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Howardevansite, $\mathrm{NaCu^{2+}Fe^{3+}_2(VO_4)^{3-}_3}$, a new fumarolic sublimate from Izalco volcano, El Salvador: Descriptive mineralogy and crystal structure

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ABSTRACT

Howardevansite, $\mathrm{NaCu^{2+}Fe^{3+}_2(VO_4)^{3-}_3}$, has been discovered in the summit crater fumaroles of Izalco volcano, El Salvador. The mineral, which occurs with lyonsite and thenardite, formed as a sublimate from the volcanic gases. Howardevansite occurs as euhedral, black tabular crystals up to 80 μm in greatest dimension. The crystals are triclinic, $P\bar{1}$, with $a = 8.198(2)$, $b = 9.773(1)$, $c = 6.6510(8)$, $\alpha = 103.82(1)$, $\beta = 101.99(1)$, and $\gamma = 106.74(1)°$. The strongest lines in the diffraction pattern are (d, I, hkl) (3.167, 100, $1\bar{3}0$), (3.093, 100, 210), (1.659, 70, $\bar{3}51$), (3.27, 60, $01\bar{2}$), and (2.676, 60, $\bar{2}12$). The atomic arrangement of the mineral has been determined and refined to $R = 0.026$, $R_w = 0.036$. The structure is formed of ribbons in the (210) plane, consisting of $\mathrm{FeO_6}$ octahedra, $\mathrm{CuO_5}$ trigonal bipyramids, and $\mathrm{VO_4}$ tetrahedra. The ribbons terminate in chains of $\mathrm{NaO_6}$ and $\mathrm{NaO_7}$ polyhedra that extend infinitely parallel to c at 0, ½, z.

Howardevansite is opaque and has a red-brown streak and metallic luster. $Z = 2$ and $D_{\mathrm{calc}} = 3.814$ g/cm^3 for the formula $\mathrm{NaCuFe_2(VO_4)_3}$. In reflected light in air, the mineral is medium gray and exhibits moderate anisotropy. Reflectance values measured on a polished face are (wavelength, min, max) 481 nm, 15.5, 20.1%; 547 nm, 15.0, 18.4%; 591 nm, 14.1, 17.2%, and 644 nm, 13.5, 17.1%.

The mineral is named in honor of Dr. Howard T. Evans, Jr., of the U.S. Geological Survey.

INTRODUCTION

Izalco volcano, El Salvador, is a Holocene basalt-andesite volcano that has been intermittently active since its formation in 1770. The geology of the volcano is described by Meyer-Abich (1958), Rose and Stoiber (1969), and Stoiber et al. (1975).

The fumaroles of Izalco volcano have been a rich source of new, high-temperature V minerals. Hughes and Stoiber (1985) have described the conditions of mineral genesis for several new fumarolic sublimates that have been discovered at Izalco volcano. They noted that the minerals form as sublimates from a vanadium halogen or oxyhalogen gas that was exsolved from a basaltic magma when the magma was 550 m below the summit crater. As the magmatic gas rose to the fumaroles and mixed with the atmosphere, the oxygen fugacity increased from that of the magma to at least $10^{-3.5}$ bar. At the fumaroles, the V compounds sublimed at temperatures up to 800 °C.

Among the new V minerals that have been described from the fumaroles of Izalco volcano are stoiberite ($\mathrm{Cu_5V_2O_{10}}$), bannermanite ($\mathrm{[Na,K]_xV_6O_{15}}$; $0.54 \leq X \leq 0.90$), ziesite (β-$\mathrm{Cu_2V_2O_7}$), fingerite ($\mathrm{Cu_{11}O_2[VO_4]_6}$), mcbirneyite ($\mathrm{Cu_3[VO_4]_2}$), blossite ($\alpha$-$\mathrm{Cu_2V_2O_7}$), and lyonsite ($\mathrm{Cu_3Fe_4[VO_4]_6}$). To these minerals is now added $\mathrm{NaCuFe_2(VO_4)_3}$. The new mineral was collected from the "Y" fumarole of Izalco volcano by R. E. Stoiber and occurs with thenardite and lyonsite. We are pleased to name the new mineral howardevansite in honor of Dr. Howard T. Evans of the U.S. Geological Survey, Reston, Virginia 22092 U.S.A. Dr. Evans is well known to all mineralogists for his numerous contributions to mineralogy, particularly in connection with the mineralogy of V. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA.

