

## THE CRYSTAL STRUCTURE AND CRYSTAL CHEMISTRY OF FERNANDINITE AND CORVUSITE

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### ABSTRACT

Using type material of fernandinite  $(\text{Ca}, \text{Na}, \text{K})_x \text{V}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$  from Minasragra, Peru, and corvusite  $(\text{Na}, \text{Ca}, \text{K})_x \text{V}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$  from the Jack Claim, La Sal Mountains, Utah, the properties and crystal chemistry of these minerals have been determined by Rietveld analysis of the powder X-ray-diffraction patterns. The associated unit-cell parameters in space group  $C2/m$  (monoclinic) for fernandinite [corvusite] are:  $a$  11.680(2) [11.706(4)] Å,  $b$  3.6537(4) [3.644(1)] Å,  $c$  11.023(2) [11.10(1)] Å,  $\beta$  105.00(2) [103.46(7)]°. The crystal structure of both species is isotypic with the  $\text{V}_2\text{O}_5$ -type layer first found for  $\delta\text{-Ag}_{0.68}\text{V}_2\text{O}_5$ ; it consists of chains of  $\text{VO}_6$  octahedra linked by opposite corners (parallel to  $b$ ) condensed by edge-sharing to form the layer. The vanadium has average valence 4.8, and the resulting layer-charge is balanced by varying amounts of Ca, Na, and K in the interlayer region ( $x$  in the above formulas varies from 0.9 to 1.2), accompanied by labile water (amount depending on humidity and heat). This study has confirmed the validity of fernandinite as a unique mineral species. It is closely related to corvusite, from which it is distinguished on the basis of the dominant interlayer cation: Ca for fernandinite, Na for corvusite.

**Keywords:** corvusite, fernandinite, Rietveld analysis, straczekite-type structure, vanadium bronze.

### SOMMAIRE

Nous avons réussi à déterminer les propriétés et la chimie cristalline des espèces fernandinite et corvusite par analyse de Rietveld des données de diffraction X (méthode des poudres); ces analyses ont porté sur des échantillons-type de fernandinite,  $(\text{Ca}, \text{Na}, \text{K})_x \text{V}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$ , de Minasragra, au Pérou, et de corvusite,  $(\text{Na}, \text{Ca}, \text{K})_x \text{V}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$ , de Jack Claim, dans les montagnes La Sal, dans le Utah. Les paramètres réticulaires, affinés dans le groupe spatial  $C2/m$  (monoclinique) sont, pour la fernandinite [corvusite]:  $a$  11.680(2) [11.706(4)],  $b$  3.6537(4) [3.644(1)],  $c$  11.023(2) [11.10(1)] Å,  $\beta$  105.00(2) [103.46(7)]°. La structure des deux espèces est isotypique avec une couche de type  $\text{V}_2\text{O}_5$ , décrite pour la première fois dans le composé  $\delta\text{-Ag}_{0.68}\text{V}_2\text{O}_5$ ; cette couche est faite de chaînes d'octaèdres  $\text{VO}_6$  agencés par coins opposés, parallèlement à  $b$ , et accolés par partage d'arêtes pour former le feutillet. Le vanadium possède une valence moyenne de 4.8; la charge moyenne sur le feutillet est compensée par une quantité variable de Ca, Na et K entre les feuillets ( $x$  dans la formule ci-haut varie entre 0.9 et 1.2), ces atomes étant accompagnés d'eau labile (dont la proportion dépendrait de l'humidité et de la chaleur). Notre étude confirme la validité de la fernandinite comme espèce minérale unique. Elle est étroitement apparentée à la corvusite; c'est le cation dominant entre les feuillets qui les distingue, Ca dans le cas de la fernandinite, Na dans le cas de la corvusite.

(Traduit par la Rédaction)

**Mots-clés:** corvusite, fernandinite, analyse de Rietveld, structure de type straczekite, bronze vanadifère.

### INTRODUCTION

Fernandinite and corvusite belong to a family of vanadium oxide minerals referred to (Evans & White 1987) and described (Evans & Hughes 1990) as natural vanadium bronzes. According to these authors, these minerals have the characteristics of the transition metal oxide phases, known to solid state chemists as bronzes. Such compounds typically are colored, have

a submetallic luster, are semiconductors, and usually contain the metal atoms in the oxide framework in mixed valences. The oxide framework may consist of a planar or three-dimensional lattice with open passages into which cations are inserted (to balance the framework charge), as well as water molecules. Evans & Hughes (1990) recognized five different types of framework among sixteen species of vanadium bronze minerals. The two most common are the hewettite

group (including barnesite, grantsite, and hender-  
sonite) and the straczekite group (bokite, corvusite,  
and fernandinite), as determined mainly from char-  
acteristic powder-diffraction patterns (Debye-Scherrer  
and fiber patterns). The straczekite type is based on a  
particular layer-structure that will be described below.

The status of the species fernandinite (Schaller  
1915) has long been questionable, and recently chal-  
lenged (Bayliss & Freeman 1989). Herewith we report  
our study of fernandinite based on type material, using  
the Rietveld method to determine and refine its crystal  
structure. Thus, fernandinite is reaffirmed as a valid  
mineral species. Also, we describe our study of the  
closely related species corvusite using type material,  
and reveal its crystal structure. In this way, we hope to  
clarify the crystal chemistry of these poorly under-  
stood minerals.

#### HISTORY

##### *Fernandinite*

In 1906, D. Foster Hewett returned from a field  
expedition to Minasragra, Cerro de Pasco, Peru, with a  
suite of vanadium minerals. Among these were two  
lots of massive vanadium oxides which, in his report  
(Hewett 1909), he referred to as "red oxide" and  
"green oxide". The red oxide was studied by  
Hillebrand *et al.* (1914), who found it to be a calcium  
vanadium oxide hydrate,  $\text{CaV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$ , and gave it  
the name hewettite. Its crystal structure has recently  
been determined by Evans (1989). The green oxide,  
later named fernandinite by Schaller (1915), has never  
been properly described.

All of Hewett's type material is deposited in the  
collections of the National Museum of Natural History  
(NMNH, Smithsonian Institution), divided into three  
parts: (1) NMNH No. 87661 (Type Collection), 150 g  
of soft, massive but crystalline, dark green material,  
deposited by D.F. Hewett; (2) NMNH No. 96702  
(General Collection), 180 g of similar material,  
deposited by W.F. Hillebrand, and (3) NMNH  
No. R-5706 (Type Collection), 5 g of similar material,  
part of the original Roebling Collection. Hillebrand  
carried out chemical analyses for Hewett, thus  
accounting for specimen (2). The Roebling speci-  
men (3) is accompanied by a notation "analyzed by  
W. Schaller", and probably came from Schaller.

Published references to fernandinite are scarce. In  
1915, Waldemar Schaller (U.S. Geological Survey)  
published a brief note (Schaller 1915) in which he laid  
claim to four new minerals, including fernandinite  
from Minasragra, Peru. He offered a chemical formula  
for the latter,  $\text{CaO} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$ , based on  
results of his chemical analysis, but he gave no analyt-  
ical or other data. According to Ford (1915), Schaller  
took the name from Eulagio E. Fernandini, a former  
owner of the ore deposit from which the sample origi-

nated. W.E. Ford, in his Third Appendix to Dana's  
System of Mineralogy, 6th Edition (Ford 1915),  
recorded Schaller's analytical data and a few other  
properties. Palache *et al.* (1951), in the Seventh  
Edition of Dana's System, repeated this information in  
more detail (though Schaller's analytical data were  
abbreviated), but gave little essentially new data.  
Malcolm Ross (U.S. Geological Survey), in a seminal  
paper on the vanadium bronzes (Ross 1959), reported  
his findings on fernandinite using electron diffraction.  
In his examination of the type material (NMNH No.  
R-5706), he determined that fernandinite is based on a  
*C*-centered lattice, and he measured the *a* and *b* repeat  
distances.

