

WERNERBAURITE, $\{[\text{Ca}(\text{H}_2\text{O})_7]_2(\text{H}_2\text{O})_2(\text{H}_3\text{O})_2\}\{\text{V}_{10}\text{O}_{28}\}$, AND SCHINDLERITE, $\{[\text{Na}_2(\text{H}_2\text{O})_{10}](\text{H}_3\text{O})_4\}\{\text{V}_{10}\text{O}_{28}\}$, THE FIRST HYDRONIUM-BEARING DECAVANADATE MINERALS

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ABSTRACT

Wernerbaurite, $\{[\text{Ca}(\text{H}_2\text{O})_7]_2(\text{H}_2\text{O})_2(\text{H}_3\text{O})_2\}\{\text{V}_{10}\text{O}_{28}\}$, and schindlerite, $\{[\text{Na}_2(\text{H}_2\text{O})_{10}](\text{H}_3\text{O})_4\}\{\text{V}_{10}\text{O}_{28}\}$, are new mineral species from the St. Jude mine, Slick Rock district, San Miguel County, Colorado, U.S.A. Crystals of wernerbaurite are tabular on {100} with stepped faces and square to octagonal outlines, up to about 1 mm in maximum dimension; the crystals are yellow-orange and the streak is yellow. The mineral displays a subadamantine luster, and is transparent; it does not fluoresce in short- or long-wave ultraviolet radiation. Wernerbaurite has a hardness of about 2, a brittle tenacity, and irregular fracture; two good cleavages, {100} and {010}, were observed. The density calculated from the empirical formula using the single-crystal cell data is 2.352 g cm⁻³. Wernerbaurite is biaxial (-), with α 1.745(3), β 1.780(3), and γ 1.795(3); 2V 66(2)° (white light). Dispersion is $r > v$, very strong. Optical orientation: $X \wedge a = 29^\circ$, $Y \wedge c = 44^\circ$, $Z \wedge b = 46^\circ$; pleochroism: X, Z = yellow, Y = orange; $X = Z < Y$. Electron probe microanalysis and the crystal structure solution provided the empirical formula $\{(\text{Ca}_{1.88}\text{Na}_{0.14}\text{K}_{0.03}\text{Sr}_{0.02})_{22.07}(\text{H}_2\text{O})_{15.95}(\text{H}_3\text{O})_{2.05}\}\{\text{V}_{10}\text{O}_{28}\}$ (based on $\text{V}^{5+} = 10$ and $\text{O} = 46$). The simplified structural formula of wernerbaurite is $\{[\text{Ca}(\text{H}_2\text{O})_7]_2(\text{H}_2\text{O})_2(\text{H}_3\text{O})_2\}\{\text{V}_{10}\text{O}_{28}\}$. Wernerbaurite is triclinic, $P\bar{1}$, with a 9.7212(6), b 10.2598(8), c 10.5928(8) Å, α 89.999(6)°, β 77.083(7)°, γ 69.887(8)°, V 963.55(12) Å³, and $Z = 1$. The strongest four lines in the diffraction pattern [d in Å(1)(hkl)] are: 10.32(100)(001), 8.88(95)(100), 9.64(92)(010), and 6.881(70)(111). The atomic arrangement of wernerbaurite was refined to $R_1 = 0.0341$ on the basis of 3,440 diffractions with $F_o > 4\sigma F$. The structural unit is a decavanadate polyanion, $(\text{V}_{10}\text{O}_{28})^{6-}$. The interstitial unit linking the structural units has a composition of $\{[\text{Ca}(\text{H}_2\text{O})_7]_2(\text{H}_2\text{O})_2(\text{H}_3\text{O})_2\}^{6+}$, and is formed of an isolated $[\text{Ca}(\text{H}_2\text{O})_7]^{2+}$ polyhedron, a $(\text{H}_3\text{O})^+$ ion, and an isolated H_2O molecule. Wernerbaurite is named in honor of Prof. Dr. rer. nat. Werner H. Baur for his long, productive and distinguished career in mineralogical crystallography.

Crystals of schindlerite are tabular and commonly occur in stacked parallel intergrowths up to 0.3 mm in maximum dimension; the crystals are orange with a yellow streak. Schindlerite displays a subadamantine luster, and is transparent; it does not fluoresce in short- or long-wave ultraviolet radiation. Schindlerite has a hardness of about 2, a brittle tenacity, and one good cleavage on {010}. The density calculated from the empirical formula using the single-crystal cell data is 2.461 g cm⁻³. Schindlerite is biaxial (+), with α 1.74 (est), β 1.790(5), and γ 1.875 (calc); 2V (meas) = 78.1° (white light). Dispersion is $r > v$, very strong. The optical orientation is $X \wedge b = 25^\circ$, $Y \wedge c = 12^\circ$, $Z \wedge a = 3^\circ$. No pleochroism was perceptible. Electron probe microanalysis and the crystal structure solution provided the empirical formula $\{(\text{Na}_{1.58}\text{K}_{0.35}\text{Ca}_{0.02}\text{Sr}_{0.01})_{21.96}(\text{H}_2\text{O})_{10.00}\}(\text{H}_3\text{O})_4\}\{\text{V}_{10}\text{O}_{28}\}$ (based on $\text{V}^{5+} = 10$ and $\text{O} = 42$). The simplified structural formula of schindlerite is $\{[\text{Na}_2(\text{H}_2\text{O})_{10}](\text{H}_3\text{O})_4\}\{\text{V}_{10}\text{O}_{28}\}$. Schindlerite is triclinic, $P\bar{1}$, with a 8.5143(3), b 10.4283(5), c 11.2827(8) Å, α 68.595(5)°, β 87.253(6)°, γ 67.112(5)°, V 854.08(8) Å³, and $Z = 1$. The strongest four lines in the diffraction pattern [d in Å(1)(hkl)] are: 8.68(100)(010, 011), 10.51(94)(001), 7.70(86)(100, 110), and 6.73(61)(111, $\bar{1}01$). The atomic arrangement of schindlerite was refined to $R_1 = 0.0399$. The structural unit is a decavanadate

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polyanion, $(V_{10}O_{28})^{6-}$. The interstitial unit linking the structural units has a composition of $\{[Na_2(H_2O)_{10}](H_3O)_4\}^{6+}$, and is formed of a $[Na_2(H_2O)_{10}]$ dimer decorated with four hydronium ions. As in wernerbaurite, an extensive network of hydrogen bonding links the interstitial unit to the structural unit in schindlerite. Schindlerite is named in honor of Dr. Michael Schindler, Associate Professor for Environmental Mineralogy at Laurentian University, Sudbury, Ontario, who has contributed greatly to our understanding of vanadium mineralogy. Wernerbaurite and schindlerite are the first hydronium-bearing decavanadate minerals, and both minerals are natural analogs of previously described synthetic phases.

Keywords: wernerbaurite, schindlerite; new mineral; decavanadate; hydronium; crystal structure; St. Jude mine, Slick Rock district, Colorado

INTRODUCTION

The uranium and vanadium deposits of western Colorado and eastern Utah have been a rich source of ore for these metals. The uranium- and vanadium-bearing minerals occur in bedded or roll-front deposits in the sandstone of the Salt Wash member of the Jurassic Morrison Formation (Carter & Gualtieri 1965, Shawe 2011). Recent collecting at these deposits by one of the authors (JM) has revealed numerous secondary vanadium minerals that result from oxidation of vanadium ore bodies under near-surface conditions. With the exceptions of martyrite, $Zn_3(V_2O_7)(OH)_2 \cdot 2H_2O$ (Kampf & Steele 2008b), which contains the $(V_2O_7)^{4-}$ divanadate group, and dickthomssenite, $Mg(V_2O_6) \cdot 7H_2O$ (Hughes *et al.* 2001), and calciodelrioite, $Ca(VO_3)_2(H_2O)_4$ (Kampf *et al.* 2012a), which contain $(VO_3)^-$ vanadate chains, all of the recently described species contain the decavanadate anionic complex, $(V_{10}O_{28})^{6-}$, found in the pascoite family of minerals (Hughes *et al.* 2005). Table 1 lists the minerals of the pascoite family, including those that contain the $(V_{10}O_{28})^{6-}$ polyanion *sensu stricto*, those that contain $(H_xV_{10}O_{28})^{(6-x)-}$ protonated decavanadate polyanions, and that which contains the mixed-valence $[(V^{4+}V^{5+}_9)O_{28}]^{7-}$ polyanion. Recent collecting also yielded well-crystallized examples of the decavanadate huemulite,

$\{[Na_4(H_2O)_{14}][Mg(H_2O)_6](H_2O)_4\}\{V_{10}O_{28}\}$ (Gordillo *et al.* 1966), which have proved suitable for structure determination (Colombo *et al.* 2011). The only other previously known pascoite-family mineral, hummerite, $\{[KMg(H_2O)_8]_2\}\{V_{10}O_{28}\}$ (Hughes *et al.* 2002), also comes from these deposits, as does sherwoodite, which contains a mixed-valence 14-vanadoaluminate complex anion of $(AlV_{14}O_{40})^{9-}$ composition (Evans & Konnerth 1978).

