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Schubnelite, $[Fe^{3+}(V^{5+}O_4)(H_2O)]$, a novel heteropolyhedral framework mineral

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ABSTRACT

Schubnelite from the U deposit of Mounana, Gabon, crystallizes in space group $P\bar{1}$ with a = 5.466(1), b = 5.675(2), c = 6.610(1) Å, α =101.02(1), β = 95.10(1), γ = 107.31(1)°, and V = 189.8(2) Å^3. The structure of schubnelite $[Fe^{3+}(V^{5+}O_4)(H_2O)]$ contains isolated (VO_4) tetrahedra and edge-sharing $(Fe\phi_6)$ octahedra (ϕ = unspecified anion) and is isostructural with $[M(TO_4)(H_2O)]$ compounds with M = Mg,Mn and T = Mo,W. The topology of the schubnelite framework can be described as an arrangement of mutually orthogonal 6^3 and 4^4 nets. The fundamental building block (FBB) of the schubnelite structure does not occur in any other $M^{[6]}T^{[4]}\phi$ mineral. Many stoichiometrically similar compounds $[M(TO_4)(H_2O)]$ crystallize in the kieserite structure-type, including the synthetic compounds $V^{3+}(PO_4)(H_2O)$ and $Mn^{3+}(PO_4)(H_2O)$. The kieserite arrangement has a $^{[6]}M^{3+}$-(H_2O)-$^{[6]}M^{3+}$ bridge. Both $V^{3+}(3d^2)$ and $Mn^{3+}(3d^4)$ have electronic degeneracies that drive spontaneous distortions resulting in satisfaction of the incident bond-valence requirements around the bridging H_2O group. For Fe^{3+} $(3d^5)$ in schubnelite, there is no electronic degeneracy and hence no spontaneous local distortion of the environment around the Fe^{3+} cation. Hence, an Fe^{3+}-(H_2O)-Fe^{3+} bridge cannot form and schubnelite is forced to crystallize in a different arrangement.

INTRODUCTION

Schubnelite was first described from the U deposit of Mounana, Gabon, by Cesbron (1970) and named after H.J. Schubnel. Schubnelite occurs as green crystals with (001) pinacoids and (010) and (100) prisms, and is extensively twinned on $(21\bar{2})$. It occurs with fervanite, $Fe_4(VO_4)_4\cdot5H_2O$, at the base of the oxidized zone of the U deposit.

Cesbron (1970) reported the composition as $Fe^{3+}_{1.93}V^{4+}_{0.77}V^{5+}_{1.30}O_{7.69}\cdot2H_2O$. He proposed the presence of a $[V_2O_8]$ unit with two V^{4+}/V^{5+} pyramids connected by a common edge, based on the structures of some well-known vanadium-bearing minerals (carnotite, vanuralite, curienite, and francevillite), which contain such edge-sharing $[V_2O_8]$ groups. Evans and Hughes (1990) quote Cesbron's formula of schubnelite as $Fe_2V_2O_8\cdot4H_2O$; this is presumably a misprint as they propose recasting the formula as $Fe_2V_2O_4(OH)_4$. However, if the V is recast as all V^{5+}, the simple formula $Fe^{3+}(V^{5+}O_4)(H_2O)$ results. This paper reports the structure of schubnelite and examines why the chemical composition $[Fe^{3+}(V^{5+}O_4)(H_2O)]$ does not occur in the kieserite structure type.

EXPERIMENTAL METHODS

A crystal from Mounana, Gabon, was mounted on a glass fiber and X-ray data were collected on a Nicolet R3m automated four-circle diffractometer. Eighteen reflections were centered using graphite-monochromated Mo$K\alpha$ X-radiation; the resulting cell dimensions are given in Table 1. A total of 1117 symmetry-independent reflections was measured $(3 \le 2\theta \le 60°)$, with index ranges $-9 \le h \le 9$, $-7 \le k \le 7$, $-9 \le l \le 9$, according to the method of Burns et al. (1994a). The intensity data were corrected for absorption (psi-scan method), Lorentz, polarization, and background effects, and reduced to structure factors. A reflection was considered as observed if the magnitude of the structure factor exceeded that of five standard deviations above background on the basis of counting statistics.

Table 1 lists the experimental data for the X-ray measurements. The E-statistics indicated the presence of a center of symmetry; the structure was solved by direct methods and difference-Fourier synthesis; and the H atoms were located in the end stages of refinement. The structure was refined using scattering factors for neutral atoms, together with anomalous-dispersion corrections, from Cromer and Mann (1968) and Cromer and Liberman (1970), respectively. The displacement factors of the H atoms H1 and H2 are isotropic and were constrained to be equal during refinement; the O5-H1 and O5-H2 bond lengths were softly constrained to the value 0.98 Å.