Hundreds of crystals of howardevansite are available, all less than 100 μm in greatest dimension. Samples have been contributed to the NMNH, Smithsonian Institution.

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TABLE 1. Electron-microprobe analyses (in wt%) of howardevansite

	(1)	(2)
Na_2O	5.6(07)	5.70
K_2O	0.60(1)	—
CuO	17.29(26)	14.65
Fe_2O_3	23.92(24)	29.41
Al_2O_3	2.01(3)	—
Mn_2O_3	0.73(2)	—
TiO_2	0.80(1)	—
V_2O_5	49.17(25)	50.24
Total	100.12	100.00

Note: Number in parentheses denotes 1σ of least units cited. Columns are (1) Mean of 30 analyses of howardevansite. Formula (basis: O = 12): $(Na_{0.98}K_{0.07})_{\Sigma-1.05}Cu_{1.06}(Fe_{1.63}Al_{0.21}Mn_{0.05}Ti_{0.05}Cu_{0.12})_{\Sigma=2.06}V_{2.94}O_{12}$; (2) Ideal $NaCu^{2+}Fe_2^{3+}(VO_4)_3$.

TABLE 2. X-ray diffraction pattern and unit-cell parameters for howardevansite

d_{obs} (Å)	d_{calc} (Å)	I_{obs}	I_{calc}	*hkl*
7.51	7.495	10	19.8	100
7.06	7.104	30	24.8	$\bar{1}10$
4.82	4.824	20	8.6	$11\bar{1}$
3.27	3.251	60	43.6	$01\bar{2}$
3.21	3.206	45	25.3	$10\bar{2}$
3.167	3.161	100	93.8	$1\bar{3}0$
3.093	3.082	100	100.0	210
2.851	2.853	40	17.2	$12\bar{2}$
2.676	2.677	60	11.3	$\bar{2}12$
2.603	2.609	60	19.3	$3\bar{2}0$
2.334	2.338	20	3.8	$04\bar{1}$
2.217	2.209	30	12.9	310
2.050	2.041	50	10.3	221
	2.043		5.6	$32\bar{1}$
1.872	1.874	40	6.0	400
1.659	1.659	70	18.2	$\bar{3}51$
	1.658		24.2	$11\bar{4}$
1.573	1.573	20	3.1	$\bar{5}10$
	1.575		2.6	$\bar{1}33$
1.543	1.540	10	3.8	$\bar{5}02$
	1.541		2.2	420
1.433	1.428	60	8.1	104
	1.431		1.8	$\bar{2}43$
	1.434		2.0	151

a	= 8.198(2) Å	α	= 103.82(1)°
b	= 9.773(1) Å	β	= 101.99(1)°
c	= 6.6510(8) Å	γ	= 106.74(1)°

CHEMISTRY

Crystals of howardevansite were mounted and polished for electron-probe microanalysis. Preliminary qualitative energy-dispersive analyses showed that of elements with Z > 8, only Na, K, Cu, Fe, Ti, Al, Mn, and V were present above background. Subsequent quantitative analyses by wavelength- and energy-dispersive methods were done on three different electron microprobes using well-analyzed standards (full details of analyses available from J.W.D.). An average of 30 analyses is contained in Table 1. Based on knowledge of the conditions of mineral genesis and associated phases, all metals were assumed to be fully oxidized; the subsequent crystal-structure determination confirmed the presence of Cu^{2+}, Fe^{3+}, and V^{5+} in howardevansite, and the substituent metals are also assumed to be fully oxidized.

The empirical formula obtained from the electron-probe microanalysis gives the formula $(Na_{0.98}K_{0.07})_{\Sigma=1.05}Cu_{1.18}(Fe_{1.63}Al_{0.21}Mn_{0.05}Ti_{0.05})_{\Sigma=1.94}V_{2.94}O_{12}$ on the basis of O = 12. The crystal-structure calculations were done assuming the ideal formula of $NaCuFe_2V_3O_{12}$. Note that the slight excess in Cu is nearly equal to the deficiency in the Fe octahedral site, suggesting that some Cu may also substitute for Fe^{3+} in its octahedron. The empirical formula can thus be recast as $(Na_{0.98}K_{0.07})Cu_{1.06}(Fe_{1.63}Al_{0.21}Mn_{0.05}Ti_{0.05}Cu_{0.12})_{\Sigma=2.06}V_{2.94}O_{12}$.

