Na, Ca, K, Ba, Fe, etc., which is typical of natural bronzes. We suggest that the name "corvusite" be associated with the Na-rich phases and the name "fernandinite" with the Ca-rich phases.

Bokite. Ankinovich (1963) described two V-oxide minerals from Kurumsak area, Kazakhstan, one of which she called corvusite-like, and a new mineral which she named "bokite," after the Kazakhstan geologist I. I. Bokii. Bokite is distinguished in containing considerable amounts of Al and Fe. Ankinovich showed that the X-ray powder-diffraction patterns of the corvusite-like mineral and bokite are distinctly different. Nevertheless, the fiber pattern of bokite (Table 6) bears a striking similarity to the straczekite-type pattern, and we therefore place the mineral in the straczekite group. In writing a formula we have divided Fe between the vanadate layer and interlayer components. Because of its lower average V valence of 4.77 and its distinct chemical composition, the mineral clearly represents a separate and valid species.

By analogy with the straczekite crystallographic properties, we have indexed the powder-diffraction data obtained for type bokite (USNM No. 139767), which agree well with those of Ankinovich (1963) (Table 6). The unit-cell parameters refined from these data by least-squares analysis are given in Table 3. On the basis of X-ray powder-diffraction patterns we have identified bokite in specimens from Arizona and Arkansas. All give sharp patterns in contrast to the generally diffuse patterns produced by corvusite. Excellent fiber patterns have facilitated the indexing of these patterns and measurement of the corresponding unit cells.

The bokite from Arkansas was found by Charles Milton at the Union Carbide V mine at Wilson Springs. The material from Arizona came from the Monument No. 2 mine and was found on a specimen labeled "navajoite" (USNM No. 138478). The various patterns show no appreciable variation, indicating that bokite is a discrete, well-crystallized phase.

The chemical analysis reported by Ankinovich (1963) shows 14.3 wt% H_2O. As in the case of fernandinite, this amount of water cannot be contained in the determined unit cell. We feel that the original analysis for water is somehow exaggerated, as the powder-diffraction data are of good quality for all localities and do not suggest the occurrence of dehydration from a more highly hydrated phase.

Bariandite. Cesbron and Vachey (1971) described this mineral from Mounana, Gabon, as $V_{10}O_{24}\cdot nH_2O$. Like all members of the straczekite group, the mineral has a *C*-centered lattice and $a = 11.7$ Å, $b = 3.65$ Å. The *c*-axis is significantly larger (29.06 Å) than that of other straczekite group minerals, suggesting that there is an ordering of interlayer constituents that encompasses two V_8O_{20} layers. The formula given in Table 4 is based on this proposal and volume considerations. As shown in Table 4, Al and H_2O are the dominant interlayer constituents in bariandite. The density calculated for the determined unit cell with the new formula is 2.50 g/cm³. The authors report "environ" 2.7 g/cm³, but their formula is wholly inconsistent with this value.

Other V bronze minerals

Navajoite. Navajoite was originally described by Weeks et al. (1955) from its occurrence at Monument No. 2 mine, Apache County, Arizona. An X-ray powder diffractogram was tentatively indexed on a monoclinic unit cell, with $a = 17.43$ Å, $b = 3.65$ Å, $c = 12.25$ Å, and $\beta = 97°$, although the authors noted that larger crystals were needed to confirm the crystallographic data. Subsequent-

