VESUVIANITE FROM PAJSBERG, SWEDEN, AND THE ROLE OF Be IN THE VESUVIANITE STRUCTURE

Sharon FITZGERALD

University Museums, University of Delaware, Newark, Delaware 19716 U.S.A.

Peter B. LEAVENS[§]

Department of Geosciences, University of Delaware, Newark, Delaware 19716 U.S.A.

George R. ROSSMAN

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125-2500 U.S.A.

Glenn P.A. YAP

Department of Chemistry and Biochemistry, University of Delaware, Newark Delaware 19716 U.S.A.

Timothy ROSE

Department of Mineral Sciences, Smithsonian Institution, PO Box 37012, MRC 119, Washington, DC 20013-7012 U.S.A.

ABSTRACT

Vesuvianite from Pajsberg, Sweden contains about one atom of Mn, based on 50 cations per formula unit, and small amounts of Be, B, and As. Optical absorption analysis suggests that the Mn is predominantly or entirely trivalent. Crystal-structure analysis indicates that Mn is housed at the general octahedral site Y3, which exhibits only minor distortion from ideal octahedral symmetry. Arsenic is housed at Y2 and Z2, and the formula derived from electron microprobe and LA-ICP-MS analyses suggests minor substitution of Al for Si, also at Z2. Beryllium and B are at T1, between the edge-sharing trimers Y3Y2Y3, as is the case for B in the boron-dominant vesuvianite species wiluite. The total content at T1 is interpreted as 0.82Be, 0.34B, and $0.037Fe^{3+}$.

Keywords: vesuvianite, optical spectra, crystal structure, Be As.

INTRODUCTION

Vesuvianite is one of the most chemically and structurally complex of the silicate minerals. The formula for most vesuvianites may be written as

$$X1_2X2_8X3_8X4Y1Y2_4Y3_8T1_4(SiO_4)_{10}(Si_2O_7)_4$$
$$(O, OH, F)_{10}$$
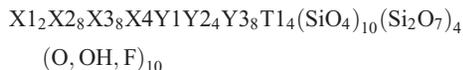
(Groat & Hawthorne 1992), where the X sites are eight-coordinated, Y sites six or five-coordinated, and Z and T sites four coordinated; more compactly, it may be written as

$$X_{19}Y_{13}T_4Si_{18}O_{68}(O, OH, F)_{10}$$

where $X = Ca$, Na, and REE, chiefly Ce (Fitzgerald *et al.* 1987); $Y1 = Cu^{2+}$, Mn^{3+}, Fe^{3+}, or Al (Rucklidge *et al.* 1975, Fitzgerald *et al.* 1986a, b, Armbruster *et al.* 2002); $Y2 = Al$; $Y3 = Al$, Fe^{3+}, Fe^{2+}, Mg, Mn^{2+}, Ti, Zn, with divalent cations ideally $= 2$; and T being vacant, or occupied by B (Groat *et al.* 1994b), or small amounts of Al or other Y-group cations (Groat *et al.* 1994a). Additionally, vesuvianite may contain B, Cl,

§ *Corresponding author e-mail address*: pbl@udel.edu

or Bi at additional positions, and an additional oxygen atom (O12) to help charge-balance them (Groat *et al*. 1994b, Groat & Evans 2012.)

The dark, brownish-red vesuvianite from Pajsberg, Sweden, has been anomalous since it was first analyzed by Flink (1887, reported in Dana 1893), who found 12.49% MnO. The analysis cannot be converted into a plausible vesuvianite formula; on the basis of 50 X + Y + Si cations, Ca = 15.74 *apfu* (atoms per formula unit) instead of the expected 19 *apfu*, and Si = 18.36 *apfu*.

Fitzgerald *et al*. (1992) found only 2.92 and 2.41% MnO by microprobe analyses in two samples of Pajsberg vesuvianite, in line with vesuvianite from Franklin, New Jersey and other localities, and they were unable to create an entirely satisfactory empirical formula for the material. If the formulae are calculated on the basis of 50 X + Y + Si cations, Ca + Na are substantially below the ideal 19 *apfu* and Si even further below the ideal 18 *apfu*. These anomalies suggested that the Pajsberg vesuvianite contains excess Y-group cations (Groat *et al*. 1994a). If the formulae are calculated on the basis of 19 Ca + Na, or full occupancy of the X-sites, Si is still below the expected 18 *apfu*, and Y-group cations are in excess of 13 *apfu* by about 1.5. These uncertainties regarding the composition and crystal chemistry of the Pajsberg vesuvianite prompted this detailed study.