Finally, Bayliss & Freeman (1989), reporting their  
examination of a portion of Smithsonian specimen  
NMNH No. R-5706 (see above) but without giving  
any specific supporting data, proposed that fernan-  
dinite is a mixture of bariandite, roscoelite, and  
gypsum.

##### *Corvusite*

Corvusite was first recognized and described as  
a new mineral by Henderson & Hess (1933). The type  
material was collected by R.G. Hart at "the Jack  
Claim... on the east side of La Sal Mountains, Grand  
County, Utah, and about 10 miles west of Gateway,  
Colo..." It was found in Morrison sandstone beside  
a petrified log. The mineral is massive and has a  
purplish black luster, hence the name (*L. corvus*,  
raven). F.L. Hess obtained the specimen, which is now  
preserved in the National Museum of Natural History  
(NMNH No. 96806).

Henderson & Hess (1933) also studied another  
specimen obtained at the Ponto No. 3 claim on the  
north wall of Gypsum Valley, San Miguel County,  
Colorado, 65 km south of the Jack Claim. This mate-  
rial is dark brown with a dull appearance. Our X-ray  
tests of the brown corvusite (NMNH No. 96807) show  
that it contains a considerable amount of admixed  
roscoelite, which probably accounts for most of the  
21.52% insoluble remainder reported in Henderson's  
analysis. We have not studied this material further.

Many references to corvusite or "corvusite-like"  
minerals appear in the literature, but usually only  
tentatively identified because of the incomplete  
chemical characterization (by modern standards) in the  
type description. Although the chemical data reported  
by Henderson & Hess (1933) list small amounts of  
Fe, Ca, K, and Na, the authors excluded these  
elements from their tentatively proposed formula:  
 $\text{V}_2\text{O}_4 \cdot 6\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ . Such "corvusite-like" material is  
commonly found in weathered zones rich in van-  
adium, such as on the Colorado Plateau.

In our work reported here, we find fernandinite to  
be a valid mineral species as proposed by Schaller and  
confirmed by Evans & Hughes (1990). Also, we have

studied type corvusite, and found that it has properties and crystal structure closely related to those of fernandinite, but it differs in the proportions of the interlayer cations.

#### PHYSICAL AND CHEMICAL PROPERTIES OF FERNANDINITE AND CORVUSITE

##### *Fernandinite*

The three type specimens of fernandinite (see History above) are indistinguishable in appearance and properties, and presumably all came from Hewett's

original lot. The mineral consists of a soft, dark green mass. It can readily be separated (with care) into pieces revealing flaky, crystalline surfaces (Fig. 1A). Any pressure with an instrument immediately distorts this texture and leaves smooth surfaces that have a submetallic luster. The mass is evidently quite porous, as immersion in toluene produces an extensive evolution of air bubbles. The porous and flaky nature of broken surfaces is apparent in the scanning electron microscope image shown in Figure 1A. Occasional microscopic red fibers may be encountered, which are undoubtedly hewettite. Quartz grains are also commonly present, as shown by the appearance of sharp,

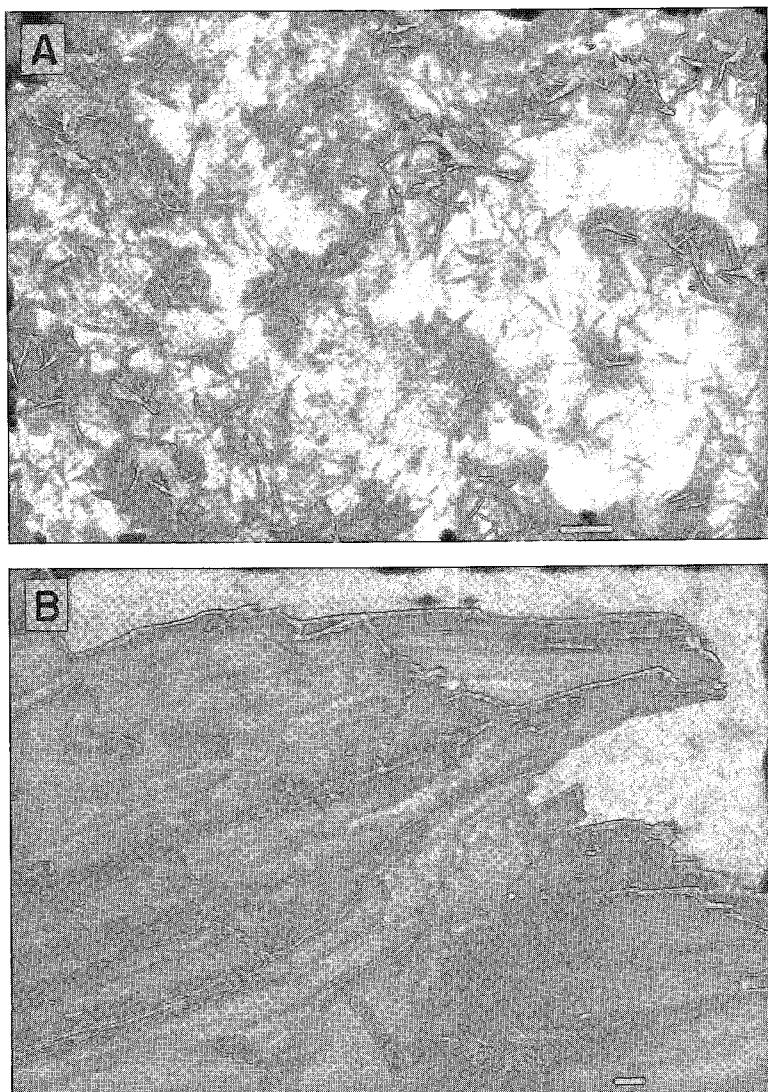


FIG. 1. Scanning electron image of (A) fernandinite, and (B) corvusite. White bar at lower right in each photograph represents 10  $\mu\text{m}$ .

characteristic lines in the X-ray powder pattern.

Optically, very thin flakes have a deep, olive green color. They are birefringent and have very high indices of refraction [Palache *et al.* (1951) stated that E.S. Larsen, Jr. estimated the mean index of refraction to be 2.05], but are too small to permit further optical characterization. The density measured in toluene on the Berman balance is  $2.78 \pm 0.05 \text{ g/cm}^3$  (Hewett found  $2.52 \text{ g/cm}^3$ ). The density calculated from the unit-cell content (see next section) is  $3.07 \text{ g/cm}^3$ , and the mean index of refraction predicted by the Gladstone-Dale relationship based on the calculated density is 2.03. The low measured densities are clearly affected by the porosity of the mineral mass.

Results of two chemical analyses of fernandinite have been published, one by W.F. Hillebrand reported by Hewett (1909), and one by W.T. Schaller (Ford 1915). The former shows the presence of 19.53%  $\text{Fe}_2\text{O}_3$ , which clearly represents a gross impurity; thus it is not considered further. Schaller's analytical data are shown in Table 1.

Electron-microprobe analyses were carried out on samples from each of the three NMNH specimens. The standard procedure for mounting the samples (embedding in epoxy resin and polishing) gave inconsistent results because of the rupture of the soft, polished surface and intrusion of the resin. Spectra taken from surfaces obtained by simply pressing with a glass plate small lumps of material glued to a glass substrate seemed to be more reproducible and reliable. Using this technique, five analyses were obtained for NMNH No. 87661, five for NMNH No. 96702, and ten for NMNH No. R-5706. Average compositions for these three runs are listed in Table 1.

All these compositions show evidence of admixed impurities, and varying amounts of water (totals are deficient by 5 to 15%). Quartz commonly is present, (observed in the X-ray powder patterns). The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio remains quite constant over the range of compositions (5/3, 0.5 to 5.1 %  $\text{SiO}_2$ ), and is considered to represent an impurity; Ti is smaller in amount and is assumed to follow vanadium. Fe is assumed to substitute for V.