Herein we describe two new secondary minerals from the uranium and vanadium deposits of western Colorado and eastern Utah, the first decavanadate minerals found to contain the hydronium ion. The new species were discovered in the St. Jude mine, Slick Rock district, San Miguel County, Colorado, U.S.A. The minerals are named *wernerbaurite* and *schindlerite* in honor of Prof. Dr. rer. nat. Werner H. Baur (b. 1931), and Dr. Michael Schindler (b. 1966), respectively. Dr. Baur is known for his long, productive and distinguished career in mineralogical crystallography. He has had appointments at various institutions, but most notably he served with distinction on the faculty of the Geological Sciences Department of the University of Illinois, Chicago from 1965 to 1986, in positions as Associate Professor, Professor, Department Head, and Associate Dean. Dr. Schindler has worked extensively on the structures of vanadium minerals, including

TABLE 1. THE PASCOITE FAMILY OF MINERALS

| | $\{V_{10}O_{28}\}^{6-}$ Decavanadates | |
|------------------|--|------------------------------|
| huemulite | $\{[Na_4(H_2O)_{14}][Mg(H_2O)_6](H_2O)_4\}\{V_{10}O_{28}\}$ | Colombo <i>et al.</i> (2011) |
| hughesite | $\{[Na_3(H_2O)_{12}][Al(H_2O)_6](H_2O)_4\}\{V_{10}O_{28}\}$ | Rakovan <i>et al.</i> (2011) |
| hummerite | $\{[KMg(H_2O)_8]_2\}\{V_{10}O_{28}\}$ | Hughes <i>et al.</i> (2002) |
| lasalite | $\{[Mg(H_2O)_6]_2[Na_2(H_2O)_6](H_2O)_2\}\{V_{10}O_{28}\}$ | Hughes <i>et al.</i> (2008) |
| magnesiopascoite | $\{[Mg(H_2O)_6][Ca_2(H_2O)_5]_2\}\{V_{10}O_{28}\}$ | Kampf & Steele (2008a) |
| pascoite | $\{Ca_3(H_2O)_{17}\}\{V_{10}O_{28}\}$ | Hughes <i>et al.</i> (2005) |
| postite | $\{[Mg(H_2O)_6][Al_2(OH)_2(H_2O)_6](H_2O)_{13}\}\{V_{10}O_{28}\}$ | Kampf <i>et al.</i> (2012b) |
| schindlerite | $\{[Na_2(H_2O)_{10}](H_3O)_4\}\{V_{10}O_{28}\}$ | This work |
| wernerbaurite | $\{[Ca(H_2O)_7]_2(H_2O)_2(H_3O)_2\}\{V_{10}O_{28}\}$ | This work |
| | $\{H_xV_{10}O_{28}\}^{(6-x)-}$ Protonated Decavanadates | |
| gunterite | $\{[Na_4(H_2O)_{16}](H_2O)_6\}\{H_2V_{10}O_{28}\}$ | Kampf <i>et al.</i> (2011b) |
| rakovanite | $\{[Na_3(H_2O)_{15}](H_3O)_1\}\{V_{10}O_{28}\}$ | Kampf <i>et al.</i> (2011a) |
| | Mixed-Valence $\{(V^{4+}_xV^{5+}_{10-x})O_{28}\}^{(6+x)-}$ Vanadylvanadate | |
| nashite | $\{[Na_{31}Ca_2(H_2O)_{22}](H_2O)_2\}\{(V^{4+}_xV^{5+}_9)O_{28}\}$ | Kampf <i>et al.</i> (2013) |

bobjonesite, hummerite, orthominasragrite, pascoite, and schubnelite, as well as other inorganic vanadium phases, and he was the 2006 recipient of the Young Scientist Award from the Mineralogical Association of Canada. Both Dr. Baur and Dr. Schindler have agreed to have the minerals named in their honor.

The new minerals and mineral names were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (wernerbaurite, IMA 2012–064; schindlerite, IMA 2012–063). Three cotype specimens of wernerbaurite are deposited in the collections of the Natural History Museum of Los Angeles County, catalogue numbers 64002, 64003, and 64004, and three cotype specimens of schindlerite are deposited in the same collection under catalogue numbers 64005, 64006, and 64007.

OCCURRENCE

Wernerbaurite and schindlerite were found in the western portion of the St. Jude mine, Gypsum Valley, Slick Rock district, San Miguel County, Colorado, U.S.A. (38° 04' 31.93"N; 108°48'52.74"W). The discovery site is a stope not far from the interconnected West Sunday and Sunday mines. All three mines are currently inactive and their entrances are sealed. The new minerals are rare. The minerals were found growing on corvusite-montroseite-bearing sandstone blocks and are closely associated with calciodelirioite (Kampf *et al.* 2012a), gypsum, huemulite, hughesite (Rakovan *et al.* 2011), metarossite, pascoite, and rossite; the minerals have not been found on the same specimen. Other minerals found in the same area in the St. Jude mine include delirioite, hendersonite, nashite (Kampf *et al.* 2013), and powellite. Other minerals found nearby in adjacent areas of the West Sunday mine are andersonite, gunterite (Kampf *et al.* 2011b), hewettite, munirite,

natrozippeite, pyrite, rakovanite (Kampf *et al.* 2011a), sherwoodite, and tyuyamunitite.

The minerals form from the oxidation of montroseite-corvusite assemblages in a moist environment. Mining operations have exposed unoxidized and oxidized phases. Under ambient temperatures and generally oxidizing near-surface environments, water reacts with pyrite in the deposit to form aqueous solutions with relatively low pH. The various secondary vanadate phases that formed depend upon the Eh-pH conditions and presence of other cations (*e.g.*, Na⁺, Ca²⁺, Mg²⁺, Al³⁺) (Evans and Garrels 1958).

Both minerals have been previously synthesized; wernerbaurite is the natural equivalent of the synthetic phase described by Strukan *et al.* (1999), and schindlerite is the natural equivalent of the synthetic phase described by Zhang *et al.* (1985).

PHYSICAL PROPERTIES

Wernerbaurite

Crystals of wernerbaurite occur in thin tablets flattened on {100}, with stepped faces and square to octagonal outlines, up to ~1 mm in maximum dimension. Crystals exhibit the forms {100}, {010}, {001}, {011}, and {111}. Crystals are often aligned approximately perpendicular to the surface on which they are growing and subparallel to one another (Figs. 1 and 2).

Wernerbaurite is yellow-orange with a yellow streak. The mineral displays a subadamantine luster, and is transparent; it does not fluoresce in short- or long-wave ultraviolet radiation. Wernerbaurite has a Mohs hardness of about 2, a brittle tenacity, and two good cleavages, {100} and {010}. The density could not be measured because the mineral dissolves in available aqueous density liquids, *e.g.*, Clerici solution and an aqueous solution of sodium polytungstate, and there

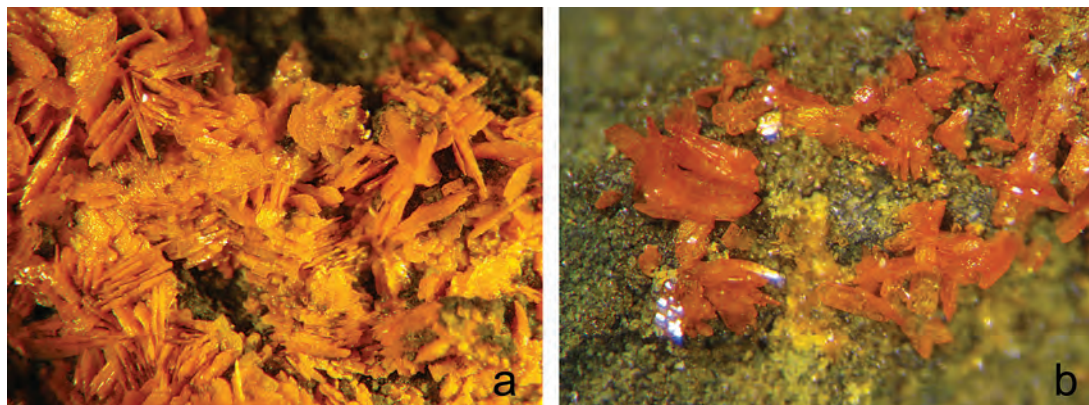


Fig. 1. Crystals of (a) wernerbaurite (to 1 mm) and (b) schindlerite (to 0.5 mm).