OCCURRENCE

The Pajsberg mine is a small deposit near the town of Persberg, Varmland County, Sweden, that produced about 3500 tons of manganese ore and 8500 tons of iron ore, closing in 1887. The manganese ore was granular, banded hausmannite in dolomite and the iron ore was quartz-hematite-magnetite. Pajsberg is one of the Långban-type ore deposits of the Bergslagen district of Sweden (Moore 1970). Långban-type deposits contain separated but associated zones of iron and manganese oxide ores, enclosed in Precambrian dolomitic marble. They are believed to be sedimentary-exhalative in origin, but have undergone high-grade metamorphism; several contain secondary, lower-temperature veins in which an enormous variety of unusual to unique mineral species have been found.

Two specimens of vesuvianite which were previously analyzed by Fitzgerald *et al*. (1992) were examined for this study. Both are from the Carl Bosch collection, now at the Smithsonian Institution; the catalog numbers are B20761 and B20770. Both consist of euhedral, cinnamon-red crystals of vesuvianite to 3 mm in size associated with pink olivine in the forsterite–tephroite series, in calcite-filled veins cutting granular, gneissic magnetite-quartz ore. The calcite is Mn-rich and fluoresces bright red in shortwave ultraviolet light. The specimens are each about 5 cm in maximum dimension, and the veins are about 0.5 cm wide. B20761, the chemically more anomalous of the two (Fitzgerald *et al*. 1992), was the focus of the study. An additional piece of B20761 obtained from the Smithsonian Institution was used for the spectroscopic studies. The study involved many false starts and blind paths and included efforts by a number of contributors over several years.

METHODS

Chemistry

A crystal from B20761 was analyzed at Elemental Research Incorporated by laser ablation, induction-coupled plasma, mass spectrometry (LA-ICP-MS), using pc detection mode and NBS612 glass standard for the trace elements. Major elements were analyzed by analog mode and are only semiquantitative. The results of this analysis are given in Table 1. The ESDs were not provided.

New electron microprobe analyses were obtained from newly mounted grains of each specimen at the Department of Mineral Sciences, Smithsonian Institution, using a JEOL 8900 Superprobe, operated at 15 kV and 20 nA. Primary standards used for analysis were: Kakanui hornblende (NMNH 143965) for Si, Al, Fe, Mg, Ca, and Ti; manganite (NMNH 157872) for Mn; and arsenic metal for As. Secondary standards used were: diopside (NMNH 117733) for Si, Al, Fe, and Mg; Kakanui augite (NMNH 122142) for Si, Al, Fe, Mg, Ca, Ti, and Mn; and fluorapatite (NMNH 104021) for As. Analytical uncertainty is about 1–3%. Unfortunately, there was a miscommunication in the discussion of elements to be analyzed, and fluorine was not included in the new analyses. The analytical results are given in Table 2.

X-ray crystallography

A single crystal of B20761 was selected from the sectioned samples, mounted with viscous oil, cooled to the 200 K data-collection temperature by a chilled nitrogen stream, and subjected to diffraction using a Bruker AXS SmartApex CCD diffractometer with graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). Crystal data and structure refinement information are given in Table 3, and structure refinement data in Table 4 [Table 4 is available from the MAC Depository of Unpublished Data, document vesuvianite CM54-6_10.3749/canmin.1500051]. The data were treated with absorption corrections based on redundant multiscan data (Bruker 2007). Unit-cell parameters were determined by sampling three

TABLE 1. LA-ICP-MS ANALYSIS OF VESUVIANITE FROM PAJSBERG, SWEDEN IN PPM BY WEIGHT

Lithium	0.3	Antimony	31.8
Beryllium	2510	Tellurium	2.4
Boron	1270	Iodine	10.5
Sodium	33.6	Cesium	<0.1
Manganese	33300		
Aluminum	maj. cmp.	Barium	0.3
Silicon	maj. cmp.	Lanthanum	45.7
Phosphorous	89.6	Cerium	74.2
Calcium	maj. cmp.	Praseodymium	6.2
Scandium	6.6	Neodymium	19.0
Titanium	290		
Vanadium	22.5	Europium	2.1
Chromium	72.5	Samarium	4.6
Manganese	maj cmp.	Gadolinium	23.6
Iron	maj. cmp.	Terbium	0.9
Cobalt	17.9	Dysprosium	4.3
Nickel	17.2		
Copper	261	Holmium	0.7
Zinc	156	Erbium	1.9
Gallium	7.8	Thulium	0.2
Gremanium	190	Ytterbium	1.8
Arsenic	2820	Lutetium	0.2
Selenium	<0.1		
Rubidium	<0.1	Hafnium	0.8
Strontium	88.2	Tantalum	<0.1
		Tungsten	<0.1
Yttrium	19.7	Rhenium	<0.1
Zirconium	7.8	Osmium	<0.1
Niobium	0.4		
Molybdenum	0.3	Iridium	<0.1
Ruthenium	<0.1	Platinum	<0.1
		Gold	<0.1
Rhodium	0.4	Mercury	1.3
Palladium	0.2	Thalium	<0.1
Silver	<0.1		
Cadmium	0.2	Lead	1700
Indium	0.8	Bismuth	23.3
		Thorium	0.2
Tin	4.0	Uranium	12.1