The atomic ratios are best obtained by combining (Fe,Ti) with V, and (Ca,Na) with K, although the role of Fe is always ambiguous. Whereas Hillebrand (Hewett 1909) found nearly 20%  $\text{Fe}_2\text{O}_3$ , Schaller (Ford 1915) found only 0.79%  $\text{Fe}_2\text{O}_3$ , but reported 12.18% insoluble matter. His determination of a  $\text{V}^{4+}/\text{V}^{5+}$  ratio of 0.204 is probably significant; we have not tried to measure this ratio directly. We found neither Mo nor U, and the presence of these elements in the results of Hillebrand and Schaller cannot be accounted for. The general formula we find for fernandinite is:  $(\text{Ca},\text{Na},\text{K})_x(\text{V},\text{Fe},\text{Ti})_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$ . Schaller (Ford 1915) determined the  $\text{V}^{4+}/\text{V}^{5+}$  ratio directly in his analysis, but we calculated this ratio from the interlayer charge, assuming that  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$  replace V in the layer structure. The various molar proportions of the components of the formula are given in Table 2 for each of the three lots of fernandinite in the NMNH collections.

#### *Corvusite*

As reported by Henderson & Hess (1933), corvusite is optically opaque, occurring as lustrous, purplish blue-black masses that commonly show striations, suggesting a fibrous character. They reported a hardness of 2.5-3, and a specific gravity of 2.82. The density calculated from the unit-cell content is  $3.02 \text{ g/cm}^3$ .

TABLE 1. CHEMICAL COMPOSITION OF FERNANDINITE AND CORVUSITE

Oxides	Sch.*	Fernandinite			Corvusite			esd
		1	2	3	Hnd.**	4	5	
$\text{V}_2\text{O}_4$	10.18				9.67			
$\text{V}_2\text{O}_5$	55.42	83.7	75.7	76.6	64.89	84.7	85.9	2.2
$\text{Fe}_2\text{O}_3$	0.79	0.5	0.4	1.5	5.82	2.0	2.0	0.2
$\text{TiO}_2$	—	0.17	0.34	0.40	—	—	—	0.2
$\text{CaO}$	3.35	5.6	5.0	5.7	1.98	1.5	2.0	0.3
$\text{Na}_2\text{O}$	—	0.0	0.03	0.04	1.44	2.6	3.0	
$\text{K}_2\text{O}$	0.52	0.2	0.2	0.5	1.06	0.9	0.8	0.2
$\text{H}_2\text{O}$	15.81				11.68			
$\text{MoO}_3$	1.38	0.0	0.0	0.0	—	0.0	0.0	
$\text{UO}_2$	—	0.0	0.0	0.0	1.71	0.0	0.0	
$\text{MgO}$	—	0.0	0.1	0.0	0.27	0.03	0.08	0.03
$\text{SiO}_2$	2.3	2.9	1.0	0.30	0.0	0.0	1.4	
$\text{Al}_2\text{O}_3$	—	1.4	1.6	0.7	0.2	0.3	.8	
Insol.	12.18							
Totals	99.69	94.1	85.4	89.2	99.90	91.9	94.2	

Notes:

\* Schaller, analyst (Ford 1915).

\*\* Henderson, analyst (Henderson & Hess 1933).

esd indicates estimated standard deviations of analyses 1-5.

Microprobe analyses (all V given as  $\text{V}_2\text{O}_5$ ):

1. NMNH No. 86671, average of 5 determinations.

2. NMNH No. 96702, average of 5 determinations.

3. NMNH No. R-5706, average of 10 determinations.

4,5. NMNH No. 96806, 2 samples, average of 10 determinations.

TABLE 2. MOLAR PROPORTIONS OF CATION COMPONENTS OF FERNANDINITE AND CORVUSITE

Cations	Fernandinite			Corvusite			
	Sch.*	1	2	3	Hnd.**	4	5
$\text{V}^{4+}$	1.34	1.39	1.41	0.88	1.07	0.08	0.19
$\text{V}^{5+}$	6.62	6.48	6.45	6.73	6.54	7.52	7.42
$\text{Fe}^{2+}$	0.05	0.05	0.10	0.34	0.67	0.40	0.39
$\text{Ti}^{4+}$	—	0.02	0.04	0.05	—	—	—
$\text{Cr}^{2+}$	0.65	0.86	0.84	0.92	0.31	0.22	0.29
$\text{K}^+$	0.13	0.04	0.04	0.04	0.20	0.16	0.01
$\text{Na}^+$	—	0.00	0.01	0.01	0.41	0.68	0.78
$\text{H}_2\text{O}$	9.5	2.5	6.5	4.5	5.7	5.9	5.8
Tot. layer cations	8.02	8.00	8.00	8.00	8.32	8.00	8.00
Tot. interlayer cations	0.78	0.90	0.89	0.97	0.95	1.06	1.08
Interlayer charge	1.43	1.76	1.73	1.89	1.27	1.28	1.37
Average V valence	4.83	4.82	4.82	4.88	4.86	4.99	4.98

Notes:

\* Schaller (Ford 1915).

\*\* Henderson (Henderson & Hess 1933).

1-5. Based on corresponding microprobe analyses in Table 1, with layer cations constrained to 8.00 and layer oxygens to 20.00.

Water estimated by difference of analytical totals from 100%.

The mineral is more brittle than fernandinite, and shows a conchoidal fracture. A scanning electron microscope image of this specimen of corvusite is shown in Figure 1B.

Corvusite shows stronger absorption than fernandinite in transmitted light, but very thin lamellae are translucent. The color is greenish yellow, and thin laths show positive elongation. The indices of refraction, as with fernandinite, are very high (high relief in methylene iodide). The Gladstone-Dale relationship, based on the composition and calculated density (see below), predicts a mean index of refraction of 2.05.

Three samples taken from NMNH No. 96806 were subjected to electron-microprobe analysis. The average compositions of these samples are set forth in Table 1, along with the data reported by Henderson & Hess (1933). The composition of this material is very similar to that of fernandinite, but whereas Ca is the major interlayer cation in fernandinite, Na is the dominant cation in corvusite. This distinction is the principal criterion for the definition of the two minerals. The general formula for type corvusite is therefore:  $(Na,Ca,K)_x(V,Fe)_yO_{20} \cdot 4H_2O$ . Table 2 shows the molar proportions found in this formulation by Henderson (Henderson & Hess 1933) and for two samples of type material in the NMNH collections. Henderson measured the  $V^{4+}/V^{5+}$  ratio analytically, but we calculated this ratio from the interlayer charge, as for fernandinite.

#### CRYSTAL-STRUCTURE ANALYSIS OF FERNANDINITE AND CORVUSITE

##### Crystallography

The only crystallographic data reported for fernandinite previous to 1990 are those of Ross (1959), who found, using the electron-diffraction pattern, a centered rectangular net near the plane of the crystal flake, with dimensions  $a$  11.69(4) Å and  $b$  3.674(4) Å. Evans & Hughes (1990) discovered that the X-ray diffraction patterns of corvusite (type) and fernandinite are closely similar, and found a unit cell in space group  $C2/m$  (consistent with the data of Ross) by which they were able to index both patterns satisfactorily. The fernandinite cell, refined with 15 uniquely indexed diffraction-maxima measured from Debye-Scherrer patterns made with  $CrK\alpha$  radiation, was found to have the dimensions given in Table 3. The Rietveld analysis (see below) yielded the unit-cell dimensions also shown in Table 3. Some variation in these dimensions, especially in  $c$  and  $\beta$ , have been observed, apparently due to the degree of hydration of the crystal structure as it is affected by the humidity in the air.