TABLE 6. X-ray powder-diffraction data for bokite

		Arizona		Kazakhstan				
		Fiber*		Powder**		Powder†		
hkl	d_{cal} (Å)‡	d_{obs} (Å)	I_{rel}	d_{obs} (Å)	I_{rel}	d_{obs} (Å)	I_{rel}	*hkl*
001	10.43	10.44	100	10.47	100	10.10	100	001
200	5.541	5.53	8	5.52	4	5.80	1	200
$\bar{2}02$	4.714	4.74	3	4.73	2			$\bar{2}02$
201	4.306	4.29	4	4.30	2			201
$\bar{2}03$	3.562	3.56	3	3.57	2			$\bar{2}03$
003	3.477	3.49	14					003
110	3.460			3.452	30	3.44	9	110
$\bar{1}11$	3.398			3.396	3			$\bar{1}11$
						3.22	2	
111	3.182			3.177	9			111
$\bar{1}12$	3.041			3.040	3	3.06	1	$\bar{1}12$
$\bar{4}02$	2.907	2.919	8	2.907	12	2.92	3	$\bar{4}02$
$\bar{2}04$	2.763	2.761	10	2.760	9	2.76	4	$\bar{2}04$
$\bar{4}03$	2.677	2.688	3	2.680	4			$\bar{4}03$
004	2.608	2.609	8					004
310	2.591							310
$\bar{3}12$	2.589			2.592	12	2.61	8	$\bar{3}12$
401	2.467					2.48	10	401
204	2.093							204
005	2.081	2.088	5	2.093	4	2.08	7	005
$\bar{6}02$	1.9730	1.974	7	1.9731	7	1.976	6	$\bar{6}02$
$\bar{6}01$	1.9396	1.944	4	1.9395	4	1.938	1	$\bar{6}01$
$\bar{1}15$	1.8803			1.8866	1			$\bar{1}15$
020	1.8212			1.8208	11	1.826	5	020
021	1.7941			1.7948	2	1.799	2	021
$\bar{6}05$	1.7140			1.7136	1			$\bar{6}05$
314	1.6470			1.6457	1			314
023	1.6134			1.6127	2			023
$\bar{6}06$	1.5713			1.5722	2			$\bar{6}06$
$\bar{4}22$	1.5433			1.5429	1			$\bar{4}22$
$\bar{5}16$	1.5298			1.5302	5	1.529	2	$\bar{5}16$
024	1.4932			1.4958	1			024
421	1.4661			1.4633	1	1.467	1	421
$\bar{7}15$	1.4258			1.4270	1			$\bar{7}15$
224	1.3740			1.3745	2			224
$\bar{6}21$	1.3377			1.3377	4	1.3392	1	$\bar{6}21$
$\bar{6}22$	1.3383			1.3389	1			$\bar{6}22$

* Monument No. 2 mine, Arizona; USNM No. 138478. Cr$K\alpha$ radiaton.

** Kurumsak area, Kazakhstan, U.S.S.R. (type); USNM No. 139767. Debye-Scherrer method, Cr$K\alpha$ radiation.

† Data of Ankinovich (1963). Debye-Scherrer method, Cr$K\alpha$ radiation.

‡ Calculated from data of Note 2, with refined unit-cell parameters: $a = 11.838(5)$ Å, $b = 3.643(1)$ Å, $c = 11.142(5)$ Å, $\beta = 110.58(4)°$, $\sigma(2\theta) = 0.075°$.

ly, Ross (1959) studied some navajoite-like material from the type locality, also collected by A. D. Weeks. Electron-diffraction experiments gave unit-cell parameters a = 11.86 Å, b = 3.644 Å and showed extinctions characteristic of C centering, data which are consistent with a corvusite-like phase. Ross also found some grains that showed a completely different, centered rectangular lattice with dimensions a = 35 Å and b = 3.6 Å. These parameters are consistent with those reported by Weeks et al. (1955) if their value of a is doubled. Evidently, Ross examined a sample that contained both corvusite and navajoite. We have found that some specimens labeled "navajoite" are actually bokite or mixtures of bokite and corvusite. One specimen from Monument No. 2 mine, Arizona (USNM No. 106900, type?), gave a powder-diffraction pattern that corresponds closely with the powder-diffraction data reported by Weeks et al. (1955), which are completely different from those of bokite or corvusite. Our data are given in Table 7, together with the original data of Weeks et al. and the unit-cell parameters refined from our new data by least-squares analysis using the C-centered cell of Ross (1959). The lines at 10.54 and 3.45 Å are probably because of bokite. There is no apparent analogy in the fiber patterns with data either for the hewettite or the straczekite groups, and the structural principle of navajoite is unknown.

The best formula fitted to Sherwood's analysis (Weeks et al., 1955) and 36 O atoms (to occupy 731 Å^3 unit-cell volume) is $Ca_{0.05}(V_{9.48}Fe_{0.52})_{\Sigma 10}O_{24}\cdot 12H_2O$. This unit-cell content gives rise to a density of 2.53 g/cm^3, in good agreement with that measured by Weeks et al., 2.56 g/cm^3.

Fervanite and schubnelite. Schubnelite was described by Cesbron (1970) from Mounana, Gabon, as $Fe_2V_2O_8\cdot 4H_2O$. The triclinic crystals form long, black prisms. Chemical analysis shows a ratio of V^{5+}/V^{4+} = 1.7, inconsistent with the formula, assuming all iron to be Fe^{3+}; however, the analyses show some deficiency in the latter from stoichiometry. The water is driven off only above 200 °C, so the formula would be better written as $Fe_2V_2O_4(OH)_4$. Although the mineral shows characteris-