Note: Elements greater than 1% are only semi-quantitative; elements greater than 2% are listed as maj. cmp. (major component).

different sections of the Ewald sphere. The systematic absences in the diffraction data, unit-cell parameters, and equivalent reflections are consistent with the reported space group, $P4/ncc$ (No. 130). The structure was solved using atomic coordinates from an isomorphic Cu-rich vesuvianite from Franklin, New Jersey (Fitzgerald *et al*. 1986a), modified by the model for boron-bearing vesuvianite proposed by Groat *et al*. (1994b), and refined with full-matrix, least-squares

procedures on F^2 with anisotropic displacement parameters. Corresponding substitutionally disordered, coincident atom pairs Al1 and As; O11 and F11; Si2 and As2; and Fe2 and Mg2 were treated with equal atomic coordinates and equal atomic displacement parameters in order to refine the site occupancy ratios as independent free variables. Associated but not coincident disordered sites Fe1 and Ca4, and B1 and B2, which were freely allowed to refine in positions, were treated with equal atomic displacement parameters. Atomic scattering factors are contained in the SHELXTL program library (Sheldrick 2008).

All X sites were refined as Ca, Y1 was refined as Fe, Y2 as Al, and Y3 was split between Mg (proxying for Mg + Al) and Fe (proxying for Fe + Mn) but constrained to total 1. X4 and Y1, adjacent sites along the four-fold axis that are each normally half-occupied, were tied together with a total occupancy of 1. Beryllium and B were tentatively assigned to T1 as B. After the first round of refinement it was apparent that Si2 contained excess electron density, so it was split into Si and As but constrained to total 1. The structure failed to converge to a satisfactory degree, so Y2 was split into Al and As, following Groat *et al*. (2013), T2 was allowed to refine as B, and O(11) was split into O and F. The structure refined to a final R of 1.88%. Atomic positions and isotropic thermal parameters are given in Table 5, anisotropic temperature factors in Table 6, and selected bond lengths and angles in Table 7. Despite the low residuals attained, interpretation of the structure is not entirely straightforward because of the complexity of the substitutions involved.

Visible, near-infrared optical absorption spectroscopy

Optical absorption spectra were obtained from a crystal of B20761 with a Cary 17I spectrophotometer using a calcite Glan-Thompson polarizer. The sample was prepared as a doubly polished slab 108 μm thick which contained the **c**-axis in the plane of the slab.

Optics

Indices of refraction were determined from a grain of B20761 mounted on a spindle stage, with an estimated accuracy of ±0.002. Indices of refraction of immersion oils were determined using a Leitz Jelly refractometer.

RESULTS

Chemistry

The most notable features of the LA-ICP-MS analysis are that this vesuvianite contains ~2% As, 1250 ppm by weight B, or 0.40% by weight B_2O_3, and

TABLE 2. ELECTRON MICROPROBE COMPOSITIONS OF PAJSBERG
VESUVIANITES, AND ATOMIC PROPORTIONS CALCULATED ON THE BASIS OF 50
CATIONS

	B20761 Left core	B20761 Left rim	B20761 Right core	B20761 Right rim	B20770 core	B20770 rim
SiO_2	34.89	34.38	34.59	34.42	34.82	34.98
As_2O_5	1.20	1.63	1.47	1.59	0.99	1.15
Al_2O_3	11.05	10.17	11.38	10.49	10.19	9.91
Fe_2O_3	8.38	8.67	7.70	8.24	9.57	9.41
MgO	3.75	4.11	3.88	3.95	3.60	3.73
MnO	2.27	2.47	2.05	2.57	2.52	3.03
CaO	35.45	35.26	35.69	35.32	35.23	34.95
Total	97.02	96.78	96.79	96.66	96.93	97.17
Ca	18.96	18.95	19.02	18.97	18.9	18.73
Al	6.48	5.99	6.67	6.20	6.02	5.84
Fe	3.11	3.28	2.87	3.11	3.61	3.55
Mg	2.79	3.07	2.87	2.96	2.68	2.80
Mn	0.93	1.06	0.87	1.09	1.08	1.29
Si	17.43	17.22	17.31	17.26	17.45	17.50
As	0.30	0.42	0.39	0.42	0.27	0.30
Charge	145.34	145.10	145.35	145.24	145.37	145.31