A heating experiment was executed with the Guinier-Lenne camera (Nonius), in which the variation of the powder pattern ( $CuK\alpha$ ) of fernandinite in

TABLE 3. UNIT CELLS OF FERNANDINITE, CORVUSITE,  
AND OTHER SYNTHETIC ANALOGS

	$a$ , Å	$b$ , Å	$c$ , Å	$\beta$ , deg.	$V$ , Å <sup>3</sup>
<b>Fernandinite</b>					
Evans & Hughes (1990)	11.704(6)	3.671(1)	11.021(11)	105.10(7)	457.
This work, Rietveld	11.680(1)	3.6537(4)	11.023(2)	105.00(2)	454.
Heating experiment (Guinier-Lenne method; see text)					
Phase I (15 lines)	11.65(2)	3.651(3)	10.99(2)	105.2(3)	451.
Phase II (13 lines)	11.69(1)	3.657(3)	9.52(1)	102.0(1)	398.
Phase III (8 lines)	11.77(1)	3.638(2)	9.27(1)	104.0(1)	385.
<b>Corvusite</b>					
Evans & Hughes (1990)	11.977(6)	3.636(2)	11.263(7)	106.62(7)	470.
This work, Rietveld	11.706(4)	3.644(1)	11.11(1)	103.46(7)	461.
<b>Other δ-type bronzes</b>					
$Ag_{2.72}V_8O_{20}$ (1)	11.744(6)	3.667(2)	8.737(8)	90.46(7)	376.3
$Ca_{2.4}V_8O_{20}$ (2)	11.805(2)	3.709(2)	9.270(2)	101.87(3)	397.2
$Na_{2.24}V_8O_{20}$ (3)	11.663(9)	3.6532(7)	8.92(1)	90.91(4)	379.9
$K_{2.0}V_8O_{20}$ (Cmm) <sup>(4)</sup>	11.6120(7)	3.6784(9)	18.6332(9)	90.	795.9

##### References (synthetic bronzes)

(1) Andersson (1965); powder data recalculated.

(2) Kotoglu (1983).

(3) Kanke et al. (1990a).

(4) Kanke et al. (1990b); transformed by 010/100/001.

air over the temperature range 20°C to 600°C was recorded. Two abrupt changes in volume were found, from phase I to phase II at 130°C, and phase II to phase III at 205°C. Similar monoclinic unit-cells were derived for phases II and III by least-squares analysis of 8 to 13 unambiguously indexed reflections for each phase, and are shown listed in Table 3. The volume changes suggest a loss of two molecules of water from I to II, and one more from II to III. The fernandinite phase III decomposes in air at 380°C, yielding a product similar to  $Ca(VO_3)_2$ ; at 500°C a prominent pattern of  $V_2O_5$  appears.

Evans & Hughes (1990) established that fernandinite has a layer structure based on densely edge-shared  $VO_6$  octahedra. This structure type was first found by Andersson (1965) for the anhydrous compound  $\delta$ - $Ag_{0.6}V_2O_5$ . Evans et al. (1984) postulated that straczekite,  $(Ca,Ba,K)_2V_8O_{20} \cdot 6H_2O$ , has a structure based on this type of layer, and on the basis of characteristic fiber-patterns, Evans & Hughes (1990) found that corvusite and, by extension, fernandinite (which gives no fiber pattern), also has this type of layer. Meanwhile, Kotoglu (1983) made a precise single-crystal refinement of an analogous structure of synthetic, anhydrous  $Ca_{2.4}V_8O_{20}$  [space group  $C2/m$ ,  $a$  11.805(2),  $b$  3.709(1),  $c$  9.270(2) Å,  $\beta$  101.87(3)°,  $R$  0.036].

Corvusite gives weaker and more diffuse patterns than fernandinite, but Evans & Hughes (1990) were able to measure sufficient Bragg data to determine the unit-cell parameters of this monoclinic phase. This process was facilitated for corvusite by the capability of obtaining fiber patterns, which show only the  $h0l$  reflections. From the type corvusite from Utah (Henderson & Hess 1933; NMNH No. 96806), Evans & Hughes obtained by least-squares analysis of 12 Bragg reflections the unit cell given in Table 3. Our Rietveld analysis of a diffraction pattern of the same

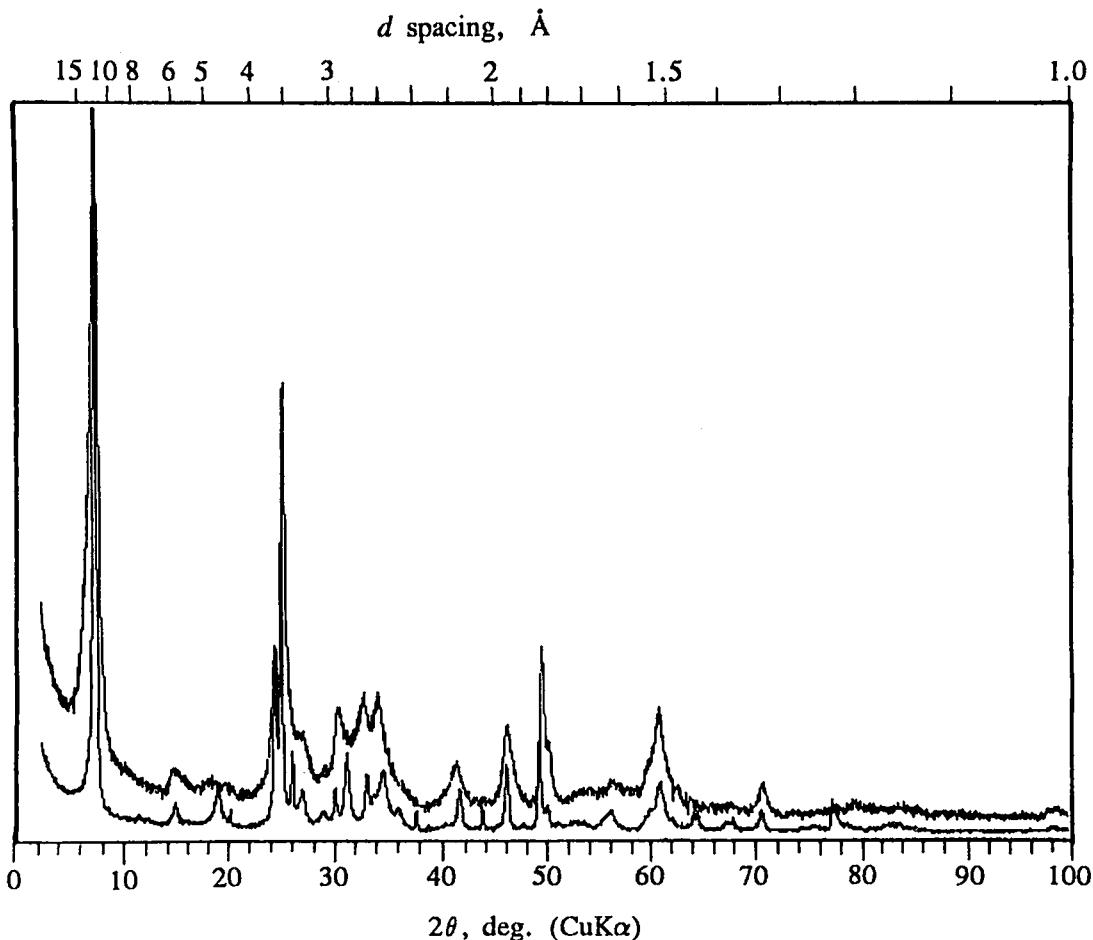


FIG. 2. X-ray powder-diffraction trace of corvusite (top) superposed on and slightly displaced above that of fernandinite.

material yielded a unit cell also shown in Table 3. As with fernandinite, variations in these parameters are ascribed to varying amounts and type of interlayer cations and water.

Figure 2 shows the powder-diffraction profiles of fernandinite and corvusite superimposed at comparable scales. The shapes of the profiles are dramatically parallel, providing conclusive evidence of closely similar crystal structures. The principal differences are: (1) a greater diffuseness of the peaks in the corvusite pattern, and (2) a substantially higher background for corvusite than that of fernandinite.