X-RAY CRYSTALLOGRAPHY

Howardevansite was first recognized as a new mineral by its Gandolfi pattern, which does not match any natural or synthetic phase in the JCPDS file. Gandolfi patterns were obtained with Ni-filtered Cu radiation, in vacuo, with a 114-mm Gandolfi camera. The indexed diffraction pattern is given in Table 2.

Single-crystal studies of howardevansite were done using a precession camera and four-circle diffractometer. Precession studies were done using unfiltered Mo radiation. Using standard methods, a reduced triclinic cell was defined. Precession and cone-axis photographs (*b* and *c* axes) were taken and allowed calculation of the unit-cell parameters, which were refined with the diffraction angles calculated from the Gandolfi photographs. Subsequently, a crystal was mounted on an automated single-crystal diffractometer; the lattice parameters (Table 2) were independently determined by an automatic-indexing procedure and were refined from 25 diffraction angles.

CRYSTAL STRUCTURE

Experimental details

Two sets of three-dimensional X-ray diffraction data were collected on single crystals of howardevansite. The first data set was collected on a Nicolet R3 four-circle diffractometer (Nicolet). The data set (1510 reflections) was collected from the hemisphere of reciprocal space comprising $\pm h$, $\pm k$, and $+l$ and the usual corrections were made. Using this data set, the phase problem was solved in space group $P\bar{1}$ using direct methods as implemented in the SHELXTL (version 4.1) package of computer programs, written by G. M. Sheldrick. The phase set with second-highest combined figure-of-merit, in combination with Fourier syntheses and difference maps, ultimately revealed the positions of all atoms.

A second data set was collected on an Enraf-Nonius CAD-4 automated diffractometer (Miami University). It was with that data set that the final refinement reported herein was undertaken; thus those complete experimental details are reported. A euhedral single crystal measuring approximately 0.08 × 0.08 × 0.05 mm was mounted on the instrument, and the unit-cell parameters were refined by least squares from diffraction angles measured for 25 reflections ($13° < 2\theta < 45°$) obtained with graphite-monochromated Mo$K\alpha$ X-radiation. Intensity data were collected from the hemisphere of reciprocal space comprising $\pm h$, $+k$, $\pm l$ to 50° 2θ, using a $\theta/2\theta$ scan technique, with theta scan widths determined by the relationship $\theta = 0.70° + 0.34(\tan \theta)$. A prescan of each peak during data collection determined counting time, with a

TABLE 3. Atomic coordinates and equivalent isotropic B for atoms in howardevansite

Atom	x	y	z	B (Å^2)
Cu	0.78675(8)	0.79562(8)	0.7765(1)	1.40(1)
Fe(1)	0.54817(9)	0.39238(8)	0.1191(1)	0.65(1)
Fe(2)	0.29616(9)	0.98522(8)	0.4553(1)	0.76(1)
V(1)	0.4101(1)	0.66723(9)	0.3893(1)	0.55(2)
V(2)	0.8383(1)	0.73926(9)	0.2755(1)	0.53(2)
V(3)	0.7710(1)	0.12589(9)	0.0913(1)	0.52(2)
Na(1)	0	½	½	4.44(7)
Na(2)	0.0234(9)	0.5509(7)	−0.016(1)	2.8(1)
O(1)	0.4450(4)	0.8570(4)	0.4201(5)	0.62(7)
O(2)	0.4821(4)	0.3502(4)	0.3713(5)	0.93(7)
O(3)	0.8014(5)	0.5556(4)	0.2637(6)	1.11(8)
O(4)	0.2201(4)	1.1642(4)	0.5035(5)	0.86(7)
O(5)	0.2729(5)	0.0075(4)	0.1599(5)	1.02(7)
O(6)	0.4729(4)	0.5794(4)	0.1701(5)	0.82(7)
O(7)	0.7287(4)	0.7421(4)	0.0244(5)	1.00(7)
O(8)	0.0552(4)	0.8210(4)	0.3184(6)	1.24(8)
O(9)	0.1981(5)	0.5800(4)	0.3385(6)	1.65(9)
O(10)	0.9907(5)	0.2365(4)	0.1897(6)	1.46(8)
O(11)	0.7176(5)	0.0361(4)	0.2674(5)	1.22(8)
O(12)	0.6592(5)	0.2444(4)	0.0678(6)	1.25(8)

Note: Numbers in parentheses denote one esd of least units cited.

maximum of 4 min per reflection. One-third of the total counting time was spent determining background on both sides of the peak. Three intensity standards were monitored every 4 h, and three orientation standards were monitored every 150 reflections. No significant deviation of intensity or orientation was noted during data collection (~5 d).