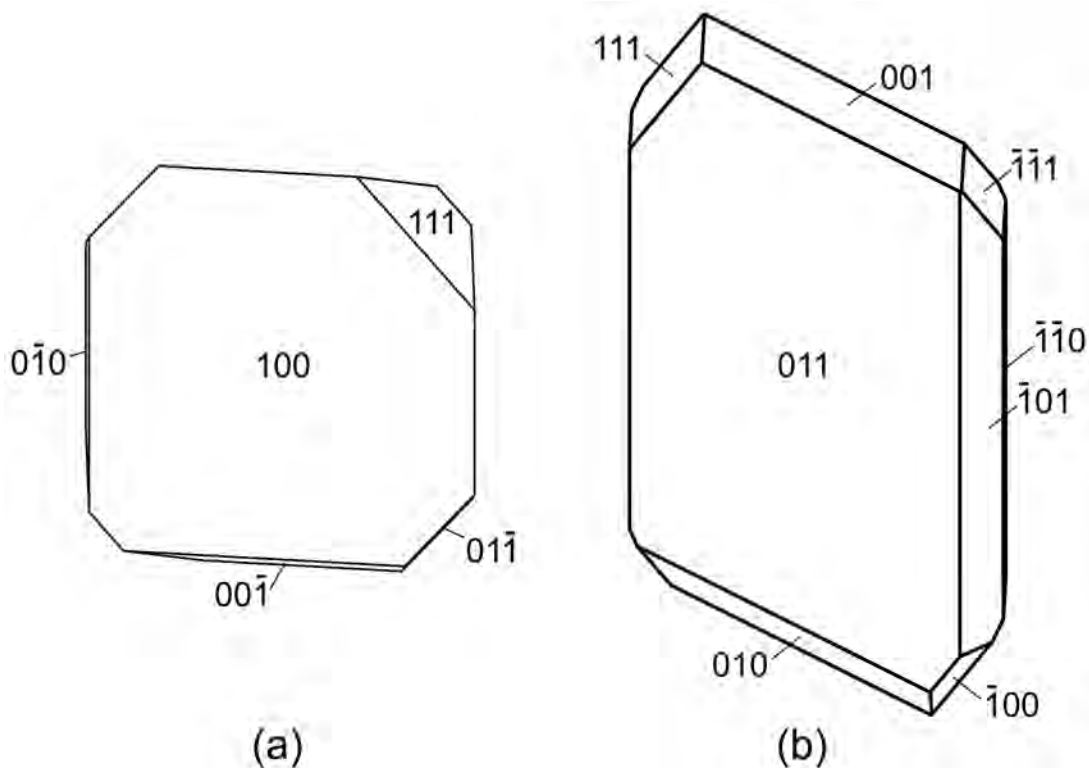


Fig. 2. Crystal drawings (clinographic projection) of (a) wernerbaurite (standard orientation) and (b) schindlerite (nonstandard orientation, with $[111]$ vertical).

is insufficient material for direct measurement. The density calculated from the empirical formula and the refined cell dimensions from the single-crystal study is 2.352 g/cm^3 . Wernerbaurite dissolves instantly in cold, dilute HCl and slowly in water.

Schindlerite

Crystals of schindlerite are tabular on $\{011\}$ and often occur in stacked parallel intergrowths. Individual crystals are up to 0.3 mm in maximum dimension and exhibit the forms $\{100\}$, $\{010\}$, $\{001\}$, $\{110\}$, $\{011\}$, $\{111\}$, and $\{1\bar{1}\bar{1}\}$ (Figs. 1 and 2). The mineral is orange with a yellow streak. It displays a subadamantine luster, is transparent, and does not fluoresce in short- or long-wave ultraviolet radiation. Schindlerite has a Mohs hardness of about 2, a brittle tenacity, and one good cleavage on $\{010\}$. The density could not be measured because the mineral dissolves in available aqueous density liquids and there is insufficient material for direct measurement. The density calculated from the empirical formula and the refined cell dimensions from the single-crystal study is 2.461 g/cm^3 . Schindlerite

dissolves instantly in cold, dilute HCl and slowly in water.

OPTICAL PROPERTIES

Wernerbaurite

The optical properties of wernerbaurite and schindlerite were determined in white light. Wernerbaurite is biaxial (-). The indices of refraction are $\alpha = 1.745(3)$, $\beta = 1.780(3)$, and $\gamma = 1.795(3)$; the optical orientation is $X \wedge a = 29^\circ$, $Y \wedge c = 44^\circ$, $Z \wedge b = 46^\circ$. The value of $2V$ was measured on a spindle stage using conoscopy, yielding $66(2)^\circ$; $2V(\text{calc}) = 65.3^\circ$. Dispersion is $r > v$, very strong; note that, because one optic axis is only about 10° from the perpendicular to the plane of the tablet, the very strong dispersion produces anomalous red-orange and blue-green interference colors near the extinction positions. The mineral is pleochroic: $X, Z = \text{yellow}$, $Y = \text{orange}$; $X = Z < Y$. The calculated Gladstone-Dale compatibility, $1 - (K_p/K_c)$, is superior (0.001) using the empirical formula and the refined cell dimensions from the single-crystal study.

Schindlerite

Schindlerite is biaxial (+). The indices of refraction are $\alpha = 1.74$ (est), $\beta = 1.790(5)$ and $\gamma = 1.875$ (calc). The value of $2V$ was determined from spindle stage extinction data using EXCALIBRW (Gunter *et al.* 2004) providing $78(1)^\circ$. The optical determinations were problematic for several reasons, including unfavorable orientation of X and the fact that crystals react in index liquids with $n > 1.80$. The unfavorable orientation of X allowed us only to estimate α . Because the crystals react in index liquids with $n > 1.80$, γ was calculated from α , β , and $2V$. Dispersion is $r > v$, very strong. The optical orientation is $X \wedge \mathbf{b} = 25^\circ$, $Y \wedge \mathbf{c} = 12^\circ$, $Z \wedge \mathbf{a} = 3^\circ$. No pleochroism was perceptible. The calculated Gladstone-Dale compatibility, $1 - (K_p/K_c)$, is superior (0.019) for the empirical formula and the refined cell dimensions from the single-crystal study.

CHEMICAL ANALYSIS OF
WERNERBAURITE AND SCHINDLERITE

Chemical analyses of wernerbaurite ($n = 12$ from three crystals) and schindlerite ($n = 21$ from nine crystals) were performed at the University of Utah using a Cameca SX-50 electron microprobe with four wavelength-dispersive spectrometers (Table 2). Analytical conditions were 15 KeV accelerating voltage, 10 nA beam current and a beam diameter of 10–20 μm . Counting times were 10 seconds for each element except Na, which was analyzed with five second count times. In the analytical routine, Na, Ca, and V were counted simultaneously, *i.e.*, first on their respective spectrometers. Raw X-ray intensities were corrected

for matrix effects with a phi-rho-z algorithm (Pouchou & Pichoir 1991).

There was no visible damage to wernerbaurite or schindlerite from the electron beam; however, as is typical of decavanadate phases (*i.e.*, postite, rakovanite, hughesite, gunterite, and lasalite), wernerbaurite and schindlerite partially dehydrate under the vacuum of the microprobe chamber. This H_2O loss results in higher concentrations for the remaining constituents than are to be expected for the fully hydrated phase. Because insufficient material is available for a direct determination of H_2O , the H_2O content has been calculated based upon the structure determination. The analyzed constituents (Table 2) have subsequently been normalized to provide a total of 100% when combined with the calculated H_2O , in order to account for the concentration increases in cations due to dehydration.

For wernerbaurite, the empirical formula (based on $\text{V}^{5+} = 10$ and $\text{O} = 46$) is $\{(\text{Ca}_{1.88}\text{Na}_{0.14}\text{K}_{0.03}\text{Sr}_{0.02})_{\Sigma 2.07}(\text{H}_2\text{O})_{15.95}(\text{H}_3\text{O})_{2.05}\}\{\text{V}_{10}\text{O}_{28}\}$, and the simplified structural formula is $\{[\text{Ca}(\text{H}_2\text{O})_7]_2(\text{H}_2\text{O})_2(\text{H}_3\text{O})_2\}\{\text{V}_{10}\text{O}_{28}\}$.

For schindlerite, the empirical formula (based on $\text{V}^{5+} = 10$ and $\text{O} = 42$) is: $\{[(\text{Na}_{1.58}\text{K}_{0.35}\text{Ca}_{0.02}\text{Sr}_{0.01})_{\Sigma 1.96}(\text{H}_2\text{O})_{10.00}][(\text{H}_3\text{O})_4]\}\{\text{V}_{10}\text{O}_{28}\}$, and the simplified structural formula is $\{[\text{Na}_2(\text{H}_2\text{O})_{10}](\text{H}_3\text{O})_4\}\{\text{V}_{10}\text{O}_{28}\}$.

CRYSTAL STRUCTURE: EXPERIMENTAL

Powder and single-crystal X-ray diffraction data were obtained with a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer using monochromatized $\text{MoK}\alpha$ radiation. The powder data presented in Table 3 for wernerbaurite and schindlerite are in good

TABLE 2. CHEMICAL ANALYSES OF WERNERBAURITE AND SCHINDLERITE

| wernerbaurite | | | | | | |
|------------------------|--------------------|-------------|------|--------------------|------------|-------------------|
| Oxide | wt.% | Range | S.D. | Norm. wt.% | Ideal wt.% | Probe Standard |
| Na_2O | 0.37 | 0.13–0.91 | 0.25 | 0.33 | | albite |
| K_2O | 0.10 | 0.05–0.13 | 0.03 | 0.09 | | sanidine |
| CaO | 8.76 | 8.16–9.25 | 0.32 | 7.70 | 8.22 | diopside |
| SrO | 0.16 | 0.04–0.30 | 0.07 | 0.14 | | Sr titanate (syn) |
| V_2O_5 | 75.76 | 74.25–77.72 | 1.09 | 66.63 | 66.68 | Y vanadate (syn) |
| H_2O | 14.85 [†] | | | 25.11 [§] | 25.10 | |
| Total | 100 | | | 100 | 100 | |
| schindlerite | | | | | | |
| Oxide | wt.% | Range | S.D. | Norm. wt.% | Ideal wt.% | Probe Standard |
| Na_2O | 4.08 | 3.47–4.87 | 0.36 | 3.87 | 4.92 | albite |
| K_2O | 1.37 | 1.19–1.69 | 0.14 | 1.30 | | sanidine |
| CaO | 0.08 | 0.02–0.19 | 0.04 | 0.08 | | diopside |
| SrO | 0.10 | 0.00–0.16 | 0.10 | 0.09 | | Sr titanate (syn) |
| V_2O_5 | 75.80 | 73.16–81.60 | 2.32 | 71.88 | 72.20 | Y vanadate (syn) |
| H_2O | 18.57 [†] | | | 22.78 [§] | 22.88 | |
| Total | 100 | | | 100 | 100 | |

[†] By difference; [§] Difference of normalized oxides.