The structure converged to an R-index of 2.1%. The positional parameters and the equivalent isotropic-displacement factors are shown in Table 2. Table 3 lists selected bond distances and angles and Table 4 contains the bond-valence analysis. The solution and refinement of the structure were done with the SHELXTL PC PLUS software (Sheldrick 1990). Bond distances and angles were calculated with SADIAN 90 (Baur and Kassner 1991).

CRYSTAL STRUCTURE

Cation coordination

There is one tetrahedrally coordinated site with a mean bond length of 1.72 Å; this was assigned to V and the refined equivalent isotropic-displacement factor is in accord with this assignment. The chemical analysis reported by Cesbron (1970) con-

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TABLE 1. Experimental data for schubnelite [$Fe(VO_4)(H_2O)$]

a (Å)	5.466(1)	Crystal size	0.042 mm × 0.084 mm × 0.126 mm
b (Å)	5.675(2)	Wavelength	Mo*K*α (0.71073 Å)
c (Å)	6.610(1)	Absorption factor (mμ)	6.17
α (°)	101.02(1)	*D*(calc) (g/cm^3)	3.225
β (°)	95.10(1)	no. of I	2234
γ (°)	107.32(1)	no. of unique $\lvert F_O \rvert$	1117
V (Å^3)	189.8(2)	no. of $\lvert F_O \rvert > 5\sigma$	990
Z	2	R_{int}(%)	1.3
Space group	$P\bar{1}$	*R* (%)	2.1
Crystal system	triclinic	*Rw* (%)	1.9

Notes: $R = \sum(|F_0| - |F_c|)/\sum|F_0|$, and $wR = [\sum w(|F_0| - |F_c|)^2/\sum F^2_o\ ]^{1/2}, w = 1$.

TABLE 2. Positional coordinates (*x*,*y*,*z*) and equivalent isotropic-displacement factors (U_{eq}) of schubnelite

Site	*x*	*y*	*z*	U_{eq}
Fe	0.36433(6)	0.78290(6)	0.30176(5)	0.0085(1)
V	0.73916(7)	0.37789(6)	0.24560(5)	0.0057(1)
O1	0.3859(3)	0.7399(3)	0.0055(3)	0.0162(5)
O2	0.6377(3)	0.6283(3)	0.3370(3)	0.0133(5)
O3	0.3718(3)	0.8667(3)	0.6174(2)	0.0104(4)
O4	0.0717(3)	0.4778(3)	0.2737(3)	0.0138(5)
O5	0.0976(3)	0.9719(3)	0.2604(3)	0.0207(6)
H1	0.12(1)	0.153(2)	0.288(8)	0.06(1)
H2	0.924(4)	0.897(9)	0.292(8)	0.06(1)

TABLE 3. Bond lengths [Å] and angles [˚] of schubnelite

Fe-O4	1.941(1)	V-O1	1.665(2)
Fe-O1	1.945(2)	V-O2	1.701(1)
Fe-O2	1.936(1)	V-O4	1.716(6)
Fe-O3	2.017(1)	V-O3	1.787(1)
Fe-O3	2.043(1)	<V-O>	1.717(1)
Fe-O5	2.080(1)		
<Fe-O>	1.988(1)		
H1-O5	0.98(1)	H2-O5-H1	103(1)
H2-O5	0.98(1)	H2-O5-H1	162(4)
H1-H2	1.53(4)	O5-H2-O2	155(2)
H1-O4	1.95(2)		
H2-O2	1.92(3)		

TABLE 4. Bond valences for schubnelite

	Fe^{3+}*	V^{5+}†	H1	H2	Sum
O1	0.58	1.45			2.03
O2	0.56	1.32		0.15	2.03
O3	0.48 ×2→	1.04			2.00
O4	0.60	1.26	0.2		2.06
O5	0.41		0.8	0.85	2.05
Sum	3.08	5.07	1	1	

*Bond-valence curves from Brown (1981).