A total of 1779 reflections were collected. The intensity data were reduced to structure factors and corrected for Lorentz and polarization effects. The data were corrected for absorption by an empirical technique using intensity data obtained from 360° psi scans at 10° intervals for four reflections. Data with $I < 3\sigma_I$ were considered unobserved. The final reflection list yielded 1455 reflections. Least-squares structure refinement was initiated using the atomic positions obtained from the SHELXTL crystal-structure solution and the Enraf-Nonius SDP-Plus set of computer programs. The quantity $\Sigma\, w(|F_o| - |F_c|)^2$ was minimized by full-matrix least-squares refinement, with weights proportional to σ_F^{-2}. Neutral-atom scattering factors, including terms for anomalous extinction, were used in the refinement.

After several cyles of least-squares refinement, it was observed that Na(2) had an unusually large U_{22} thermal parameter, suggesting that the atom did not actually lie at the center of symmetry at 0,½,0. Both Na atoms were then removed from the atom list and a difference-Fourier map was calculated. The map showed two large peaks (~19 e/Å^3) corresponding to the removed Na atoms. One peak was observed on the special position at 0,½,½, corresponding to Na(1). The second peak, corresponding to Na(2), was significantly off the special position at 0,½,0, in accord with the unusually large thermal parameter for the atom. The atom was thus placed in a half-occupied general position.

Least-squares refinement was then continued by successively fixing all atomic parameters except those of Na(1) and Na(2) [with Na(1) fixed at the special position] and then fixing the Na atoms and refining all other atoms (positional and thermal parameters). During the refinement of Na(2) positional and thermal parameters, apparent large correlations among parameters necessitated separate refinement of the positional and thermal parameters, except during the last cycle of refinement.

Final refinement of all possible variables converged to $R = 0.026$, $R_w = 0.036$ with a goodness-of-fit of 1.944 for the 1455 "observed" data. The shift/error in the final cycle for all variables was <0.07. A difference-Fourier map calculated from the final parameters gave the largest positive peak as 1.766 e/Å^3 and the largest negative peak as 0.776 e/Å^3. Refinement using all 1651 reflections with $I > 0$ yielded $R = 0.036$, $R_w = 0.039$, and parameter shifts (compared to the $I > 3\sigma_I$ data) in the fifth decimal place for non-oxygen-atom positional parameters and in the fourth decimal place for oxygen-atom positional parameters.

Throughout the refinement cycles, the Na(1) atom yielded thermal parameters that describe a nonpositive definite ellipsoid. The site is the smaller of the two Na sites and is deemed too small to include some of the substituent K that is observed in the microprobe analyses. The nonpositive definite refinement of Na(1) suggests that the howardevansite structure model is at the limits of its resolution with the available crystals.

Table 3 contains atomic coordinates and equivalent isotropic

TABLE 4. Anisotropic thermal parameters for atoms in howardevansite

Atom	$\beta_{(1,1)}$	$\beta_{(2,2)}$	$\beta_{(3,3)}$	$\beta_{(1,2)}$	$\beta_{(1,3)}$	$\beta_{(2,3)}$
V(1)	0.0033(1)	0.00146(8)	0.0035(2)	0.0020(2)	0.0029(2)	0.0019(2)
V(2)	0.0029(1)	0.00186(8)	0.0030(2)	0.0020(2)	0.0029(2)	0.0018(2)
V(3)	0.0029(1)	0.00194(8)	0.0029(2)	0.0023(2)	0.0030(2)	0.0023(2)
Fe(1)	0.0037(1)	0.00217(7)	0.0040(2)	0.0029(1)	0.0034(2)	0.0029(2)
Fe(2)	0.0037(1)	0.00238(7)	0.0052(2)	0.0024(1)	0.0032(2)	0.0028(2)
Cu	0.00664(9)	0.00777(7)	0.0072(1)	0.0089(1)	0.0079(2)	0.0105(2)
O(1)	0.0022(5)	0.0017(3)	0.0059(8)	0.0025(6)	0.002(1)	0.0014(9)
O(2)	0.0048(5)	0.0034(4)	0.0049(7)	0.0022(7)	0.004(1)	0.0045(9)
O(3)	0.0056(5)	0.0033(4)	0.0086(8)	0.0042(7)	0.006(1)	0.0045(9)
O(4)	0.0061(5)	0.0036(4)	0.0040(7)	0.0062(7)	0.006(1)	0.0051(8)
O(5)	0.0068(5)	0.0040(4)	0.0045(7)	0.0057(7)	0.005(1)	0.0055(9)
O(6)	0.0067(5)	0.0020(3)	0.0032(7)	0.0039(7)	0.004(1)	0.0023(8)
O(7)	0.0056(5)	0.0039(4)	0.0054(8)	0.0047(7)	0.005(1)	0.0047(9)
O(8)	0.0040(6)	0.0040(4)	0.0080(8)	−0.0006(8)	0.004(1)	0.003(1)
O(9)	0.0037(6)	0.0040(4)	0.016(1)	0.0011(8)	0.000(1)	0.005(1)
O(10)	0.0039(6)	0.0061(4)	0.0080(9)	0.0008(8)	0.001(1)	0.005(1)
O(11)	0.0079(6)	0.0044(4)	0.0042(8)	0.0038(8)	0.006(1)	0.0044(9)
O(12)	0.0065(5)	0.0042(4)	0.0074(8)	0.0072(7)	0.003(1)	0.002(1)
Na1*	0.0026(4)	0.0314(4)	0.0514(8)	0.0230(7)	0.0288(9)	0.0814(7)
Na2	0.0089(1)	0.0130(1)	0.0083(1)	0.0130(1)	−0.0069(1)	−0.0070(1)