TABLE 3. CRYSTAL DATA AND STRUCTURE REFINEMENT PROCEDURES FOR
PAJSBERG VESUVIANITE B20761

Identification code	petl006q
Empirical formula	$Al_{3.93}As_{0.41}B_{1.23}Ca_{19.06}F_{2.23}Fe_{3.84}Mg_{5.11}O_{75.78}Si_{17.70}$
Formula weight	3004.39
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system, space group	Tetragonal, $P4/nnc$
Unit cell dimensions	$a = 15.6644(8)$ Å $\alpha = 90°$
	$b = 15.6644(8)$ Å $\beta = 90°$
	$c = 11.8434(6)$ Å $\gamma = 90°$
Volume	2906.1(3) Å^3
Z, Calculated density	2, 3.433 Mg/m^3
Absorption coefficient	3.521 mm^{-1}
F(000)	2974
Crystal size	$0.132 \times 0.110 \times 0.066$ mm
Theta range for data collection	2.601 to 27.521 deg.
Limiting indices	$-19 \leq h \leq 20, -20 \leq k \leq 20, -15 \leq l \leq 15$
Reflections collected / unique	35276 / 1684 [R(int) = 0.0313]
Completeness to theta = 25.000	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8022 and 0.6557
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1684 / 0 / 162
Goodness-of-fit on F^2	1.101
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0188$, w$R_2 = 0.0512$
R indices (all data)	$R_1 = 0.0211$, w$R_2 = 0.0526$
Extinction coefficient	n/a
Largest diff. peak and hole	0.422 and -0.740 e Å^{-3}

TABLE 5. ATOMIC POSITIONS AND THERMAL PARAMETERS FOR PAJSBERG VESUVIANITE B20761

	x	y	z	$U_{(eq)}$
Ca1	7500	2500	2500	10(1)
Ca2	8106(1)	454(1)	3789(1)	8(1)
Ca3	8989(1)	8200(1)	8932(1)	16(1)
Ca4	7500	7500	1448(1)	13(1)
Fe1	7500	7500	435(1)	13(1)
Al1	0	0	0	7(1)
As1	0	0	0	7(1)
Fe2	8888(1)	1206(1)	1266(1)	5(1)
Mg2	8888(1)	1206(1)	1266(1)	5(1)
Si1	7500	2500	0	7(1)
Si2	8201(1)	399(1)	8718(1)	6(1)
As2	8201(1)	399(1)	8718(1)	6(1)
Si3	9156(1)	8495(1)	3638(1)	8(1)
B1	576(5)	576(5)	2500	17(3)
B2	2500	2500	2500	17(3)
O1	7784(1)	1727(1)	853(1)	10(1)
O2	8820(1)	1613(1)	2820(1)	10(1)
O3	9559(1)	2240(1)	741(1)	10(1)
O4	9399(1)	1051(1)	4689(1)	9(1)
O5	8282(1)	116(1)	1802(1)	11(1)
O6	8786(1)	7252(1)	559(1)	14(1)
O7	8298(1)	9446(1)	8178(1)	18(1)
O8	9398(1)	9081(1)	689(1)	9(1)
O9	8532(1)	8532(1)	2500	11(1)
O10	7500	7500	8666(2)	16(1)
O11	9986(1)	608(1)	1364(1)	13(1)
F11	9986(1)	608(1)	1364(1)	13(1)

Note: Displacement parameters ($\mathring{A}^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 6. ATOMIC POSITIONS AND THERMAL PARAMETERS FOR PAJSBERG VESUVIANITE B20761