TABLE 3. POWDER X-RAY DATA FOR WERNERBAURITE AND SCHINDLERITE

| l_{obs} | $d_{\text{obs}}(\text{\AA})$ | $d_{\text{calc}}(\text{\AA})$ | l_{calc} | hkl | l_{obs} | $d_{\text{obs}}(\text{\AA})$ | $d_{\text{calc}}(\text{\AA})$ | l_{calc} | hkl |
|------------------|------------------------------|-------------------------------|-------------------|-------------------|------------------|------------------------------|-------------------------------|-------------------|-------------------|
| wernerbaurite | | | | | | | | | |
| 100 | 10.32(4) | 10.2883 | 100 | 001 | | | 2.8069 | 3 | $2\bar{1}3$ |
| 92 | 9.64(5) | 9.6001 | 98 | 010 | | | 2.7280 | 2 | $1\bar{3}1$ |
| 95 | 8.88(2) | 8.8660 | 96 | 100 | | | 2.7192 | 8 | $\bar{3}10$ |
| 58 | 8.10(2) | 8.0892 | 64 | 110 | 20 | 2.714(6) | 2.7073 | 6 | $3\bar{3}1$ |
| | | 7.6810 | 9 | 101 | | | 2.6964 | 2 | 330 |
| 10 | 7.48(8) | 7.3328 | 8 | 011 | | | 2.6953 | 2 | $\bar{1}13$ |
| 70 | 6.881(16) | 6.8663 | 58 | 111 | | | 2.6858 | 4 | 023 |
| | | 6.7423 | 18 | 011 | 9 | 2.661(12) | 2.6764 | 2 | 301 |
| 39 | 6.031(14) | 6.0425 | 29 | $\bar{1}01$ | | | 2.6444 | 5 | 104 |
| | | 5.9497 | 16 | $\bar{1}\bar{1}1$ | 23 | 2.550(3) | 2.5541 | 13 | $3\bar{1}2$ |
| 14 | 5.41(2) | 5.3924 | 14 | $\bar{1}\bar{1}1$ | | | 2.5399 | 2 | $\bar{1}31$ |
| | | 5.0288 | 2 | 120 | | | 2.5372 | 6 | $1\bar{1}4$ |
| 5 | 5.01(6) | 4.9955 | 3 | 102 | 12 | 2.430(4) | 2.4451 | 3 | $\bar{2}\bar{2}3$ |
| 17 | 4.80(5) | 4.8000 | 15 | 020 | | | 2.4241 | 6 | 133 |
| 12 | 4.69(8) | 4.7058 | 4 | 210 | | | 2.4190 | 2 | $\bar{1}33$ |
| | | 4.7015 | 6 | $0\bar{1}2$ | 4 | 2.348(16) | 2.3508 | 2 | $0\bar{2}4$ |
| | | 4.6608 | 3 | 112 | 8 | 2.30(2) | 2.3076 | 6 | $\bar{1}42$ |
| 7 | 4.51(6) | 4.5535 | 3 | $\bar{1}11$ | 4 | 2.27(7) | 2.2815 | 4 | 401 |
| | | 4.4768 | 2 | 201 | | | 2.2474 | 6 | 033 |
| 4 | 4.38(8) | 4.3836 | 2 | 012 | | | 2.2472 | 2 | $3\bar{2}1$ |
| | | 4.0505 | 9 | $\bar{1}02$ | 23 | 2.242(8) | 2.2384 | 8 | 402 |
| 11 | 4.06(3) | 4.0446 | 3 | 220 | | | 2.2369 | 5 | $\bar{2}\bar{3}3$ |
| | | 3.9733 | 4 | $\bar{2}\bar{1}1$ | | | 2.2182 | 3 | $\bar{2}42$ |
| 17 | 3.97(2) | 3.9672 | 13 | 221 | 13 | 2.196(5) | 2.1918 | 10 | 024 |
| | | 3.8405 | 3 | 202 | | | 2.1038 | 5 | 403 |
| 8 | 3.77(2) | 3.7589 | 6 | $\bar{2}01$ | 11 | 2.099(5) | 2.0915 | 2 | 234 |
| | | 3.7087 | 2 | $\bar{1}20$ | | | 2.0748 | 2 | $\bar{2}43$ |
| 4 | 3.66(3) | 3.6664 | 3 | $0\bar{2}2$ | | | 2.0697 | 6 | $\bar{1}43$ |
| | | 3.5894 | 2 | $\bar{2}\bar{2}1$ | | | 2.0654 | 7 | $4\bar{1}1$ |
| 6 | 3.454(19) | 3.4332 | 4 | 222 | 32 | 2.059(2) | 2.0577 | 9 | 134 |
| | | 3.3379 | 4 | 113 | | | 2.0535 | 3 | $\bar{1}\bar{3}4$ |
| 11 | 3.339(12) | 3.3191 | 4 | $0\bar{1}3$ | | | 2.0404 | 5 | $4\bar{1}2$ |
| | | 3.2473 | 2 | 131 | 26 | 1.9869(19) | 1.9837 | 19 | $\bar{2}43$ |
| | | 3.2281 | 4 | 311 | | | 1.9541 | 2 | 424 |
| 21 | 3.219(8) | 3.2253 | 10 | $\bar{1}\bar{1}3$ | 13 | 1.927(4) | 1.9273 | 7 | 034 |
| | | 3.2000 | 3 | 030 | | | 1.9157 | 2 | 511 |
| | | 3.1814 | 2 | 230 | 6 | 1.897(9) | 1.9019 | 2 | 512 |
| | | 3.1556 | 7 | $\bar{2}\bar{1}2$ | 12 | 1.815(5) | 1.8148 | 10 | 502 |
| 25 | 3.126(7) | 3.1311 | 10 | $0\bar{3}1$ | 6 | 1.794(11) | 1.7942 | 5 | 144 |
| | | 3.1172 | 3 | 231 | 11 | 1.761(3) | 1.7628 | 5 | $\bar{5}\bar{3}1$ |
| | | 3.0920 | 5 | 203 | 4 | 1.716(7) | 1.7147 | 2 | 006 |
| | | 3.0810 | 6 | 321 | | | 1.7099 | 2 | 260 |
| | | 3.0407 | 2 | 320 | | | 1.6976 | 2 | $\bar{4}21$ |
| 29 | 3.028(5) | 3.0389 | 6 | 301 | 7 | 1.687(4) | 1.6874 | 4 | $\bar{2}61$ |
| | | 3.0212 | 18 | $\bar{2}02$ | 7 | 1.654(5) | 1.6528 | 4 | 332 |
| | | 2.9671 | 2 | $\bar{2}\bar{3}1$ | | | 1.6373 | 2 | $\bar{2}44$ |
| | | 2.9553 | 5 | 300 | 6 | 1.632(6) | 1.6297 | 3 | $\bar{1}\bar{1}6$ |
| 14 | 2.911(9) | 2.8975 | 11 | 123 | 4 | 1.574(5) | 1.5749 | 2 | 623 |
| | | 2.8752 | 3 | 302 | 7 | 1.546(6) | 1.5384 | 4 | 535 |
| | | 2.8507 | 4 | $\bar{2}\bar{2}1$ | 5 | 1.528(11) | 1.5203 | 2 | 640 |
| 29 | 2.842(5) | 2.8452 | 14 | $\bar{1}\bar{3}2$ | 7 | 1.507(5) | 1.5062 | 2 | 245 |
| | | 2.8181 | 7 | 232 | | | | | |

TABLE 3 (continued).