†Bond-valence curves from Brown and Altermatt (1985).

tains significant VO_2, resulting in a V^{4+} content of 0.77 atoms per formula unit (apfu). Mineral structures and many recently synthesized vanadium phosphate structures have V^{4+} in [4+1+1] or [4+1] coordination with O; [4+1+1] and [4+1] indicates that the central V^{4+} cation is surrounded by four O atoms at distances from 1.9 to 2.1 Å, one O atom at 1.5 to 1.7 Å, and another O atom from 2.0 to 2.4 Å. This type of coordination does not occur in schubnelite (Table 3). Furthermore, the geometry of the V site is consistent with the occurrence of V^{5+} at this site. Using the bond-valence parameters of Brown and Altermatt (1985), the sum of the bond-valences incident at the V site is 5.07 vu, in accord with the occurrence of a pentavalent cation at this site. The (VO_4) tetrahedron shows strong distortion with a range in bond lengths from 1.665 to 1.787 Å. The mean <V-O> bond length of 1.717(1) Å is close to the calculated grand <$^{[4]}V^{5+}$-O> distance of 1.72(1) Å (Shannon and Calvo 1973). The distortion of the (VO_4) tetrahedron is caused by the coordination details of the O1 and O3 anions. The O1-V distance is very short (1.665 Å) because O1 is bonded to one Fe^{3+} and one V^{5+} cations. The O3-V distance is much longer (1.787 Å) because O3 is bonded to two Fe^{3+} and one V^{5+} cations (Table 4), and can accept only ~1 vu from the V^{5+} cation.

There is one octahedrally coordinated site with a mean bond length of ~2.00 Å; this was assigned to Fe. The ($Fe\phi_6$) octahedron is somewhat distorted, with Fe-O distances in the range 1.94 to 2.08 Å, typical for sixfold-coordinated Fe^{3+}. Any attempt to put V^{4+} at the Fe site results in nonsensical bond-valence sums at some of the sites in the structures. Thus, we can conclude from the refinement of the X-ray data that the chemical formula of schubnelite is [$Fe^{3+}(V^{5+}O_4)(H_2O)$].

The H_2O group occurs at the free apex of the ($Fe\phi_6$) octahedron. The two H atoms of the H_2O group form hydrogen bonds to O2 and O4. Bond-valence calculation shows that O2 and O4 are weakly bonded acceptor anions that require the hydrogen bond to satisfy their bond-valence requirements.

Structure and topology

The structure of schubnelite consists of edge-sharing pairs of (FeO_6) octahedra connected by isolated (VO_4) tetrahedra (Fig. 1). The three-dimensional framework is isostructural with the [$M(TO_4)(H_2O)$] type, where M is Mg,Mn and T is Mo,W (Amberg et al. 1988; Clearfield et al. 1985). The structure can be described as a three-dimensional arrangement of octahedral-tetrahedral double layers parallel to (001) (Fig. 1a). The layers consist of double six-membered rings, where each six-membered ring has the sequence Oc-T-Oc-T-Oc-T, where T stands for tetrahedral and Oc for octa-

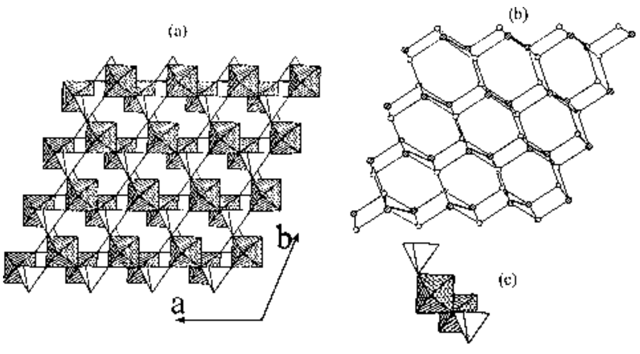

FIGURE 1. The structure of schubnelite. (**a**) Projected onto (001), showing one double layer of edge-sharing octahedra and isolated (VO_4) tetrahedra. (**b**) The schubnelite framework with a two-dimensional 6^3 net parallel to (001) and 4^4 nets parallel to (100) and (010). The shared octahedral edge is shown as a bold line between octahedral nodes. (**c**) The FBB of the schubnelite structure.

hedral coordination. This arrangement can be described as a 6^3 net. The thickness of the double layer is defined by the pair of edge-sharing octahedra and represents the size of the unit cell in the *c* direction. The free apices of the tetrahedra in the [001] direction share corners with the pair of octahedra from the adjacent double layer.