Table 7. X-ray powder-diffraction data for navajoite from Arizona

		Fiber*		Powder**		Powder†		
hkl	d_{cal} (Å)‡	d_{obs} (Å)	I_{rel}	d_{obs} (Å)	I_{rel}	d_{obs} (Å)	*I*	*hkl*
200	17.33	17.38	20	17.38	7			200
001	11.71	11.69	100	11.79	100	12.11	VS	001
		10.44	50	10.54	3	10.61	M	
201	9.239	9.29	9	9.22	1	9.41	F	201
400	8.665	8.72	6	8.59	1	8.67	F	400
$\bar{4}01$	7.367	7.34	6	7.33	2	7.44	F	$\bar{4}01$
401	6.623	6.62	1					401
600	5.777	5.78	15	5.79	6	5.79	Wb	600
800	4.333	4.34	4			4.35	W	800
801	3.924	3.93	7			3.95	F	801
210	3.522			3.53	1			210
10,0,0	3.466	3.45				3.47	W	10,0,0
$\bar{6}03$	3.412	3.41	5	3.41	20			$\bar{6}03$
802	3.312	3.34	5					802
510	3.193			3.18	8			510
$\bar{8}03$	3.075	3.06	7			3.10	Wb	$\bar{8}03$
710	2.910			2.90	3	2.90	M	710
12,0,0	2.888	2.89	10	2.88	3			12,0,0
803	2.752	2.77	3			2.79	F	803
404	2.684	2.69	1			2.68	F	404
910	2.629			2.63	1			910
213	2.586			2.59	2			213
$\overline{14},0,1$	2.479	2.48	6	2.48	1	2.49	W	14,0,1
$\overline{14},0,2$	2.377	2.375	1	2.377	2	2.39	VF	$\overline{14},0,2$
						2.18	F	
$\overline{16},0,2$	2.109	2.109	7	2.102	2	2.12	M	$\overline{16},0,2$
$\overline{16},0,3$	1.990	1.989	5	1.992	4	1.99	W	$\overline{16},0,3$
16,0,3	1.820	1.818	2					16,0,3
020	1.799			1.799	3	1.80	F	020
606	1.790	1.798	3					606
021	1.778			1.777	1			021

* Monument No. 2 mine, Arizona (type?); USNM No. 106900. Cr$K\alpha$ radiation.

** USNM No. 106900. Debye-Scherrer method, Cr$K\alpha$ radiation.

† Monument No. 2 mine, Arizona, data of Weeks et al. (1955). Cu$K\alpha$ radiation.

‡ Calculated from data of Note 2, with refined unit-cell parameters for $C2/m$: a = 34.94(2) Å, b = 3.597(2) Å, c = 11.79(1) Å, β = 95.98(6)°, $\sigma(2\theta)$ = 0.077°.

tics of an oxide bronze, a structure analysis will be needed to define its true nature.

The same can be said for fervanite, first described by Hess and Henderson (1931) from the Colorado Plateau as $Fe_4V_4O_{12} \cdot 5H_2O$. The mineral occurs in seams as lustrous golden yellow fibers in mineralized sandstone. It is clearly based on an unknown type of chain structure containing fully oxidized cations. Our powder-diffraction data for this mineral agree with those reported for fervanite associated with schubnelite from Mounana by Cesbron (1970).

Melanovanadite. Although this mineral was described nearly 70 years ago by Lindgren et al. (1922), its crystal-chemical nature remained obscure until the crystal-structure study of Konnert and Evans (1987) was reported. Lindgren et al. proposed the formula $Ca_2V_{10}O_{25}$ (based on analyses of evidently impure material), but the structure analysis established a vanadate layer structure with composition $CaV_4O_{10} \cdot 5H_2O$. The water is highly labile and can be easily removed or replaced. The layer is not based on cross-linked vanadate chains as in the fibrous vanadium bronzes, but rather on a network of VO_4 tetrahedra and V_2O_8 double square pyramids. The crystals are lustrous black prisms, and the average V valence is 4.5. Thus, the mineral corresponds to a typical V bronze. Details of the crystal chemistry of melanovanadite are fully described by Konnert and Evans (1987).

Shcherbinaite and bannermanite. These two V-oxide minerals were found by R. E. Stoiber in volcanic fumeroles at Izalco volcano, El Salvador. Shcherbinaite was found to consist of pure V_2O_5 crystals forming golden yellow, orthorhombic laths (Hughes and Finger, 1983b). No additional cations were found in sensitive tests. The mineral corresponds to the phase α-$Na_xV_2O_5$ as described by Hagenmuller (1973), which has the structure illustrated in Figure 7. The mineral was also found at the Bezymyenny volcano, Kamchatka (Borisenko et al., 1970).

Bannermanite also has a composition $Na_xV_2O_5$, but with x varying from 0.54 to 0.70; a small amount of K is also present (Hughes and Finger, 1983a). The mineral corresponds to the phase β-$Na_xV_2O_5$ (Hagenmuller, 1973), with the structure shown in Figure 6. These minerals are typical fibrous V bronzes.

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