	x	y	z	$U_{(eq)}$
X1	7500	2500	2500	10(1)
X2	8106(1)	454(1)	3789(1)	8(1)
X3	8989(1)	8200(1)	8932(1)	16(1)
X4	7500	7500	1448(1)	13(1)
Y1	7500	7500	435(1)	13(1)
Y2	0	0	0	7(1)
Y3	8888(1)	1206(1)	1266(1)	5(1)
Z1	7500	2500	0	7(1)
Z2	8201(1)	399(1)	8718(1)	6(1)
Z3	9156(1)	8495(1)	3638(1)	8(1)
T1	576(5)	576(5)	2500	17(3)
T2	2500	2500	2500	17(3)
O1	7784(1)	1727(1)	853(1)	10(1)
O2	8820(1)	1613(1)	2820(1)	10(1)
O3	9559(1)	2240(1)	741(1)	10(1)
O4	9399(1)	1051(1)	4689(1)	9(1)
O5	8282(1)	116(1)	1802(1)	11(1)
O6	8786(1)	7252(1)	559(1)	14(1)
O7	8298(1)	9446(1)	8178(1)	18(1)
O8	9398(1)	9081(1)	689(1)	9(1)
O9	8532(1)	8532(1)	2500	11(1)
O10	7500	7500	8666(2)	16(1)
O11	9986(1)	608(1)	1364(1)	13(1)
F11	9986(1)	608(1)	1364(1)	13(1)

Note: Displacement parameters ($\mathring{A}^2 \times 10^3$). $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

2450 ppm Be, or 0.87 wt.% BeO. Arsenic has been reported in vesuvianite by Pan & Fleet (1992), Groat & Evans (2012), and Groat et al. (2013) in amounts up to 1.71% As_2O_5. Beryllium has been reported previously in amounts greater than 1% BeO in vesuvianite from Franklin, New Jersey (Palache 1935, Palache & Bauer 1930, Hurlbut 1955); Turnback Lake, Canada (Meen 1939); and Iron Mountains, New Mexico (Glass et al. 1944), but its location in the structure has not been determined.

Several differences between the EMP analyses in Fitzgerald et al. (1992) and these new ones are apparent: the totals are higher by about 2%, CaO is higher by about 1%, and both SiO_2 and Al_2O_3 are somewhat higher; other elements are less strongly affected. The new chemical analyses that include As provide a basis for a new interpretation of the formula. Based on the optical spectroscopy (discussed below), Fe is considered exclusively Fe^{3+} and Mn exclusively

Mn^{3+}. The electron microprobe analyses can be converted to formulae by normalizing either to 19 Ca or to 50 cations, excluding Be + B. Normalizing to 19 Ca gives an excess of about 0.1 Y-group cations (Groat et al. 1994a); however, normalizing to 50 cations gives a slight deficiency in Ca for the rims of both samples. The LA-ICP-MS analysis found 1700 ppm Pb, which would substitute for Ca. As Mn varies inversely with Ca between the cores and the rims, a small amount of Mn may also substitute for Ca, at least in the rims, as previously suggested by Fitzgerald et al. (1992). We feel that normalizing to 50 cations gives the most coherent results; however, the differences between the two normalizing schemes are minor.

From the LA-ICP-MS analysis, B20761 also contains 2510 ppm Be, 1270 ppm B, and 1700 ppm Pb by weight. These are discussed below. The problems encountered by Fitzgerald et al. (1992) in normalizing the analyses to formulae are resolved by the new analyses; the new compositions of B20761 and B20770 are also not very different.

TABLE 7. SELECTED BOND LENGTHS AND ANGLES FOR PAJSBERG VESUVIANITE B20761

X1–O1	2.3383(13)
X1–O1	2.3383(13)
X1–O1	2.3383(13)
X1–O1	2.3383(13)
X1–O2	2.5196(12)
X1–O2	2.5196(13)
X1–O2	2.5196(12)
X1–O2	2.5196(13)
X2–O8	2.3344(13)
X2–O5	2.3440(13)
X2–O3	2.3743(13)
X2–O2	2.4208(13)
X2–O5	2.4274(13)
X2–O1	2.4704(13)
X2–O4	2.4734(13)
X2–O6	3.0352(15)
X3–O7	2.4044(14)
X3–O3	2.4077(13)
X3–O6	2.4548(14)
X3–F11	2.4866(13)
X3–O11	2.4866(13)
X3–O8	2.5774(13)
X3–O10	2.5972(6)
X3–O7	2.6035(15)
X3–O7	2.6106(16)
X3–O6	2.8870(14)
X4–O6	2.3061(15)
X4–O6	2.3061(15)
X4–O6	2.3061(15)
X4–O6	2.3061(15)
X4–O9	2.6045(18)
X4–O9	2.6045(18)
X4–O9	2.6045(18)
X4–O9	2.6045(18)
Y1–O6	2.0571(14)
Y1–O6	2.0571(14)
Y1–O6	2.0571(14)
Y1–O6	2.0571(14)
Y1–O10	2.094(3)
Y2–O11	1.8757(13)
Y2–O11	1.8757(13)
Y2–O8	1.9052(12)
Y2–O8	1.9052(12)
Y2–O4	1.9317(12)
Y2–O4	1.9317(12)
Y3–O2	1.9505(13)
Y3–O11	1.9615(13)
Y3–O1	1.9732(13)
Y3–O3	2.0292(14)
Y3–O5	2.0549(14)
Y3–O4	2.0970(13)
Z1–O1	1.6389(13)