#### Rietveld structure-refinement

The success of this study depended primarily on X-ray powder-diffraction analysis, and especially the Rietveld method of pattern-profile analysis (Rietveld

1969; reviewed by Post & Bish 1989). As the minerals are very soft and easily deformed with pressure, particular care was needed in preparation of samples for the diffractometer. Examination of fernandinite by scanning electron microscope (J.J. McGee, USGS) revealed thin plates 5 to 10  $\mu\text{m}$  across, and for corvusite, fibrous masses extending to 1 mm or more (Fig. 1); thus, a risk of significant preferred orientation was indicated. The samples selected for profile analysis were gently crushed under acetone to reduce smearing of the soft crystallites. The powders were sifted onto glass-fiber filters in order to minimize preferred orientation, a procedure that has been found to be effective in many other similar cases. Powder X-ray-diffraction data were collected using  $\text{CuK}\alpha$  radiation with an automated Scintag Pad-V diffractometer fitted with an intrinsic-Ge solid-state detector and incident-beam and diffracted-beam soller slits.

The Rietveld refinement was performed using the computer program GSAS (Larson & Von Dreele 1990). A trial model based on the  $V_4O_{10}$  layer structure of  $Ca_{1.2}V_4O_{10}$  reported by Kotoglu (1983) was assumed, and the ambiguity with respect to  $+β$  or  $-β$  readily resolved. In the initial stages of computing, only the scale factor and three background parameters were refined. In successive cycles, two additional background parameters were refined, along with unit-cell parameters, a sample-displacement correction parameter, the Lorentzian broadening term of the pseudo-Voigt profile function, but not the V and O positional parameters. A comparison of the observed and calculated powder-diffraction patterns at this stage of the refinement revealed marked anisotropic broadening of the Bragg reflections for fernandinite, and even more for corvusite. Consequently, an anisotropic broadening coefficient was introduced and refined with the unique direction along [001]. This correction is usually related to a crystal strain effect, which in this case does not apply to the (00l) reflections, but nevertheless agreement with the observed pattern was significantly improved. The Lorentzian broadening terms that were refined suggest the presence of crystallites  $\sim 80$  and  $420$  Å perpendicular and parallel to

TABLE 4. DATA COLLECTION AND REFINEMENT PARAMETERS FOR FERNANDINITE

Data collection		Profile parameters*	
2θ range	20-90°	No. background	coeff. 4
Step size	0.03°	Profile coeff.	
Count time	20 s/step	GU	1.0
		GV	-0.9
		GW	5.5
Structure refinement		LX	21.1(4)
No. Bragg refl.	141	LY	3.2
No. var. param.	34	STEC	104(4)
$Chi^2$	10.5	SPEC	0
$R_{wp}$	0.126	SPTEC	0
$R_{Bragg}$	0.04	GP	0

\*Coefficients for pseudo-Voigt profile function employed in GSAS Rietveld Refinement Package (Larson & Von Dreele 1990); values for GU, GV, GW, and LY were fixed to those refined for  $LaB_6$  standard. Only LX and STEC (i.e., the Lorentz and related anisotropic broadening terms) were refined with the structure.

the c axis, respectively. A summary of the profile and background parameters applied in this analysis is given in Table 4.

The presence of a minor amount of quartz impurity was detected in the residual plot. Therefore, the final Rietveld refinement included peak-profile and scale-factor parameters for this phase.

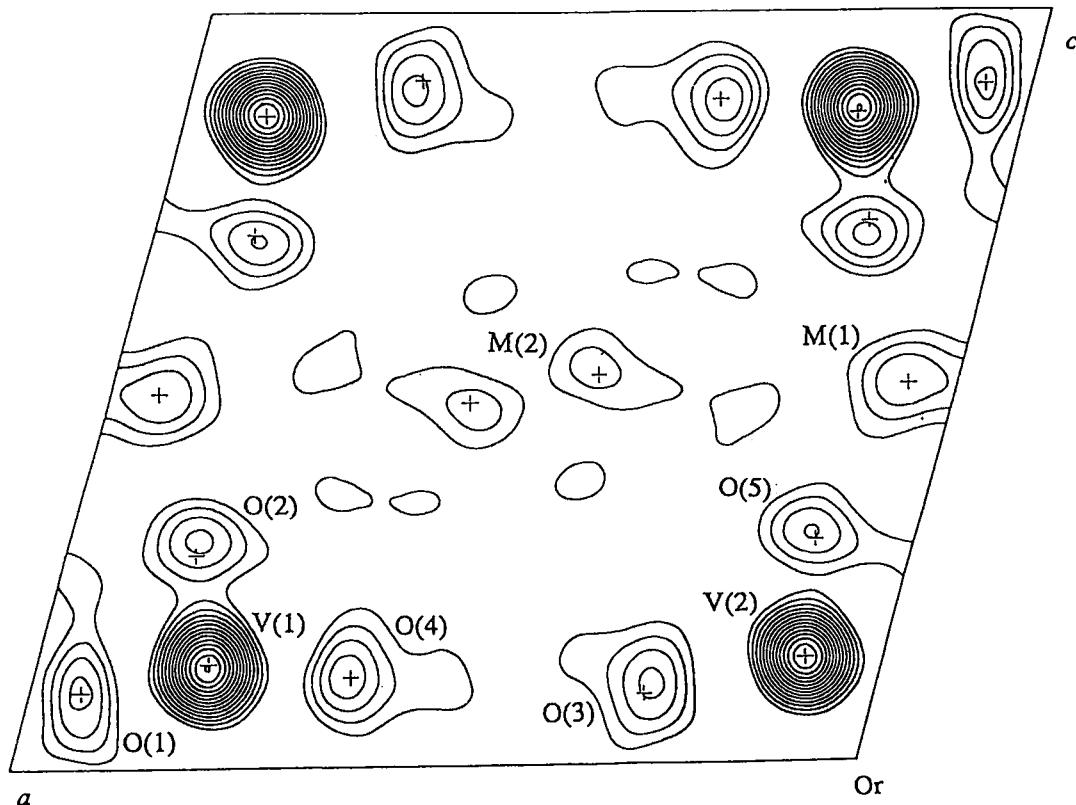


FIG. 3. Electron-density section of fernandinite at  $y = 0$ . First contour at  $2 e/\text{\AA}^3$ , contour interval  $2 e/\text{\AA}^3$ .