| l_{obs} | $d_{\text{obs}} (\text{\AA})$ | $d_{\text{calc}} (\text{\AA})$ | l_{calc} | $h k l$ | l_{obs} | $d_{\text{obs}} (\text{\AA})$ | $d_{\text{calc}} (\text{\AA})$ | l_{calc} | $h k l$ |
|------------------|-------------------------------|--------------------------------|-------------------|---------------------|------------------|-------------------------------|--------------------------------|-------------------|---------------------|
| schindlerite | | | | | | | | | |
| 94 | 10.51(4) | 10.4412 | 100 | 0 0 1 | 19 | 2.328(3) | 2.3259 | 19 | $\bar{2} \bar{3} 2$ |
| 100 | 8.68(2) | 8.9009 | 46 | 0 1 0 | 9 | 2.233(5) | 2.3235 | 3 | $\bar{2} \bar{2} 3$ |
| | | 8.5449 | 90 | 0 1 1 | | | 2.2343 | 5 | 1 4 4 |
| 86 | 7.70(2) | 7.7967 | 60 | 1 0 0 | 29 | 2.131(2) | 2.2310 | 7 | 3 0 2 |
| | | 7.5460 | 60 | 1 1 0 | | | 2.1362 | 11 | 0 4 4 |
| 61 | 6.73(2) | 6.8473 | 37 | 1 1 1 | 7 | 2.062(6) | 2.1293 | 17 | $\bar{3} \bar{1} 1$ |
| | | 6.6038 | 45 | $\bar{1} 0 1$ | | | 2.0980 | 6 | $\bar{3} \bar{3} 2$ |
| 6 | 5.79(7) | 5.7837 | 6 | 0 $\bar{1}$ 1 | 13 | 1.994(3) | 2.0568 | 3 | $\bar{3} \bar{2} 3$ |
| 3 | 5.47(15) | 5.4952 | 2 | 0 1 2 | | | 2.0015 | 4 | $\bar{2} \bar{3} 3$ |
| 7 | 5.19(6) | 5.2206 | 5 | 0 0 2 | 12 | 1.935 (3) | 1.9875 | 5 | 1 4 5 |
| 9 | 4.81(3) | 4.7967 | 4 | 0 2 1 | | | 1.9809 | 4 | 3 0 3 |
| 7 | 4.50(4) | 4.4505 | 4 | 0 2 0 | 10 | 1.858(3) | 1.9453 | 5 | $\bar{3} \bar{1} 2$ |
| 12 | 4.26(2) | 4.2724 | 3 | 0 2 2 | | | 1.9270 | 6 | 0 4 5 |
| 4 | 4.07(5) | 4.0639 | 3 | 1 $\bar{1}$ 1 | 15 | 1.769(2) | 1.8593 | 8 | $\bar{3} \bar{3} 3$ |
| 24 | 3.815(9) | 3.8178 | 13 | 2 2 1 | | | 1.8343 | 3 | $\bar{3} \bar{4} 2$ |
| | | 3.7908 | 10 | $\bar{2} 0 1$ | 1.7824 | 5 | 1 5 5 | | |
| 10 | 3.445(16) | 3.7561 | 3 | 0 1 3 | 5 | 1.693(7) | 1.7728 | 2 | 3 2 5 |
| | | 3.4804 | 5 | 0 0 3 | | | 1.7651 | 4 | $\bar{2} 4 2$ |
| 13 | 3.316(12) | 3.4237 | 8 | 2 2 2 | 9 | 1.668(4) | 1.7638 | 6 | 4 0 2 |
| | | 3.3019 | 11 | $\bar{2} 0 2$ | | | 1.7346 | 3 | 2 6 2 |
| 50 | 2.993(4) | 3.0559 | 10 | 1 0 3 | 4 | 1.597(5) | 1.6885 | 4 | $\bar{2} 1 6$ |
| | | 3.0261 | 12 | 2 3 2 | | | 1.6724 | 3 | 0 $\bar{3} 4$ |
| 24 | 2.787(5) | 2.9992 | 17 | $\bar{2} 1 2$ | 9 | 1.464(8) | 1.6700 | 4 | $\bar{5} \bar{2} 1$ |
| | | 2.9714 | 17 | 2 0 2 | | | 1.6577 | 2 | 3 6 1 |
| 7 | 2.612(9) | 2.9670 | 21 | 0 3 0 | 4 | 1.440(3) | 1.5993 | 2 | 3 3 6 |
| | | 2.8931 | 5 | 0 $\bar{1}$ 3 | | | 1.5443 | 2 | 1 $\bar{3} 4$ |
| 24 | 2.787(5) | 2.8062 | 3 | 0 1 4 | 4 | 1.503(7) | 1.5412 | 2 | 5 2 3 |
| | | 2.7890 | 13 | $\bar{2} \bar{2} 2$ | | | 1.5053 | 2 | $\bar{2} \bar{5} 3$ |
| 7 | 2.612(9) | 2.7754 | 2 | 2 1 3 | 9 | 1.481(7) | 1.5010 | 2 | $\bar{3} 4 2$ |
| | | 2.7679 | 8 | 3 2 1 | | | 1.4919 | 3 | $\bar{3} 4 3$ |
| 22 | 2.472(4) | 2.7101 | 3 | 2 3 3 | 7 | 1.464(8) | 1.4800 | 3 | $\bar{2} 1 7$ |
| | | 2.6163 | 2 | $\bar{2} \bar{1} 3$ | | | 1.4690 | 2 | $\bar{2} 4 6$ |
| 7 | 2.612(9) | 2.6103 | 7 | 0 0 4 | 10 | 1.440(3) | 1.4676 | 3 | 3 7 2 |
| | | 2.6103 | 7 | 0 0 4 | | | 1.4459 | 2 | 0 4 4 |
| 22 | 2.472(4) | 2.4756 | 18 | 0 3 4 | 10 | 1.440(3) | 1.4412 | 4 | 4 4 6 |
| | | 2.4610 | 11 | 2 $\bar{1}$ 2 | | | | | |

agreement with those calculated from the structure data. Observed d values and intensities were derived by profile fitting using JADE 2010 software.

The Rigaku CrystalClear software package was used for reducing X-ray intensity data to structure factors, including corrections for Lorentz and polarization effects, and the application of empirical absorption corrections; the structures were solved by direct methods using SIR2004 (Burla *et al.* 2005). The SHELXL-97 software (Sheldrick 2008) was used for the structure refinements, utilizing neutral-atom scattering factors. Hydrogen atoms were located using difference Fourier maps, and were refined using O-H and H-H distance constraints. Details of the data collections and structure refinements are provided in Table 4, and the atom coordinates and equivalent displacement

parameters are in Table 5. Table 6 lists the anisotropic displacement parameters, and selected interatomic distances and bond valences are listed in Table 7. A copy of Table 6, tables of structure factors, and cif files for wernerbaurite and schindlerite are available from the Depository of Unpublished Data on the MAC website [document Wernerbaurite CM51_297; <http://www.mineralogicalassociation.ca/index.php?p=144>].

ATOMIC ARRANGEMENTS OF WERNERBAURITE AND SCHINDLERITE

Minerals containing the $(V_{10}O_{28})^{6-}$ decavanadate group can be considered members of the pascoite family (Table 1), pascoite being the first decavanadate-bearing mineral described (Hillebrand *et al.* 1914). All minerals

of the pascoite family are bipartite structures that consist of a *structural unit* and an *interstitial unit*, as elucidated by Hawthorne (1983). The $(V_{10}O_{28})^{6-}$ polyanion defines the structural unit, the anhydrous anionic portion of the structure (note that in this paper we denote {structural units} and {interstitial units} with braces in the chemical formulas). These more rigid structural units are linked by the interstitial units, the cationic portions of the structures, *via* bonds of lower bond-valence linking alkalis, alkaline earths, and Al to O atoms of the structural units and interstitial H_2O groups, hydroxyls, and/or hydronium ions (Hughes *et al.* 2008). The minerals of the pascoite family differ in the composition and structure of the interstitial units, the +6 charge of which balances the charge of the decavanadate polyanions. The recent characterization of rakovanite (Kampf *et al.* 2011a) and gunterite (Kampf *et al.* 2011b) demonstrated that in some decavanadates, protonation of the

decavanadate polyanion occurs, as has been described in synthetic compounds by Duraisamy *et al.* (2000). In addition, the recently described phase nashite (Kampf *et al.* 2013) illustrates that a mixed-valence $(V_{10}O_{28})$ group can also occur, with a $\{(V^{4+}_1V^{5+}_9)O_{28}\}^{7-}$ vanadylnonavanadate structural unit.

The structural unit in wernerbaurite and schindlerite

The structural unit in wernerbaurite and schindlerite consists of a decavanadate polyanion similar to that found in other decavanadate-bearing minerals (Fig. 3). The decavanadate polyanion consists of ten distorted, edge-sharing octahedra, eight of which contain one vanadyl bond, defined as a $V^{5+}-O$ bond less than 1.74 Å in length (Schindler *et al.* 2000); the remaining two octahedra have two vanadyl bonds. In all cases, the vanadyl bond is *trans* to the longest V–O bond(s) of

TABLE 4. DATA COLLECTION AND STRUCTURE REFINEMENT DETAILS FOR WERNERBAURITE AND SCHINDLERITE.

| | Wernerbaurite | Schindlerite |
|---|--|--|
| Diffractometer | Rigaku R-Axis Rapid II | Rigaku R-Axis Rapid II |
| X-ray radiation / power | MoK α ($\lambda = 0.71075$ Å) | MoK α ($\lambda = 0.71075$ Å) |
| X-ray power | 50 kV, 40 mA | 50 kV, 40 mA |
| Temperature | 298(2) K | 298(2) K |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions (Å°) | $a = 9.7212(6)$ $b = 10.2598(8)$ $c = 10.5928(8)$ $\alpha = 89.999(6)$ $\beta = 77.083(7)$ $\gamma = 69.887(8)$ | $a = 8.5143(3)$ $b = 10.4283(5)$ $c = 11.2827(8)$ $\alpha = 68.595(5)$ $\beta = 87.253(6)$ $\gamma = 67.112(5)$ |
| V (Å ³) | 963.55(12) | 854.08(8) |
| Z | 1 | 1 |
| Density (g/cm ³), calc. | 2.350 | 2.449 |
| Absorption coefficient (mm ⁻¹) | 2.709 | 2.765 |
| F(000) | 676 | 620 |
| Crystal size (μ m) | 40 x 220 x 220 | 40 x 90 x 180 |
| θ range (°) | 3.02 to 27.49 | 3.08 to 27.49 |
| Index ranges | $\bar{12} \leq h \leq 12$ $\bar{13} \leq k \leq 13$ $\bar{13} \leq l \leq 11$ | $\bar{10} \leq h \leq 11$ $\bar{13} \leq k \leq 13$ $\bar{13} \leq l \leq 14$ |
| Reflections collected / unique | 18571 / 4396 [$R_{int} = 0.0429$] | 10928 / 3880 [$R_{int} = 0.0360$] |
| Reflections $F_o > 4\sigma F$ | 3440 | 2888 |
| Completeness | 99.3% | 99.2% |
| Max. and min. transmission | 0.4663 and 0.2661 | 0.9094 and 0.6359 |
| Refinement method | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 |
| Parameters refined | 319 | 292 |
| GoF | 1.061 | 1.071 |
| Final R indices [$F_o > 4\sigma F$] | $R_1 = 0.0341$, $wR_2 = 0.0853$ | $R_1 = 0.0399$, $wR_2 = 0.0993$ |
| R indices (all data) | $R_1 = 0.0475$, $wR_2 = 0.0920$ | $R_1 = 0.0575$, $wR_2 = 0.1105$ |
| Largest diff. peak / hole (e/Å ³) | +0.574 / -0.575 | +0.634 / -0.655 |

Notes: $R_{int} = \sum[F_o^2 - F_o^2(\text{mean})]/\sum[F_o^2]$. $GoF = S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$. $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_c^2) + (aP)^2 + bP]$ where P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$; for wernerbaurite a is 0.0485 and b is 0.1073; for schindlerite a is 0.0614 and b is 0.