Figure 1b shows the topology of the schubnelite structure parallel to (001). In this representation, each central cation is connected to the cations of the adjacent polyhedra by the edges of the net. The edge-sharing pair of octahedra are marked by a bold line. The O atom common to one tetrahedron and two octahedra is represented by a triangle and not as a solid line. Thus each T-node represents a tetrahedron and is surrounded by five neighbors (representing the octahedra). The M-nodes represent the octahedra, and have the additional diagonal connection to the adjacent M-node. The (001) nets are connected in the [010] and [100] directions by four-membered rings, forming 4^4 nets. The four-membered rings are arranged in double-crankshaft chains parallel to [100] and [010]. In the [100] direction, every second four-membered ring is divided by the bold diagonal line representing the edge-sharing octahedra. The maximal symmetry possible for this framework is *Cmmm*. If we do not consider the different cations and the common octahedral edge, we would have a simple five-connected three-dimensional net with space group symmetry *P*6/*mmm*; each node is the Wyckoff position 2c and has site symmetry $\bar{6}m2$.

Fundamental building block

Hawthorne (1979, 1983, 1985, 1990, 1992) and Moore (1970, 1974, 1984) have examined crystal-structure topology in terms of fundamental building blocks (FBB). In particular, Hawthorne (1983, 1985) proposed that higher bond-valence polyhedra form homo- or heteropolyhedral clusters that constitute the FBB of the structure. This FBB is repeated (often polymerized) by translational symmetry operators to form the structural unit. Hawthorne (1990) derived possible clusters of $[M^{[6]}_2 T^{[4]}_2\phi_n]$ stoichiometry using graph theoretic and combinatorial techniques. Excluding unlikely polyhedral linkages (such as face-sharing tetrahedra), he found 76 completely connected clusters of $[M^{[6]}_2 T^{[4]}_2\phi_n]$ stoichiometry, but only six occur in his structural hierarchy of 96 minerals of corresponding composition.

The FBB of the schubnelite structure is shown in Figure 1c. This FBB does not occur in any of the 96 mineral structures listed by Hawthorne (1990). In particular, all other minerals with $[M(TO_4)(H_2O)]$ stoichiometry occur in the kieserite structure-type and contain an FBB very common in mineral structures (Fig. 2b).

Chemical composition

The formula of schubnelite indicated by the structure solution is $Fe^{3+}(V^{5+}O_4)(H_2O)$. Such a material should be a honey-yellow color due to absorption predominantly in the ultraviolet but extending into the violet end of the visible region. However, schubnelite is black, and pleochroic yellowish to greenish-brown in thin splinters, and it was the color that led Evans and Hughes (1990) to suggest that schubnelite is a vanadium bronze. There are two possible explanations for the dark color in schubnelite: (1) There is strong magnetic coupling between the Fe^{3+} cations of the edge-sharing octahedral dimers; (2) There is a small amount of Fe^{2+} substituting for Fe^{3+}, leading to Fe^{2+}-Fe^{3+} charge-transfer interactions; the mechanism for maintaining electroneutrality with an Fe^{2+} component must be incorporation of a hexavalent cation replacing V^{5+} in tetrahedral coordination, but we see no evidence of this.

$[M(TO_4)(H_2O)]$ compounds with the kieserite structure type

The kieserite structure-type contains corner-sharing octahedra that form chains parallel to [001]. Each chain is connected by tetrahedral groups that bridge two octahedra from one chain to two other chains, building up a three-dimensional framework (Fig. 2a). The chains have a repeat distance of approximately 7 Å (the length of the two octahedra in the FBB); Moore (1970) called this a 7 Å chain. The H_2O groups occur at the common vertex of two octahedra. Minerals of the kieserite structure-type are kieserite $[Mg(SO_4)(H_2O)]$, dwornikite $[Ni^{2+}(SO_4)(H_2O]$, gunningite $[Zn(SO_4)(H_2O)]$, poitevinite $[Cu^{2+}(SO_4)(H_2O)]$, szimikite $[Mn^{2+}(SO_4)(H_2O)]$, and szomolnokite $[Fe^{2+}(SO_4)(H_2O)]$ (Hawthorne et al. 1987; Wildner and Giester 1991; Le Fur et al. 1966). Structurally related synthetic compounds are $[V^{3+}(PO_4)(H_2O)]$ (Vaughey et al. 1994) and $[Mn^{3+}(PO_4)(H_2O)]$ (Lightfoot et al. 1987).

Why does $[Fe^{3+}(VO_4)(H_2O)]$ not occur in the kieserite structure type?