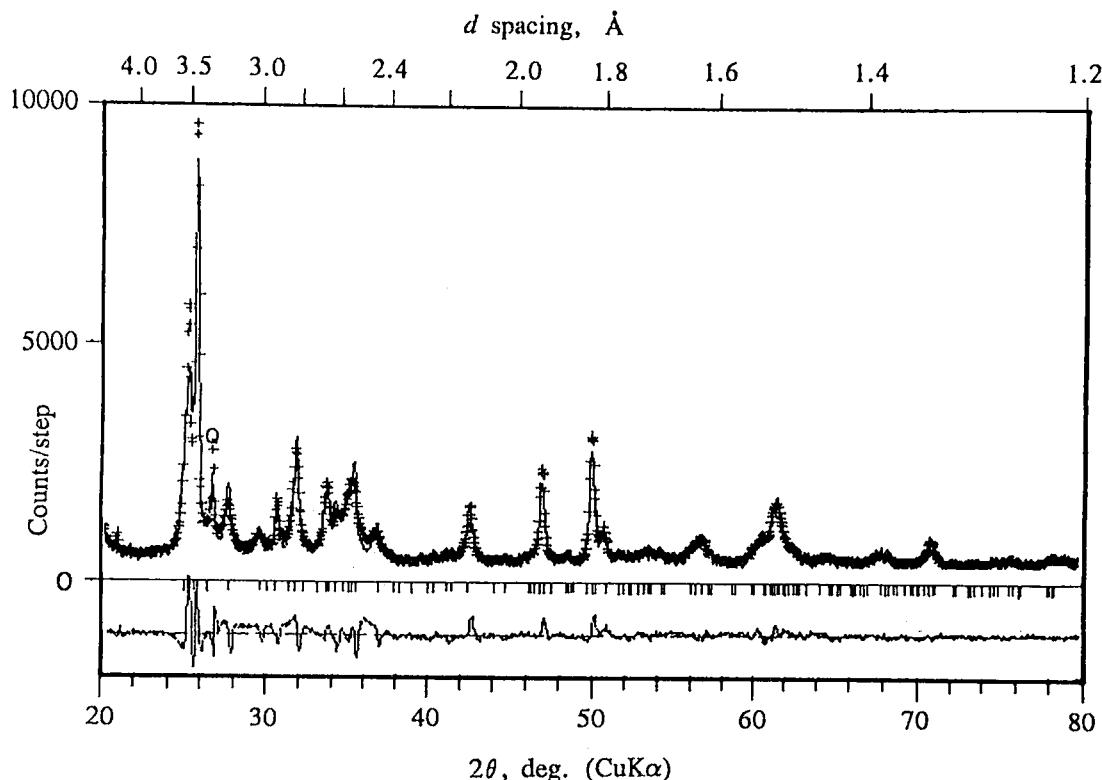


FIG. 4. X-ray powder-diffraction trace of fernandinite (CuK $\alpha$  radiation). Crosses are observed intensities, solid line is the calculated trace. Difference trace at bottom is at the same scale as profile at top.

After convergence of the refinement of the V<sub>8</sub>O<sub>20</sub> layer structure (weighted profile agreement factor  $R_{wp} = 0.17$ ), a difference Fourier map based on 141 extracted Bragg intensities revealed the locations of some interlayer cations and water molecules. The only prominent electron-density peaks attributed to the interlayer appeared near  $x,y,z = 0,0,\frac{1}{2}$  and  $\frac{1}{2},0,\frac{1}{2}$ . These sites were designated M1 and M2 (where M may be Ca, Na, K, or H<sub>2</sub>O) and were refined with Ca in both M1 and M2 ( $R = 0.13$ ). For the final cycles of refinement, all of the atom positions were allowed to vary, along with occupancy parameters for M1 and M2, and the thermal parameters were held fixed at  $U = 0.01$  for all layer atoms, and 0.02 for Ca in the M sites.

The final electron-density section at  $y = 0$  was calculated for fernandinite using the XTAL program system (Hall & Stewart 1988), and is shown in Figure 3. The observed diffraction-pattern is shown with the calculated pattern superposed in Figure 4. The structural coordinates are listed in Table 5, and the details of the structure are discussed in the next section.

The structure parameters obtained in the analysis of the fernandinite pattern were used to initiate the

procedure for corvusite. Again, refinement based on the layer structure alone led to convergence at  $R_{wp} = 0.19$ . The subsequent electron-density map was found to be very similar to that of fernandinite, showing peaks near  $0,0,\frac{1}{2}$  and  $\frac{1}{2},0,\frac{1}{2}$ . Unlike fernandinite, these two peaks are practically equal in

TABLE 5. STRUCTURE PARAMETERS FOR FERNANDINITE

Space group	C2/m; all atoms in 4i; $y = 0$ for all atoms			
Atom	x	z	$U^*$	Occup.
V(1)	0.8018(7)	0.1370(9)	0.01	1.0
V(2)	0.0982(7)	0.1378(7)	0.01	1.0
O(1)	0.946(2)	0.096(2)	0.01	1.0
O(2)	0.849(2)	0.283(2)	0.01	1.0
O(3)	0.629(2)	0.120(2)	0.01	1.0
O(4)	0.274(2)	0.100(3)	0.01	1.0
O(5)	0.110(2)	0.286(3)	0.01	1.0
M(1)	0.061(2)	0.506(3)	0.02	0.46(3)
M(2)	0.568(4)	0.478(4)	0.02	0.26(3)

Note:

\* $U$  (Å<sup>2</sup>) at arbitrarily fixed values.

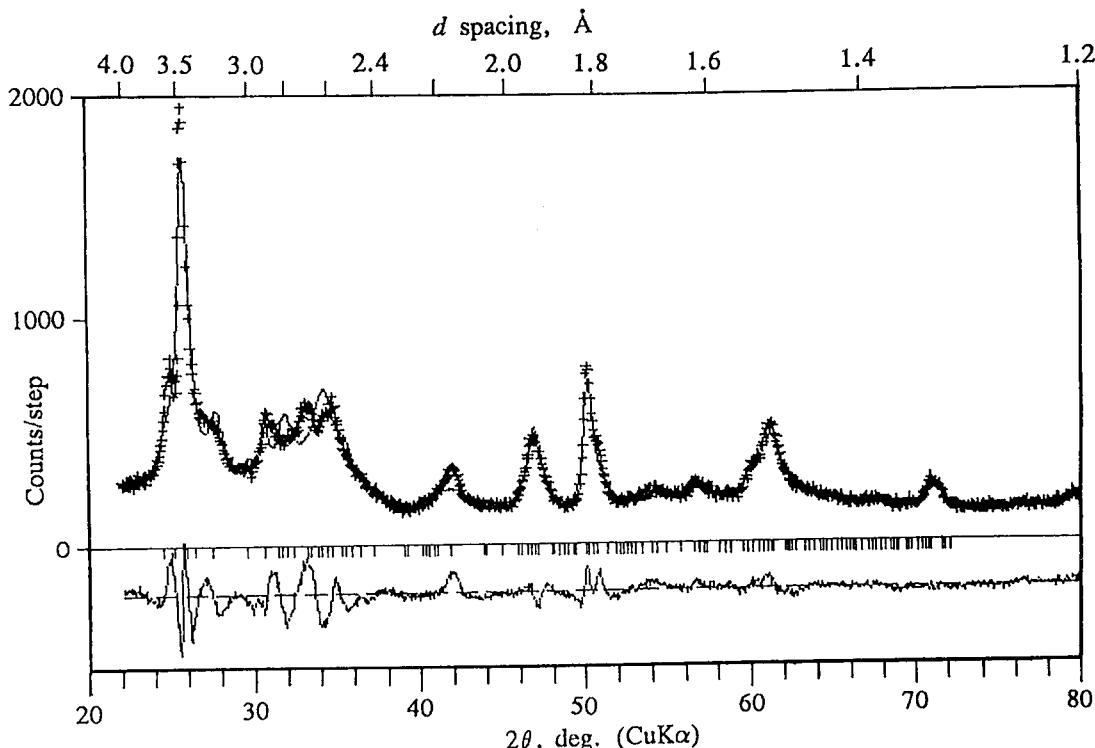


FIG. 5. X-ray powder-diffraction trace of corvusite (CuK $\alpha$  radiation), with calculated trace superposed as in Fig. 4.

height. When Na with 25% occupancy was refined at these locations, final refinement converged at  $R_{wp} = 0.16$ . Figure 5 shows the observed profile for corvusite. The theoretical profile is clearly not as satisfactory as that for fernandinite (Fig. 4), probably because of the inadequacy of the broadening function to model the more severe interlayer disorder in corvusite. Because of the poorer quality of the latter refinement, we adopt the results of the fernandinite refinement as representative of both structures, and only those are given in Tables 5 and 6.

One of the drawbacks of Rietveld refinements, especially for powder X-ray-diffraction data, is the difficulty of assessing the reliability of the estimated errors determined by the refinement. If the data are affected by systematic errors, such as preferred orientation, then the estimated standard deviations obtained might be considerably smaller than the actual errors [see, for example, review by Post & Bish (1989); also, Scott (1983)]. Consequently the errors in the bond distances may be significantly higher than those indicated in Table 6.