TABLE 5. ATOM COORDINATES AND EQUIVALENT DISPLACEMENT PARAMETERS (\AA^2) FOR WERNERBAURITE AND SCHINDLERITE

| Atom | x/a | y/b | z/c | U_{eq} |
|---------------|------------|-------------|-------------|-------------|
| wernerbaurite | | | | |
| V1 | 0.65439(5) | 0.03563(4) | 0.94782(4) | 0.01912(12) |
| V2 | 0.34785(5) | 0.27089(5) | 0.09318(5) | 0.02374(13) |
| V3 | 0.51790(5) | 0.04014(5) | 0.24712(4) | 0.02206(12) |
| V4 | 0.81413(5) | 0.80172(5) | 0.10355(5) | 0.02525(13) |
| V5 | 0.47686(5) | 0.26110(5) | 0.79393(5) | 0.02551(13) |
| Ca | 0.83962(7) | 0.26607(6) | 0.41299(6) | 0.02816(15) |
| O1 | 0.4263(2) | 0.09869(17) | 0.93156(16) | 0.0205(4) |
| O2 | 0.5596(2) | 0.15842(18) | 0.10244(17) | 0.0217(4) |
| O3 | 0.6720(2) | 0.89534(18) | 0.81782(17) | 0.0213(4) |
| O4 | 0.6755(2) | 0.15763(18) | 0.84533(18) | 0.0246(4) |
| O5 | 0.7195(2) | 0.95556(19) | 0.23251(18) | 0.0254(4) |
| O6 | 0.8241(2) | 0.95602(19) | 0.98196(18) | 0.0253(4) |
| O7 | 0.4664(2) | 0.89756(19) | 0.31933(18) | 0.0253(4) |
| O8 | 0.2763(2) | 0.30383(19) | 0.79403(19) | 0.0280(4) |
| O9 | 0.1693(2) | 0.29926(19) | 0.04793(19) | 0.0265(4) |
| O10 | 0.4241(2) | 0.35638(18) | 0.95846(19) | 0.0270(4) |
| O11 | 0.4653(2) | 0.1539(2) | 0.36944(19) | 0.0314(5) |
| O12 | 0.2999(3) | 0.3837(2) | 0.2148(2) | 0.0360(5) |
| O13 | 0.9835(2) | 0.7477(2) | 0.1212(2) | 0.0365(5) |
| O14 | 0.5284(3) | 0.3660(2) | 0.6995(2) | 0.0379(5) |
| OW1 | 0.7548(2) | 0.0726(2) | 0.4654(2) | 0.0306(5) |
| H1a | 0.742(3) | 0.030(3) | 1.398(2) | 0.037 |
| H1b | 0.673(3) | 0.088(3) | 1.529(2) | 0.037 |
| OW2 | 0.8885(3) | 0.1343(2) | 0.2015(2) | 0.0380(5) |
| H2a | 0.829(3) | 0.091(3) | 1.185(3) | 0.046 |
| H2b | 0.975(2) | 0.100(3) | 1.147(3) | 0.046 |
| OW3 | 0.0958(3) | 0.1416(3) | 0.3823(2) | 0.0490(7) |
| H3a | 1.133(4) | 0.062(3) | 1.420(3) | 0.059 |
| H3b | 1.158(4) | 0.137(4) | 1.308(2) | 0.059 |
| OW4 | 0.8363(4) | 0.7091(3) | 0.4248(3) | 0.0689(9) |
| H4a | 0.802(4) | -0.236(4) | 1.503(3) | 0.083 |
| H4b | 0.759(4) | -0.254(4) | 1.384(3) | 0.083 |
| OW5 | 0.9033(3) | 0.4104(2) | 0.2396(2) | 0.0418(6) |
| H5a | 0.981(3) | 0.380(3) | 1.174(3) | 0.05 |
| H5b | 0.863(3) | 0.5009(19) | 1.243(3) | 0.05 |
| OW6 | 0.5957(3) | 0.3612(2) | 0.3717(3) | 0.0457(6) |
| H6a | 0.529(3) | 0.318(3) | 1.389(4) | 0.055 |
| H6b | 0.540(3) | 0.4513(19) | 1.373(4) | 0.055 |
| OW7 | 0.8894(3) | 0.2086(3) | 0.6283(2) | 0.0509(7) |
| H7a | 0.951(3) | 0.251(4) | 1.637(3) | 0.061 |
| H7b | 0.826(3) | 0.216(4) | 1.704(2) | 0.061 |
| OW8 | 0.7847(4) | 0.4827(3) | 0.5249(2) | 0.0649(8) |
| H8a | 0.769(5) | 0.494(4) | 1.6093(18) | 0.078 |
| H8b | 0.809(5) | 0.551(3) | 1.487(3) | 0.078 |
| OW9 | 0.2864(3) | 0.6429(3) | 0.9472(3) | 0.0537(7) |
| H9a | 0.340(3) | 0.554(2) | 0.965(3) | 0.064 |
| H9b | 0.353(3) | 0.691(3) | 0.938(3) | 0.064 |
| H9c | 0.213(3) | 0.684(3) | 1.025(3) | 0.064 |

TABLE 5 (continued)

| Atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>U</i> _{eq} |
|--------------|-------------|-------------|-------------|------------------------|
| schindlerite | | | | |
| V1 | 0.37680(7) | 0.78287(6) | 0.49749(5) | 0.02084(15) |
| V2 | 0.69006(6) | 0.50277(6) | 0.48023(5) | 0.01792(15) |
| V3 | 0.17151(7) | 0.78389(6) | 0.27788(5) | 0.02334(16) |
| V4 | 0.52664(7) | 0.49551(6) | 0.73981(5) | 0.02051(15) |
| V5 | 0.52942(7) | 0.79132(6) | 0.23773(5) | 0.02263(16) |
| Na | 0.93135(17) | 0.66757(15) | 0.87252(13) | 0.0347(3) |
| O1 | 0.4327(2) | 0.6243(2) | 0.39448(18) | 0.0187(5) |
| O2 | 0.6031(3) | 0.6202(2) | 0.58407(19) | 0.0202(5) |
| O3 | 0.3162(3) | 0.6153(2) | 0.61469(19) | 0.0205(5) |
| O4 | 0.4829(3) | 0.8691(2) | 0.3673(2) | 0.0227(5) |
| O5 | 0.7387(3) | 0.6331(2) | 0.3597(2) | 0.0224(5) |
| O6 | 0.1704(3) | 0.8642(2) | 0.4016(2) | 0.0245(5) |
| O7 | 0.2983(3) | 0.8805(2) | 0.1776(2) | 0.0247(5) |
| O8 | 0.4388(3) | 0.3586(2) | 0.82799(19) | 0.0230(5) |
| O9 | 0.8743(3) | 0.3789(2) | 0.5742(2) | 0.0226(5) |
| O10 | 0.7492(3) | 0.3655(2) | 0.79312(19) | 0.0232(5) |
| O11 | 0.6103(3) | 0.8963(3) | 0.1390(2) | 0.0324(6) |
| O12 | 0.3420(3) | 0.8821(3) | 0.5846(2) | 0.0293(5) |
| O13 | 0.9783(3) | 0.8818(3) | 0.2096(2) | 0.0329(6) |
| O14 | 0.4922(3) | 0.5973(3) | 0.8251(2) | 0.0288(5) |
| OW1 | 0.9785(4) | 0.5105(4) | 0.7591(3) | 0.0512(8) |
| H1A | 1.069(3) | 0.467(4) | 0.724(4) | 0.061 |
| H1B | 0.908(4) | 0.462(4) | 0.765(4) | 0.061 |
| OW2 | 0.0302(4) | 0.8184(3) | 0.7038(3) | 0.0509(8) |
| H2A | 0.988(5) | 0.916(2) | 0.661(4) | 0.061 |
| H2B | 1.128(3) | 0.772(4) | 0.679(4) | 0.061 |
| OW3 | 0.2084(3) | 0.4852(3) | 0.9867(2) | 0.0369(6) |
| H3A | 1.279(4) | 0.480(4) | 1.047(3) | 0.044 |
| H3B | 1.282(4) | 0.441(4) | 0.939(3) | 0.044 |
| OW4 | 0.6565(4) | 0.8178(3) | 0.7518(3) | 0.0489(7) |
| H4A | 0.589(5) | 0.786(4) | 0.724(4) | 0.059 |
| H4B | 0.624(5) | 0.915(2) | 0.712(4) | 0.059 |
| OW5 | 0.9309(4) | 0.8282(3) | 0.9737(2) | 0.0445(7) |
| H5A | 0.927(5) | 0.801(4) | 1.0549(17) | 0.053 |
| H5B | 0.856(4) | 0.921(3) | 0.930(3) | 0.053 |
| OW6 | 0.8208(3) | 0.7906(2) | 0.5098(2) | 0.0208(5) |
| H6A | 0.767(3) | 0.8864(18) | 0.467(3) | 0.025 |
| H6B | 0.783(4) | 0.736(3) | 0.500(3) | 0.025 |
| H6C | 0.905(3) | 0.771(3) | 0.558(3) | 0.025 |
| OW7 | 0.2842(4) | 0.8239(4) | 0.9296(3) | 0.0594(9) |
| H7A | 1.330(4) | 0.780(5) | 1.014(2) | 0.071 |
| H7B | 1.352(4) | 0.760(4) | 0.892(3) | 0.071 |
| H7C | 1.178(3) | 0.824(5) | 0.928(4) | 0.071 |