TABLE 7. CONTINUED

Z1–O1	1.6389(13)
Z1–O10	1.6389(13)
Z1–O1	1.6389(13)
Z2–O7	1.6302(14)
Z2–O3	1.6364(13)
Z2–O2	1.6476(13)
Z2–O4	1.6726(13)
Z3–O6	1.6149(14)
Z3–O5	1.6265(14)
Z3–O8	1.6270(13)
Z3–O9	1.6654(8)
T1–O11	1.633(4)
T1–O11	1.633(4)
T1–O7	1.939(7)
T1–O7	1.939(7)
T2–O10	1.381(3)
T2–O10	1.381(3)
O1–X1–O1	117.63(6)
O1–X1–O1	66.97(6)
O1–X1–O1	158.03(6)
O1–X1–O1	158.03(6)
O1–X1–O1	66.97(6)
O1–X1–O1	117.63(6)
O1–X1–O2	124.58(4)
O1–X1–O2	90.21(4)
O1–X1–O2	71.56(4)
O1–X1–O2	75.23(4)
O1–X1–O2	71.56(4)
O1–X1–O2	75.23(4)
O1–X1–O2	124.58(4)
O1–X1–O2	90.21(4)
O2–X1–O2	162.67(6)
O1–X1–O2	75.23(4)
O1–X1–O2	71.56(4)
O1–X1–O2	90.21(4)
O1–X1–O2	124.58(4)
O2–X1–O2	69.76(6)
O2–X1–O2	113.03(6)
O1–X1–O2	90.21(4)
O1–X1–O2	124.58(4)
O1–X1–O2	75.23(4)
O1–X1–O2	71.56(4)
O2–X1–O2	113.04(6)
O2–X1–O2	69.76(6)
O2–X1–O2	162.67(6)
O8–X2–O5	121.70(5)
O8–X2–O3	83.44(4)
O5–X2–O3	94.41(5)
O8–X2–O2	110.79(4)
O5–X2–O2	117.12(5)
O3–X2–O2	124.97(5)
O8–X2–O5	91.61(4)
O5–X2–O5	76.48(5)

TABLE 7. CONTINUED

O3–X2–O5	165.39(5)
O2–X2–O5	69.63(4)
O8–X2–O1	153.63(4)
O5–X2–O1	73.14(4)
O3–X2–O1	73.19(4)
O2–X2–O1	74.72(4)
O5–X2–O1	113.97(4)
O8–X2–O4	67.55(4)
O5–X2–O4	166.85(5)
O3–X2–O4	76.75(4)
O2–X2–O4	62.77(4)
O5–X2–O4	114.06(4)
O1–X2–O4	94.77(4)
O8–X2–O6	67.12(4)
O5–X2–O6	58.18(4)
O3–X2–O6	69.16(4)
O2–X2–O6	165.83(4)
O5–X2–O6	96.25(4)
O1–X2–O6	113.72(4)
O4–X2–O6	125.25(4)
O7–X3–O11	68.24(5)
O3–X3–O11	68.18(4)
O6–X3–O11	130.46(5)
O7–X3–O8	88.70(4)
O3–X3–O8	77.81(4)
O6–X3–O8	73.86(4)
F11–X3–O8	63.38(4)
O11–X3–O8	63.38(4)
O7–X3–O10	83.87(4)
O3–X3–O10	138.30(4)
O6–X3–O10	73.90(6)
F11–X3–O10	151.64(5)
O11–X3–O10	151.64(5)
O8–X3–O10	123.13(6)
O7–X3–O7	73.75(6)
O3–X3–O7	84.94(4)
O6–X3–O7	145.55(5)
F11–X3–O7	69.11(5)
O11–X3–O7	69.11(5)
O8–X3–O7	132.49(5)
O10–X3–O7	98.95(7)
O7–X3–O7	136.58(7)
O3–X3–O7	62.51(4)
O6–X3–O7	76.10(4)
F11–X3–O7	116.71(5)
O11–X3–O7	116.71(5)
O8–X3–O7	133.55(4)
O10–X3–O7	79.94(4)
O70–X3–O7	69.46(5)
O7–X3–O6	71.72(5)
O3–X3–O6	128.26(4)
O6–X3–O6	65.22(5)
F11–X3–O6	106.87(4)
O11–X3–O6	106.87(4)
O8–X3–O6	57.17(4)