TABLE 6. BOND LENGTHS IN FERNANDINITE AND SYNTHETIC ANALOGS  $M_xV_2O_5$

References $M_x =$ Atoms	1 $Ag_{0.68}$	2 $Ca_{0.60}$	3 $Na_{0.56}$	4 $K_{0.50}$	Avg.*	5 FND
V(1)-O(2)	1.54(4)	1.646(4)	1.615(3)	1.605(5)	1.622 Å	1.56(3)
-O(1)	1.78(4)	1.772(3)	1.792(2)	1.805(4)	1.790	1.85(2)
(x2)-O(4)	1.89(2)	1.912(2)	1.889(1)	1.902(1)	1.901	1.88(1)
-O(3)	2.09(4)	2.063(3)	2.081(3)	2.075(5)	2.073	1.98(2)
-O(4)	2.35(4)	2.359(3)	2.374(3)	2.357(4)	2.363	2.353(3)
V(2)-O(5)	1.49(5)	1.644(4)	1.607(3)	1.600(5)	1.614	1.60(3)
-O(1)	1.85(4)	1.895(3)	1.856(3)	1.847(5)	1.866	1.72(3)
(x2)-O(3)	1.90(2)	1.932(2)	1.906(1)	1.911(1)	1.916	1.88(1)
-O(4)	1.95(4)	1.978(3)	1.989(4)	1.967(4)	1.978	2.19(2)
-O(1)	2.35(4)	2.347(3)	2.543(3)	2.570(4)	2.487	2.50(3)
O(1)-O(1)**	2.62(4)	2.640(2)	2.570(5)	2.579(4)	2.596	2.74(5)
O val.	4.84	4.40	4.72	4.75		4.80

Notes:

\* Average of three most precise values, columns 2, 3, and 4.  
\*\* Shared edge of octahedra across symmetry center.

#### References:

1. Andersson (1965).
2. Kotoglu (1983).
3. Kanke et al. (1990a).
4. Kanke et al. (1990b).
5. Fernandinite, this work.

DESCRIPTION AND DISCUSSION  
OF THE STRUCTURES

*The layer of vanadate octahedra*

As described by Evans & Hughes (1990), the  $V_8O_{20}$  ( $V_2O_5$ ) layer in fernandinite and corvusite is composed of fourfold chain elements that are made up of four chains of  $VO_6$  octahedra sharing opposite corners condensed into a compact unit by edge-sharing of the octahedra. This arrangement and the corresponding designations of atoms are shown in Figure 6. The assembled sheets and interlayer cationic sites are shown in perspective in Figure 7. Four single-crystal studies of analogous vanadium bronze structures (referred to in solid-state chemistry as  $\delta$ -phase) have been made previously. The holotype structure was determined by Andersson (1965) on  $Ag_{0.68}V_2O_5$ , based on the least-squares analysis of Weissenberg data. Modern single-crystal structure analyses have since been reported for  $Ca_{0.60}V_2O_5$  (Kotoglu 1983),  $Na_{0.56}V_2O_5$  (Kanke *et al.* 1990a), and  $K_{0.50}V_2O_5$  (Kanke *et al.* 1990b). The bond lengths in the  $V_2O_5$  layer in each of these compounds and in fernandinite are listed and compared in Table 6 according to the atom designations shown in Figure 6.

In each of the two types of octahedra, the vanadium atom is strongly displaced outward from the layer, forming a short bond with the external, unshared oxygen atom [ $V(1)-O(1)$ ,  $V(2)-O(2)$ ], which averages  $1.62 \pm 0.02$  Å for the three most precise determinations. The opposite internal bonds [to  $O(4)$ ] for the three structures vary from 2.347 to 2.570 Å. The remaining four V-O bonds, which may be considered as the basal bonds in a square pyramid with the short bond at the apex, averages 2.03 Å, ranging from 1.772 to 2.075 Å. The two atoms  $O(1)$  close to the center of symmetry form the edge of the octahedron that is shared with a similar edge in an adjacent fourfold chain to form the  $V_8O_{20}$  layer. This edge length averages 2.60 Å.

Comparing these dimensions with those found in fernandinite, we find substantial variations. (Although the calculated standard deviations of these distances is better than 0.04 Å, as mentioned above the actual errors are probably considerably larger.) A contributing factor to variations in the layer structure is probably the number of extra electrons (differences in average valence of V) in the  $V_8O_{20}$  layer. For the synthetic Ca compound (Kotoglu 1983), the average valence of V is 4.37, corresponding to a  $V^{4+}:V^{5+}$  ratio of 2:1, but for the Na and K compounds (Kanke *et al.* 1990a, b) and these two minerals, the average valence is 4.75, corresponding to a ratio of 1:3. These extra electrons may exert interactions due to attraction among the V atoms themselves, with some adjustments of the interatomic dimensions, such as  $V(2)-O(4)$  and  $O(1)-O(1)$ . Some attractive forces may

also occur to shorten distances between V atoms. Thus, the average V-V distance for three of these distances across the shared edge of the octahedra in the six structures is 3.47 Å, but the  $V(1)-V(1)$  distance across the center of symmetry is 3.25 Å, and the distance between  $V(1)$  and  $V(2)$  in adjacent levels ( $y = 0, \frac{1}{2}$ ) is 3.00 Å.

There seems to be no characteristic variation in V-V distances with average valence of V. Calculation of bond strengths ( $s$ ) from bond lengths

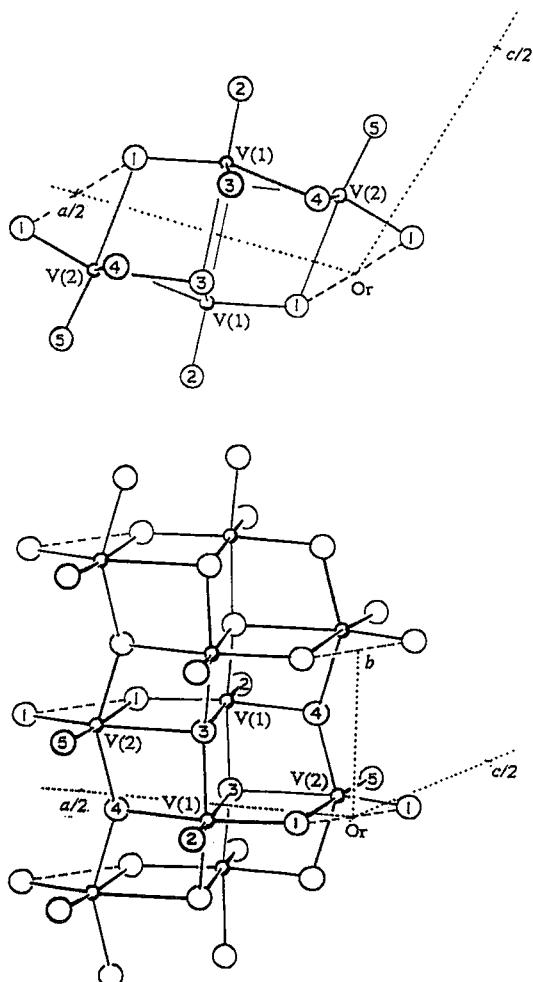


FIG. 6. Top and oblique view of fourfold chain element of  $V_2O_5$  layer in relation to the unit-cell axes, showing labeling of atoms. Dashed lines represent edges of octahedra shared with adjacent chains to form the layer.