Note: Numbers in parentheses denote one esd of least units cited.
* Displacement parameter is not positive-definite for atom Na1.

Table 5. Selected bond lengths (Å) and angles (°) for atoms in howardevansite

V(1)–0(1)	1.747(4)	O(1)–V(1)–O(2)	109.9(2)	O(2)–V(1)–O(6)	111.5(2)
–O(2)	1.725(4)	O(1)–V(1)–O(6)	112.9(2)	O(2)–V(1)–O(9)	107.7(2)
–O(6)	1.760(4)	O(1)–V(1)–O(9)	107.7(2)	O(6)–V(1)–O(9)	106.9(2)
–O(9)	1.621(4)				
Mean	1.713				
V(2)–O(3)	1.712(4)	O(3)–V(2)–O(4)	111.1(2)	O(4)–V(2)–O(7)	114.4(2)
–O(4)	1.780(4)	O(3)–V(2)–O(7)	108.5(2)	O(4)–V(2)–O(8)	108.0(2)
–O(7)	1.735(4)	O(3)–V(2)–O(8)	106.8(2)	O(7)–V(2)–O(8)	107.7(2)
–O(8)	1.656(4)				
Mean	1.721				
V(3)–O(5)	1.750(3)	O(5)–V(3)–O(10)	110.7(2)	O(10)–V(3)–O(11)	108.9(2)
–O(10)	1.700(3)	O(5)–V(3)–O(11)	109.1(2)	O(10)–V(3)–O(12)	105.7(2)
–O(11)	1.678(4)	O(5)–V(3)–O(12)	111.0(2)	O(11)–V(3)–O(12)	111.4(2)
–O(12)	1.687(4)				
Mean	1.704				
Cu–O(2)	2.116(3)	O(2)–Cu–O(4)	87.1(2)	O(4)–Cu–O(7)	165.6(1)
–O(4)	1.986(4)	O(2)–Cu–O(5)	94.8(1)	O(4)–Cu–O(10)	94.6(2)
–O(5)	2.088(4)	O(2)–Cu–O(7)	79.6(2)	O(5)–Cu–O(7)	95.4(2)
–O(7)	1.953(4)	O(2)–Cu–O(10)	133.0(2)	O(5)–Cu–O(10)	131.8(1)
–O(10)	1.916(4)	O(4)–Cu–O(5)	80.1(2)	O(7)–Cu–O(10)	98.5(2)
Mean	2.012				
Fe(1)–O(2)	1.964(4)	O(2)–Fe(1)–O(3)	101.8(1)	O(3)–Fe(1)–O(12)	88.1(2)
–O(3)	2.076(3)	O(2)–Fe(1)–O(6)	91.2(2)	O(6)–Fe(1)–O(6′)	80.4(2)
–O(6)	2.068(4)	O(2)–Fe(1)–O(6′)	160.6(2)	O(6)–Fe(1)–O(7)	87.4(1)
–O(6′)	1.987(4)	O(2)–Fe(1)–O(7)	78.9(1)	O(6)–Fe(1)–O(12)	169.0(2)
–O(7)	2.138(3)	O(2)–Fe(1)–O(12)	96.1(2)	O(6′)–Fe(1)–O(7)	83.3(1)
–O(12)	1.920(4)	O(3)–Fe(1)–O(6)	82.3(1)	O(6′)–Fe(1)–O(12)	95.0(2)
Mean	2.026	O(3)–Fe(1)–O(6′)	94.5(1)	O(7)–Fe(1)–O(12)	102.1(1)
		O(3)–Fe(1)–O(7)	169.7(2)		
Fe(2)–O(1)	1.994(4)	O(1)–Fe(2)–O(1′)	77.3(1)	O(1′)–Fe(2)–O(11)	94.1(1)
–O(1′)	2.083(3)	O(1)–Fe(2)–O(4)	161.8(1)	O(4)–Fe(2)–O(5)	81.9(2)
–O(4)	1.999(4)	O(1)–Fe(2)–O(5)	94.0(2)	O(4)–Fe(2)–O(8)	99.2(2)
–O(5)	2.004(4)	O(1)–Fe(2)–O(8)	98.1(2)	O(4)–Fe(2)–O(11)	92.9(2)
–O(8)	2.009(3)	O(1)–Fe(2)–O(11)	93.1(2)	O(5)–Fe(2)–O(8)	85.7(1)
–O(11)	1.928(4)	O(1′)–Fe(2)–O(4)	85.2(1)	O(5)–Fe(2)–O(11)	171.4(2)
Mean	2.003	O(1′)–Fe(2)–O(5)	92.3(1)	O(8)–Fe(2)–O(11)	88.4(2)
		O(1′)–Fe(2)–O(8)	174.8(2)		