TABLE 7. CONTINUED

O10–X3–O6	67.06(6)
O7–X3–O6	143.82(4)
O7–X3–O6	134.31(4)
O6–X4–O6	77.97(4)
O6–X4–O6	125.68(10)
O6–X4–O6	77.97(4)
O6–X4–O6	77.97(4)
O6–X4–O6	125.68(10)
O6–X4–O6	77.97(4)
O6–X4–O9	149.96(3)
O6–X4–O9	130.99(3)
O6–X4–O9	64.60(4)
O6–X4–O9	77.34(4)
O6–X4–O9	64.60(4)
O6–X4–O9	77.34(4)
O5–X4–O9	149.96(3)
O6–X4–O9	130.99(3)
O9–X4–O9	122.84(7)
O6–X4–O9	77.34(4)
O6–X4–O9	149.96(3)
O6–X4–O9	130.99(3)
O6–X4–O9	64.60(4)
O9–X4–O9	76.77(3)
O9–X4–O9	76.77(3)
O6–X4–O9	130.99(3)
O6–X4–O9	64.60(4)
O6–X4–O9	77.34(4)
O6–X4–O9	149.96(3)
O9–X4–O9	76.77(3)
O9–X4–O9	122.84(7)
O6–Y1–O6	171.79(10)
O6–Y1–O6	89.707(8)
O6–Y1–O6	89.706(8)
O6–Y1–O6	89.706(8)
O6–Y1–O6	89.708(8)
O6–Y1–O6	171.79(10)
O6–Y1–O10	94.10(5)
O6–Y1–O10	94.10(5)
O6–Y1–O10	94.10(5)
O6–Y1–O10	94.10(5)
O11–Y2–O11	180.00(11)
O11–Y2–O8	90.52(5)
O11–Y2–O8	89.48(5)
O11–Y2–O8	89.48(5)
O11–Y2–O8	90.52(5)
O8–Y2–O8	180.00(10)
O11–Y2–O4	95.37(5)
O11–Y2–O4	84.63(5)
O8–Y2–O4	88.42(5)
O8–Y2–O4	91.58(5)
O11–Y2–O4	84.63(5)
O11–Y2–O4	95.37(5)
O8–Y2–O4	91.58(5)
O8–Y2–O4	88.42(5)

TABLE 7. CONTINUED

O4–Y2–O4	180.00(10)
O2–Y3–O11	98.53(5)
O2–Y3–O1	92.91(5)
O11–Y3–O1	168.55(6)
O2–Y3–O3	93.30(5)
O11–Y3–O3	86.86(5)
O1–Y3–O3	92.73(5)
O2–Y3–O5	87.39(5)
O11–Y3–O5	89.43(5)
O1–Y3–O5	90.87(5)
O3–Y3–O5	176.29(5)
O2–Y3–O4	172.14(5)
O11–Y3–O4	78.27(5)
O1–Y3–O4	90.35(5)
O3–Y3–O4	93.69(5)
O5–Y3–O4	85.42(5)
O1–Z1–O1	112.35(5)
O1–Z1vO10	103.85(9)
O1–Z1–O10	112.35(5)
O1–Z1–O1	112.35(5)
O1–Z1–O1	103.85(9)
O10–Z1–O1	112.35(5)
O7–Z2–O3	106.04(8)
O7–Z2–O2	114.24(7)
O3–Z2–O2	112.71(7)
O7–Z2–O4	112.18(7)
O3–Z2–O4	111.52(7)
O2–Z2–O4	100.31(7)
O6–Z3–O5	111.79(7)
O6–Z3–O8	108.36(7)
O5–Z3–O8	113.75(7)
O6–Z3–O9	106.95(8)
O5–Z3–O9	106.85(6)
O8–Z3–O9	108.88(6)
O11–T1–O11	135.5(7)
O11–T1–O7	107.63(16)
O11–T1–O7	100.06(15)
O11–T1–O7	100.06(15)
O11–T1–O7	107.63(16)
O7–T1–O7	101.8(5)
O10–T2–O10	180.0
O10–T2–X3	123.332(9)
O10–T2–X3	56.668(9)
O10–T2–X3	56.668(9)
O10–T2–X3	123.332(9)

Note: Lengths in Angstroms, angles in degrees. ESDs in parentheses.