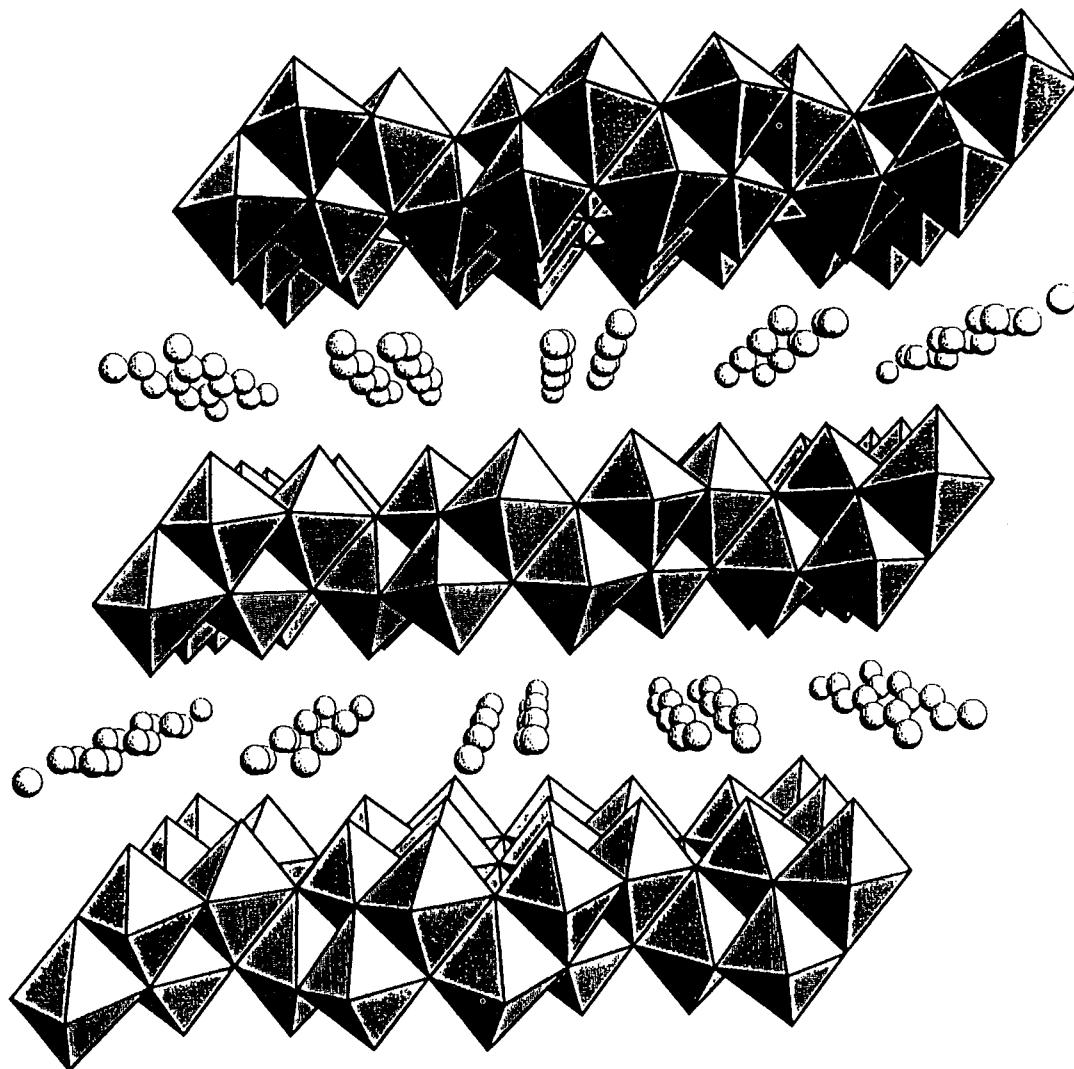


FIG. 7. Perspective view of fernandinite structure viewed along the  $b$  axis. Note: the chains of interlayer sites along  $0,y,\frac{1}{2}$  and  $\frac{1}{2},y,\frac{1}{2}$  are shown as circles, but these sites are only partially occupied by cations, and possibly some water molecules.

(R) [ $s = (R/1.791)^{-5.1}$ ; Brown 1981] gives no significant evidence for localization of extra electrons on either V(1) or V(2) in the best three determinations. The average valence of V in Kotoglu's (1983) Ca compound is 4.66, and in the Na and K compounds, 4.85 (Kanke *et al.* 1990a, b). These values are somewhat higher than the reported analytical values 4.4 and 4.8, respectively.

#### *Interlayer cations and water molecules*

Electron-density maps of the interlayer material in both fernandinite and corvusite show well-defined

peaks in zig-zag rows parallel to the  $b$  axis at  $x,z = 0,\frac{1}{2}$  and  $\frac{1}{2},\frac{1}{2}$ , separated by about 2.4 Å. In fernandinite, there are sufficient cations and sufficient room to fill alternate sites ( $x,0,z$ ;  $x,1,z$ ), with H<sub>2</sub>O in intervening sites ( $-x,\frac{1}{2},-z$ ). On the other hand, in corvusite, there is too much density in the intervening site to be assigned to water. On the assumption that only cations occupy the  $M1$  and  $M2$  sites in the structures, and using composite scattering-factors according to the chemical data, our least-squares structure analyses yield 1.4 cations in the unit cell for fernandinite, whereas the analytical value is 1.06. We may, therefore, postulate that some of

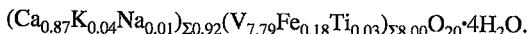
the scattering at these sites is due to substitutional H<sub>2</sub>O. We have not attempted to separate these interacting occupancy-factors further.

Aside from the water in the *M*(1) and *M*(2) sites, in neither structure can we "see" water at all; it presumably occupies the large open spaces between the cations diffusely, showing only as broad, low electron-density regions (Fig. 3). The best estimate we may have for the amount of water in the unit cell can be obtained from the cell volume, 457 Å. Assuming that the volume of the V<sub>4</sub>O<sub>10</sub> layer, as derived from the structures of the synthetic bronzes, is about 355 Å<sup>3</sup>, and the allowance for Ca is 9 Å<sup>3</sup>, 88 Å<sup>3</sup> remains for H<sub>2</sub>O, just enough for four molecules.

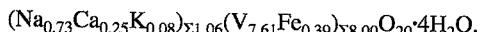
### CONCLUSIONS

Based on X-ray powder data, the unit cells of the closely related minerals fernandinite and corvusite have been refined in space group *C2/m*, using type material. Rietveld structure analyses of patterns of both minerals have confirmed that the layer structures of these minerals are exactly analogous to that of synthetic δ-Ag<sub>0.68</sub>V<sub>2</sub>O<sub>5</sub>, consisting of fourfold V<sub>4</sub>O<sub>10</sub> chains of condensed VO<sub>6</sub> octahedra (Evans & Hughes 1990) joined laterally by sharing edges of octahedra in adjacent chains to form the layers. The minerals thus belong to a group of natural vanadium bronzes previously designated as the "straczekite group", which includes bokite and probably bariandite.

The layer structures are clearly revealed in maps of the electron density, together with some information about the interlayer material. In both structures, a string of peaks in the interlayer region adjacent to the twofold axes indicate sites partially occupied by the cations, and perhaps some water molecules. Most of the water is not visible and presumably diffusely occupies open space between the cations. The general formula for these minerals has been found to be  $M_x[(V,Fe,Ti)_8O_{20}] \cdot nH_2O$ , where *M* is (Ca,Na,K) for fernandinite and (Na,Ca,K) for corvusite, *x* is near 1.0, and *n* is near 4 but variable. The average analytical formula for type fernandinite (assuming the layer contains all iron as Fe<sup>2+</sup> and all titanium as Ti<sup>4+</sup>) may be written:



Similarly, the formula for type corvusite may be written:



Based on the chemistry of the type materials, it is established that fernandinite is associated with calcium as the dominant interlayer cation, and corvusite with sodium as the dominant cation. The interlayer water is loosely bound and may be absorbed or eliminated

according to conditions of humidity and temperature. Although fernandinite has not been adequately described until now and has previously been subject to question, our study has firmly established its validity as a unique mineral species.

An unanswered question concerns the reason for the radically different habits of crystals observed in the two type minerals. Occurrences of a black "corvusite-like" mineral are nearly always described as mammillary or radiating laths or fibers emanating from the wall of a vug or a nucleus in a small cavity. It seems that the Peruvian fernandinite was formed in an entirely different manner, perhaps by sudden precipitation from a hot, saturated solution, forming solid, dense masses. Many reported occurrences of corvusite or "corvusite-like" minerals show calcium as the dominant cation. We believe that such occurrences are actually fernandinite deposited under more usual conditions by slow formation as radiating fibers on cavity walls.

### ACKNOWLEDGEMENTS

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