Na(1)–O(3)	2.295(4)(2×)	O(3)–Na(1)–O(9)	87.9(2)		
–O(9)	2.190(4)(2×)	O(3)–Na(1)–O(10)	84.3(1)		
–O(10)	2.860(4)(2×)	O(9)–Na(1)–O(10)	74.2(1)		
Mean	2.448				
Na(2)–O(3)	2.864(4)	O(3)–Na(2)–O(3′)	158.5(1)	O(8)–Na(2)–O(9)	66.1(1)
–O(3′)	2.621(4)	O(3)–Na(2)–O(8)	55.7(1)	O(8)–Na(2)–O(9′)	128.3(1)
–O(8)	2.924(4)	O(3)–Na(2)–O(9)	72.0(1)	O(8)–Na(2)–O(10)	70.5(1)
–O(9)	2.397(4)	O(3)–Na(2)–O(9′)	97.9(1)	O(8)–Na(2)–O(12)	83.1(1)
–O(9′)	2.293(3)	O(3)–Na(2)–O(10)	105.9(1)	O(9)–Na(2)–O(9′)	154.2(1)
–O(10)	2.624(5)	O(3)–Na(2)–O(12)	138.5(1)	O(9)–Na(2)–O(10)	127.6(1)
–O(12)	2.930(4)	O(3′)–Na(2)–O(8)	141.9(1)	O(9)–Na(2)–O(12)	88.6(1)
Mean	2.665	O(3′)–Na(2)–O(9)	102.2(1)	O(9′)–Na(2)–O(10)	77.6(1)
		O(3′)–Na(2)–O(9′)	78.3(1)	O(9′)–Na(2)–O(12)	112.8(1)
		O(3′)–Na(2)–O(10)	94.1(1)	O(10)–Na(2)–O(12)	57.8(1)
		O(3′)–Na(2)–O(12)	59.8(1)		

temperature factors (*B*) for all atoms in howardevansite, and Table 4 contains anisotropic thermal parameters for all atoms. Table 5 presents bond lengths and bond angles for all coordination polyhedra, and Table 6 gives the bond-valence table (Brown, 1981). Table 7[1] contains a list of observed and calculated structure factors for the mineral.

Description of the structure

The atomic arrangement of howardevansite can be described as ribbons in the (210) plane, consisting of Cu, Fe, and V atoms and coordinating oxygen atoms. The ribbons extend infinitely in the [001] direction, but terminate laterally in chains of alkali polyhedra. Figure 1 shows the location of the ribbons and chains in end view in the structure, and Figure 2 depicts the coordination polyhedra in the (210) planes. As shown in Figure 2, the (210) planes are formed of Fe(1)O$_6$ and Fe(2)O$_6$ octahedra, CuO$_5$ trigonal bipyramids, and isolated V(1)O$_4$, V(2)O$_4$, and V(3)O$_4$ tetrahedra. The plane contains four of the six oxygen atoms that coordinate the Fe atoms, three of the four oxygen atoms coordinating each of the V atoms and three of the five oxygen atoms forming the CuO$_5$ trigonal dipyramid. Adjacent (210) planes are linked through corner-sharing of the remaining oxygen atoms needed to complete the coordination polyhedra.