the octahedron, typical of the disposition of bonds in the octahedra of the decavanadate polyanion. The long V–O bond (V–O1 in all cases) in each octahedron is of interest because of the unusual coordination of that oxygen atom in the decavanadate group. Specifically, the O1 atom bonds to six vanadium atoms (Fig. 3), yet the bond valence sum for the oxygen atom totals 1.96 *v.u.* in wernerbaurite and 1.98 *v.u.* in schindlerite, attesting to the efficacy of the electrostatic valency principle, even for such an unusual oxygen coordination.

The interstitial unit in wernerbaurite

The interstitial unit that links the $\{V_{10}O_{28}\}^{6-}$ structural unit in decavanadate compounds must balance the 6– charge of the decavanadate structural unit. The interstitial unit in wernerbaurite is formed of isolated $[Ca(H_2O)_7]^{2+}$ polyhedra (Fig. 4), $(H_3O)^+$ ions, and an isolated H_2O molecule, and has a composition of $\{[Ca(H_2O)_7]_2(H_2O)_2(H_3O)_2\}^{6+}$. Wernerbaurite and schindlerite are the first decavanadate minerals known

TABLE 7. SELECTED BOND DISTANCES (Å) AND BOND VALENCE SUMS (νu) FOR ATOMS IN WERNERBAURITE AND SCHINDLERITE [BOND VALENCE PARAMETERS FROM BRESE AND O'KEEFFE (1991)]

| wernerbaurite | | | | | |
|---------------|----------|---------|-----------|----------|---------|
| V1– | d | νu | V2– | d | νu |
| O6 | 1.691(2) | 1.35 | O12 | 1.605(2) | 1.71 |
| O4 | 1.693(2) | 1.35 | O10 | 1.825(2) | 0.94 |
| O2 | 1.909(2) | 0.75 | O9 | 1.831(2) | 0.93 |
| O3 | 1.929(2) | 0.71 | O3 | 1.995(2) | 0.60 |
| O1 | 2.108(2) | 0.44 | O2 | 2.009(2) | 0.57 |
| O1' | 2.133(2) | 0.41 | O1 | 2.264(2) | 0.29 |
| Mean, sum | 1.911 | 5.01 | Mean, sum | 1.922 | 5.03 |
| V3– | d | νu | V4– | d | νu |
| O11 | 1.611(2) | 1.68 | O13 | 1.601(2) | 1.73 |
| O7 | 1.819(2) | 0.96 | O8 | 1.831(2) | 0.93 |
| O5 | 1.820(2) | 0.96 | O9 | 1.856(2) | 0.87 |
| O3 | 2.011(2) | 0.57 | O5 | 1.909(2) | 0.75 |
| O2 | 2.012(2) | 0.57 | O6 | 2.055(2) | 0.51 |
| O1 | 2.217(2) | 0.33 | O1 | 2.322(2) | 0.25 |
| Mean, sum | 1.915 | 5.06 | Mean, sum | 1.929 | 5.02 |
| V5– | d | νu | Ca– | d | νu |
| O14 | 1.600(2) | 1.73 | OW3 | 2.321(2) | 0.38 |
| O8 | 1.845(2) | 0.89 | OW8 | 2.352(2) | 0.35 |
| O7 | 1.866(2) | 0.84 | OW6 | 2.374(2) | 0.33 |
| O10 | 1.874(2) | 0.83 | OW1 | 2.419(2) | 0.29 |
| O4 | 2.053(2) | 0.51 | OW5 | 2.464(2) | 0.26 |
| O1 | 2.321(2) | 0.25 | OW7 | 2.466(3) | 0.26 |
| Mean, sum | 1.927 | 5.05 | OW2 | 2.481(2) | 0.25 |
| | | | Mean, sum | 2.411 | 2.13 |
| schindlerite | | | | | |
| V1– | d | νu | V2– | d | νu |
| O12 | 1.613(2) | 1.67 | O9 | 1.684(2) | 1.38 |
| O4 | 1.822(2) | 0.95 | O5 | 1.704(2) | 1.31 |
| O6 | 1.825(2) | 0.94 | O2 | 1.918(2) | 0.73 |
| O2 | 1.993(2) | 0.60 | O3 | 1.920(2) | 0.73 |
| O3 | 2.005(2) | 0.58 | O1 | 2.101(2) | 0.45 |
| O1 | 2.247(2) | 0.30 | O1' | 2.120(2) | 0.42 |
| Mean, sum | 1.918 | 5.04 | Mean, sum | 1.922 | 5.02 |
| V3– | d | νu | V4– | d | νu |
| O13 | 1.607(2) | 1.70 | O14 | 1.617(2) | 1.65 |
| O7 | 1.833(2) | 0.92 | O10 | 1.818(2) | 0.96 |
| O6 | 1.870(2) | 0.83 | O8 | 1.819(2) | 0.96 |
| O10 | 1.888(2) | 0.79 | O3 | 1.994(2) | 0.60 |
| O9 | 2.051(2) | 0.51 | O2 | 2.021(2) | 0.55 |
| O1 | 2.291(2) | 0.27 | O1 | 2.230(2) | 0.32 |
| Mean, sum | 1.923 | 5.03 | Mean, sum | 1.917 | 5.04 |
| V5– | d | νu | Na– | d | νu |
| O11 | 1.593(2) | 1.76 | OW1 | 2.334(3) | 0.24 |
| O7 | 1.855(2) | 0.87 | OW2 | 2.345(3) | 0.23 |
| O4 | 1.874(2) | 0.83 | OW5 | 2.345(3) | 0.23 |
| O8 | 1.888(2) | 0.79 | OW4 | 2.384(3) | 0.21 |
| O5 | 2.020(2) | 0.56 | OW3 | 2.420(3) | 0.19 |
| O1 | 2.359(2) | 0.22 | OW3' | 2.433(3) | 0.18 |
| Mean, sum | 1.932 | 5.03 | Mean, sum | 2.377 | 1.27 |

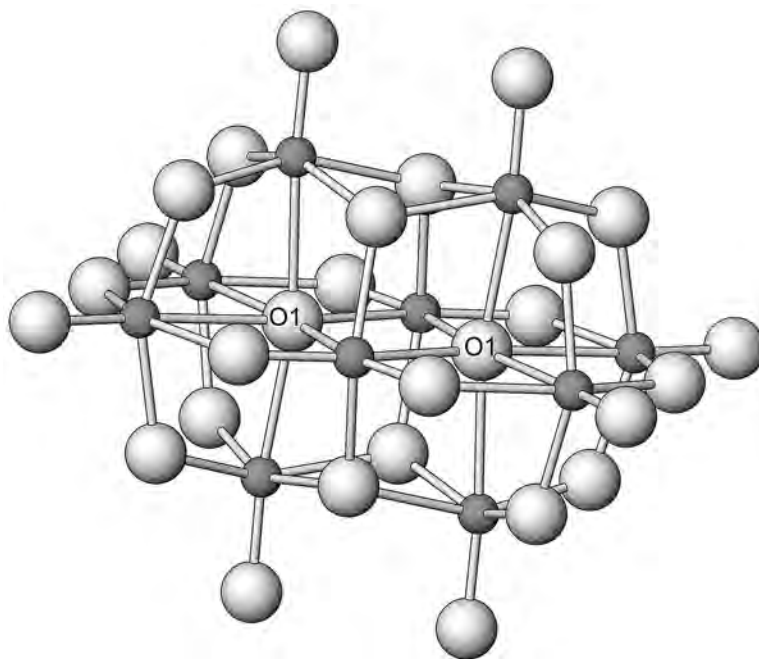


Fig. 3. The decavanadate polyanions in wernerbaurite and schindlerite. The O1 atom, discussed in the text, is labeled.