There are three structures of the form $[M^{3+}(T^{5+}O_4)(H_2O)]$: schubnelite, $[Fe^{3+}(VO_4)(H_2O)]$, and the synthetic phases $[V^{3+}(PO_4)(H_2O)]$ and $[Mn^{3+}(PO_4)(H_2O)]$. The synthetic phases crystallize in the kieserite arrangement, whereas schubnelite does not. The key to the occurrence of the kieserite arrangement is the local coordination around the (H_2O) group. In the kieserite structure-type, the (H_2O) group is bonded to two $^{[6]}M^{3+}$ cations. If the $(M^{3+}O6)$ octahedra are regular, the bridging anion [ostensibly (H_2O)] receives $0.5 \times 2 = 1$ vu from the coordinating M^{3+} cations. However, this violates the valence-sum rule (Brown 1981; Hawthorne 1994, 1997) if the linking anion is (H_2O). The only way that such an

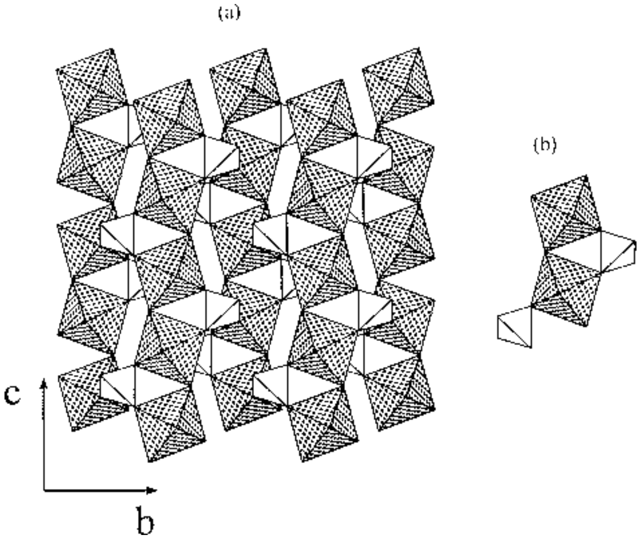

FIGURE 2. The kieserite structure type. **(a)** The framework with the characteristic 7 Å octahedral chains. **(b)** The FBB of the kieserite structure type.

TABLE 5. Bond valences for $X(PO_4)H_2O$

	X	P	H1	Sum
		$X = Mn^{3+}$		
O1	0.71 ×2Ø	1.26 ×2Ø	1.97	
O2	0.67 ×2Ø	1.25 ×2Ø	0.20	2.12
O3	0.24 ×2Ø→		0.80 ×2Ø→	2.08
Sum	3.24	5.07	1.00	
		$X = V^{3+}$		
O1	0.54 ×2↓	1.27 × 2↓		1.81
O2	0.58 ×2↓	1.13 × 2↓	0.30	2.01
O3	0.33 ×2↓→		0.70 ×2↓→	2.16
Sum	2.90	4.80	1.00	

Notes: All bond-valence curves are from Brown and Altermatt (1985).

M^{3+}-(H_2O)-M^{3+} linkage can occur is if the M^{3+}-(H_2O) bonds are greatly elongated. The [$M^{3+}(TO_4)$(H_2O)] structures with the kieserite structure have M = V^{3+} and Mn^{3+}. These cations have $3d^2$ and $3d^4$ electron arrangements, respectively. For both these cations, there is an orbital degeneracy (in the t_{2g} and e_g states, respectively), and hence both can decrease their energy by spontaneous distortions, the well known Jahn-Teller distortion of Mn^{3+} (e.g., Burns et al. 1994b). The M^{3+}-(H_2O) distances in these two structures are 2.154(3) and 2.284(3) Å, respectively, compared with the mean M^{3+}-O(meridional) distances of 1.958(4) and 1.897(3) Å, respectively. The resulting incident bond-valence sums around the bridging anion groups are compatible with the occurrence of H_2O at this site (Table 5).

The situation for [$Fe^{3+}(V^{5+}O_4)(H_2O)$] is significantly different. Trivalent iron has a $3d^5$ electron arrangement, and there is no specific electron mechanism driving the distortion required for H_2O to bridge two octahedra. Hence schubnelite cannot crystallize in the kieserite arrangement.

Chemical environment

Evans and Garrels (1958) described the occurrence of vanadate minerals in the Colorado Plateau ore deposits. They showed that the polymerization of V^{4+}/V^{5+} polyhedra increases with decreasing pH. The structure of schubnelite contains isolated (VO_4) tetrahedra, so that it can be assumed that schubnelite and the associated fervanite $Fe_4(VO_4)_4·5H_2O$ were formed in a basic environment at the oxidized zone of the uranium deposit in Mounana, Gabon.

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