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[1] A copy of Table 7 may be ordered as Document Am-88-362 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

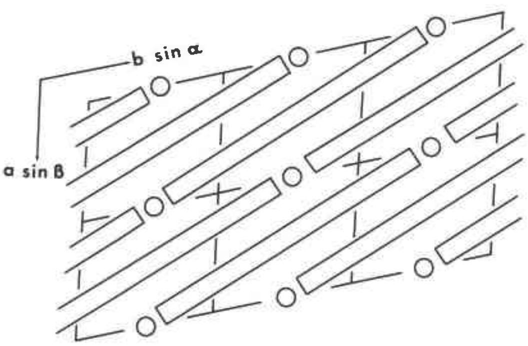

Fig. 1. Structural elements in howardevansite, projected down *c* axis. Rectangles represent (210) planes of Fe, V, and Cu coordination polyhedra; adjacent planes are linked by corner-sharing of oxygen atoms between cations in adjacent planes. Circles represent projections of Na chains.

Each (210) plane terminates laterally in chains of alkali (Na ≫ K) polyhedra (Fig. 3) that are parallel to the *c* axis of howardevansite. The alkali chains are formed of $Na(1)O_6$ octahedra, centered at 0,½,½, and $Na(2)O_7$ polyhedra located slightly off the center of symmetry at 0,½,0; together these polyhedra form infinite chains parallel to *c* at 0,½,*z*. Because of the displacement of Na(2) from the center of symmetry, the Na-Na distance in the chains deviates from *c*/2 (3.326 Å), with Na-Na distances of 3.62 and 3.09 Å. The short Na-Na distance is similar to the Na-Na distance in the NaO_6 octahedral chains in lecontite (3.15Å).

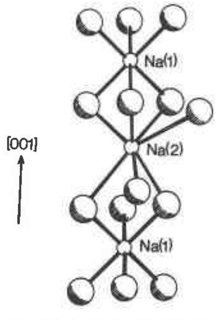

Fig. 3. $Na(1)O_6$ and $Na(2)O_7$ chains in howardevansite. Chains extend infinitely in the [001] direction.

Na(1), located at a symmetry center, is octahedrally coordinated by oxygen with two unusually short Na–O bonds at 2.19 Å. Because of these two short bonds, it is unlikely that the larger K^+ ions substitute for Na(1). Na(2) is coordinated in a trigonal prism, with a seventh bond to oxygen through a prism face. The polyhedron has a greater average bond length (2.67 vs. 2.45 Å) and bond lengths that vary from 2.29 to 2.93 Å. Thus the larger Na(2) site can more easily contain the small amounts of substituent K.