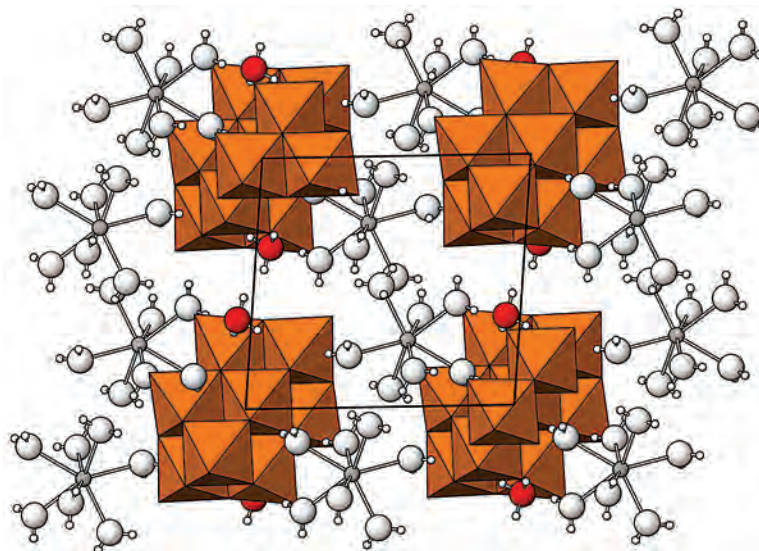


Fig. 4. The atomic arrangement of wernerbaurite viewed down [100] (*c* axis horizontal). Polyhedral groups represent the $[V_{10}O_{28}]^{6-}$ structural unit. The hydronium ion (red) and $[Ca(H_2O)_7]$ of the interstitial unit are depicted.

to contain the hydronium ion; the hydrogen atoms of the hydronium ion were easily located in difference maps. The synthetic equivalent of wernerbaurite (Strukan *et al.* 1999) was synthesized at pH 6.0; as noted previously, the natural low-temperature decavanadate phases also form in an acidic environment, under ambient temperatures and generally oxidizing near-surface environments where water reacts with pyrite in the deposit to form aqueous solutions of relatively low pH.

Like the other associated low-temperature decavanadate phases, there is extensive hydrogen bonding in the wernerbaurite atomic arrangement, predominantly between the interstitial unit and the structural unit. Table 8 lists the hydrogen bonds in the wernerbaurite atomic arrangement. The lone non-hydrogen cation in the interstitial unit, Ca^{2+} , bonds only to H_2O molecules of the interstitial unit, and does not link to the oxygen atoms of the structural unit. The only linkage between the structural unit and the interstitial unit is by the hydrogen bonds listed in Table 8. The low hardness of

wernerbaurite results from the presence of pervasive hydrogen bonds and lack of ionic bonds between the interstitial unit and the structural unit.

The interstitial unit in schindlerite

The interstitial unit in schindlerite, $\{[\text{Na}_2(\text{H}_2\text{O})_{10}](\text{H}_3\text{O})_4\}^{6+}$, is formed of an isolated $[\text{Na}_2(\text{H}_2\text{O})_{10}]$ dimer that is linked to four hydronium ions by hydrogen bonding (Fig. 5). The Na atoms bond only to water molecules of the interstitial group and not to oxygen atoms of the decavanadate structural unit. Thus, the only linkage between the structural and interstitial units is through hydrogen bonding. Table 8 lists the hydrogen bonds in the schindlerite atomic arrangement, and serves to illustrate the extensive hydrogen bonding between the structural unit and interstitial unit. Like wernerbaurite and other low-temperature decavanadates, the pervasive hydrogen bonding in schindlerite results in the low hardness of the mineral. The structural

TABLE 8. HYDROGEN BONDS[†] IN WERNERBAURITE AND SCHINDLERITE

| Acceptor | H | d (Å) | Acceptor | H | d (Å) |
|--|-----|---------|----------|-----|---------|
| wernerbaurite | | | | | |
| Hydrogen Bonding Between the Interstitial Unit and the Structural Unit | | | | | |
| O2 | H9b | 2.01(2) | O8 | H5b | 2.09(2) |
| O3 | H3b | 1.81(2) | O9 | H5a | 1.92(2) |
| O4 | H7b | 2.09(2) | O10 | H9a | 1.91(2) |
| O5 | H1a | 2.00(2) | O10 | H9b | 2.53(3) |
| O5 | H2a | 2.03(2) | O11 | H4a | 2.49(4) |
| O5 | H4b | 2.66(4) | O11 | H6a | 2.01(2) |
| O6 | H2a | 2.58(3) | O12 | H8a | 2.09(3) |
| O6 | H2b | 2.01(2) | O13 | H9c | 2.11(2) |
| O7 | H1b | 1.82(2) | O14 | H6b | 1.98(2) |
| O8 | H4b | 2.08(3) | | | |
| Hydrogen Bonding Within the Interstitial Unit | | | | | |
| OW1 | H3a | 2.03(2) | OW3 | H4a | 2.14(3) |
| OW4 | H7a | 2.20(2) | OW4 | H8b | 1.83(2) |
| schindlerite | | | | | |
| Hydrogen Bonding Between the Interstitial Unit and the Structural Unit | | | | | |
| O2 | H6b | 2.27(2) | O9 | H1b | 2.66(4) |
| O3 | H2b | 2.12(2) | O10 | H1b | 1.93(2) |
| O4 | H4b | 1.93(2) | O10 | H7a | 2.40(3) |
| O4 | H6b | 2.60(3) | O12 | H2b | 2.52(4) |
| O5 | H1a | 1.98(2) | O12 | H4a | 2.33(3) |
| O5 | H6b | 2.32(2) | O12 | H6a | 2.08(2) |
| O6 | H2a | 2.02(2) | O13 | H5a | 2.32(3) |
| O7 | H5b | 1.92(2) | O14 | H3a | 2.17(2) |
| O7 | H7a | 2.40(3) | O14 | H4a | 2.32(3) |
| O8 | H3b | 1.95(2) | O14 | H7b | 2.04(2) |
| O8 | H7a | 2.32(2) | | | |
| Hydrogen Bonding Within the Interstitial Unit | | | | | |
| OW2 | H6c | 2.29(2) | OW5 | H7c | 2.13(2) |

[†] A hydrogen bond is defined as a bond with the H...acceptor distance < 2.7 Å and a donor – H – acceptor angle > 110°.

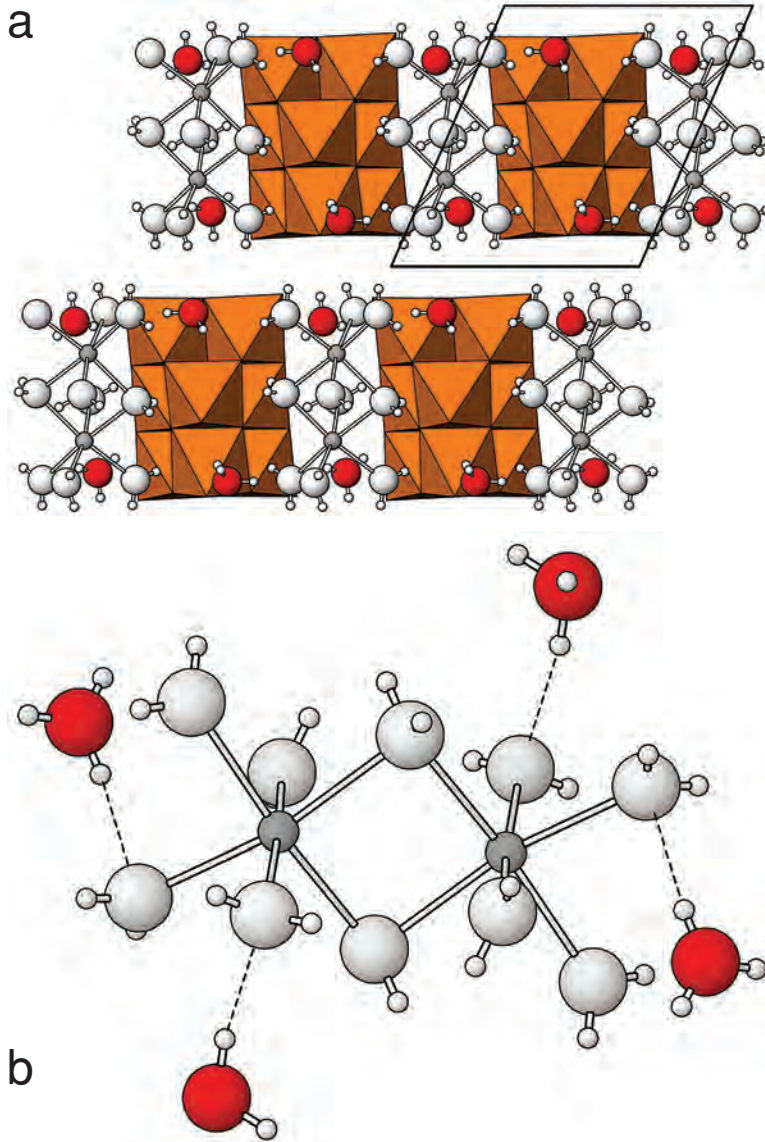


FIG. 5. (a) Atomic arrangement of schindlerite projected down [001]; the a axis is horizontal. The unit cell is shown. Polyhedral clusters are the $\{V_{10}O_{28}\}^{6-}$ structural group, and the hydronium ions in the $\{[Na_2(H_2O)_{10}](H_3O)_4\}$ interstitial group are red. (b) The $\{[Na_2(H_2O)_{10}](H_3O)_4\}$ dimer in schindlerite. Hydronium ions that decorate the dimer are red; hydrogen bonds are dashed.

units in schindlerite are linked across $\{010\}$ only by hydrogen bonds, resulting in the good $\{010\}$ cleavage.

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