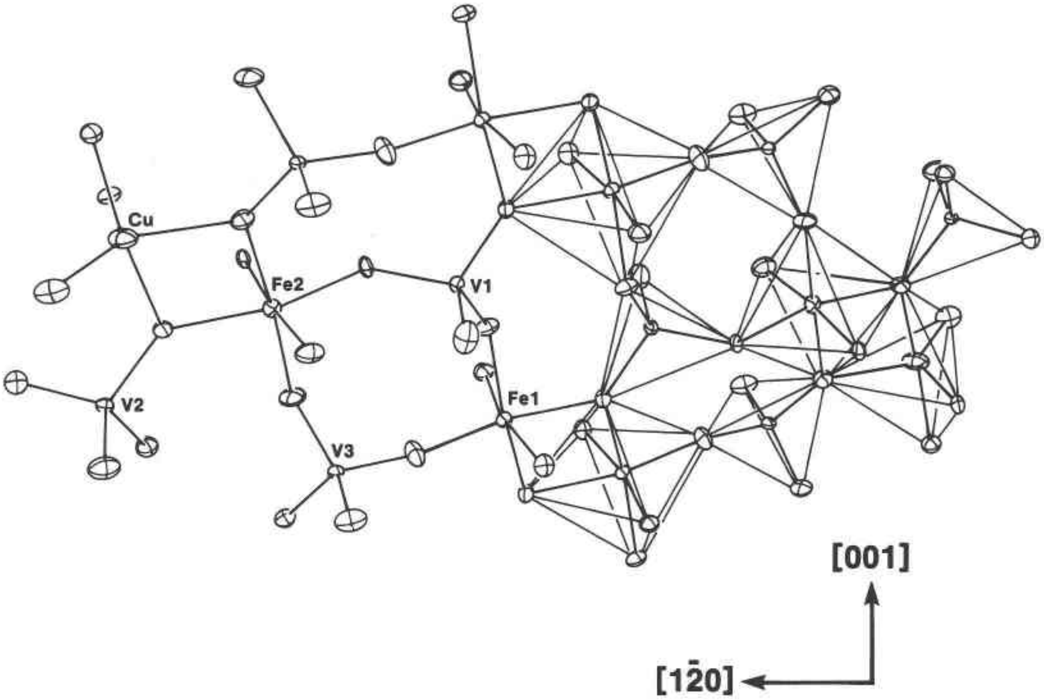

Fig. 2. ORTEP (Johnson, 1965) view of (210) ribbons in howardevansite. View is approximately perpendicular to (210), which contains the cations. Two vectors approximately in the plane of the page are noted for orientation. Planes of coordination polyhedra (VO_4 tetrahedra, CuO_5 trigonal bipyramids, and FeO_6 octahedra) extend infinitely parallel to *c*, but terminate laterally in Na chains (see Fig. 1).

TABLE 6. Bond-valence table for howardevansite

	V(1)	V(2)	V(3)	Cu	Fe(1)	Fe(2)	Na(1)	Na(2)	Oxy sum
O(1)	1.14	—	—	—	—	0.52 0.41	—	—	2.07
O(2)	1.21	—	—	0.29	0.57	—	—	—	2.07
O(3)*	—	1.26	—	—	0.42	—	0.24(2×)	0.06 0.11	2.01
O(4)	—	1.03	—	0.42	—	0.52	—	—	1.97
O(5)	—	—	1.13	0.31	—	0.51	—	—	1.95
O(6)	1.09	—	—	—	0.43 0.53	—	—	—	2.05
O(7)	—	1.18	—	0.46	0.35	—	—	—	1.99
O(8)	—	1.49	—	—	—	0.50	—	0.06	2.05
O(9)*	1.66	—	—	—	—	—	0.30(2×)	0.19 0.24	2.18
O(10)	—	—	1.30	0.52	—	—	0.07(2×)	0.11	2.00
O(11)	—	—	1.39	—	—	0.63	—	—	2.02
O(12)	—	—	1.36	—	0.65	—	—	0.06	2.07
Cation sum	5.10	4.96	5.18	2.00	2.95	3.09	1.22	0.83	

* Because of half-occupancy of Na(2), bond-valence sums for O(3) and O(9) include averaged bond-valence for two Na(2)–O bonds.

PHYSICAL PROPERTIES

Howardevansite occurs as tabular, black euhedral crystals less than 100 μm in greatest dimension. A drawing of a typical crystal showing the dominant forms is given in Figure 4. The mineral has a metallic luster. For the formula $NaCuFe_2(VO_4)_3$, $Z = 2$ and the $D_{calc} = 3.814$ g/cm^3. Howardevansite has a brittle tenacity and a red-brown streak. No distinct cleavages are apparent in the mineral.

The mineral transmits light only on the thinnest edges, with a deep red-brown color. In reflected light in air, howardevansite is medium gray, with moderate anisotropy. Reflectivity values were measured in air on a polished surface of unknown orientation, using a SiC standard. Average minimum and maximum reflectivity values for four wavelengths are 481 nm, 15.5, 20.1%; 547 nm, 15.0, 18.4%; 591 nm, 14.1, 17.2%; and 644 nm, 13.5, 17.1%.

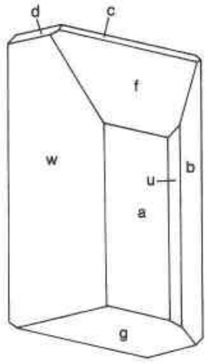

Fig. 4. Drawing of howardevansite showing dominant forms. Labeled forms are $a = (100)$; $b = (010)$; $c = (001)$; $w = (1\bar{1}0)$; $f = (101)$; $g = (\bar{1}01)$; $d = (0\bar{1}1)$. (Crystal morphology measured and figure redrawn from original by H. T. Evans, Jr., U.S. Geological Survey.)

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