Visible, near-infrared optical absorption spectroscopy

Interpretation of the optical absorption spectrum (Fig. 1) is not straightforward. In the ultraviolet range from 350 to 400 nm, the spectrum is dominated by an
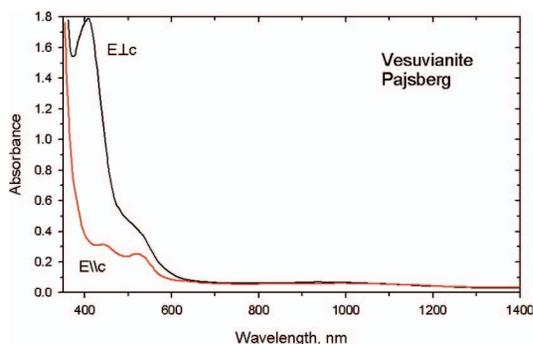
FIG. 1. Optical absorption spectrum of the Pajsberg vesuvianite obtained with light polarized parallel and perpendicular to the **c**-axis of a 0.180 mm-thick slab.

intense absorption which tails into the visible portion of the spectrum. In the visible region, the most intense band, centered at about 415 nm, is polarized in the $E\perp c$ direction. Two less-intense bands occur at 451 nm (present in the $E//c$ direction, but possibly obstructed in the $E\perp c$ direction) and at 531 nm (present in both polarizations). There is also a hint of a weak feature near 1015 nm.

First consider the role of iron. If the iron is mostly Fe^{2+}, Manning (Manning & Tricker 1975, Manning 1968) indicates that the absorption bands would be near 830 and 1110 nm. He does not provide an epsilon value for the Fe^{2+}, but typical values for Fe^{2+} in sites of low distortion are around 10. This leads to the expectation of a band of at least 0.37 absorbance units in this wavelength region. No such bands are present. And, if the iron were at sites with distorted octahedral coordination, the intensity would be even higher. Thus we can conclude that Fe^{2+} is absent, or at best only a minor component of the iron in the Pajsberg vesuvianite, possibly causing the weak feature near 1015 nm.

The optical spectra indicate that the iron is mostly Fe^{3+}. Manning (Manning 1968, Manning & Tricker 1975) established that the absorption of Fe^{3+} is at about 463 nm with greatest intensity in the $E//c$ direction with an intensity given by the epsilon value of 1.5 if the Fe^{3+} is at the octahedral sites. Given these assumptions, one can calculate from Beer's Law that a 463 nm band in the Pajsberg sample would have an absorbance of only about 0.056. Such a band would be barely seen in the spectrum of Figure 1, and, in fact, is not seen, suggesting that some of the iron is not at the octahedral sites.

The possibility arises that some of the features in the Pajsberg vesuvianite spectrum are from Mn^{2+}. At sites with approximately octahedral coordination, Mn^{2+} has a spectrum with bands near 412, 450, and

550 nm, so this possibility must be considered. Because Mn^{2+} bands are spin-forbidden, they are very weak, and, based on an intensity argument assuming a molar absorptivity (epsilon value) of 1.0 for the 411 nm band, the Pajsberg vesuvianite would have to have a Mn^{2+} concentration of at least 74 moles/liter (more than 100% MnO by weight) to provide the absorption intensity observed in its spectrum. Such a high concentration is physically impossible. Even an epsilon of 1.0 is high for many Mn^{2+} phases. For example, the epsilon of the equivalent band (at 396.5 nm) in $NaMnF_3$ at 80 K is about 0.22 (Srivastava & Mehra 1972), which would demand an even higher concentration of Mn to give the observed spectrum.

The role of Mn^{3+} is suggested by the fact that many minerals that have modest concentrations of Mn^{3+} at a six-coordinated site are red in color, as is the Palsberg vesuvianite. Such phases with Mn^{3+} are subject to Jahn-Teller distortion and commonly have an intense absorption band in their optical spectra in the 450 to 550 nm region and a weaker, lower-energy component whose separation from the dominant band depends upon the magnitude of the distortion of the site coordination from octahedral symmetry.

The feature near 531 nm in the Pajsberg vesuvianite spectrum is consistent with the dominant Mn^{3+} feature in the spectrum of lilac vesuvianite from Naslawice, Poland (Platonov et al. 1995) and in the spectrum of lilac Mn^{3+}-bearing vesuvianite from Asbestos, Quebec, Canada (Rossman 2015). However, unlike these spectra, the 531 nm band in the Pajsberg spectrum is not the most intense feature; rather, the 415 nm band is the dominant feature, which is at an unusual position for Mn^{3+}.

There are two literature spectra of vesuvianite with similar intense features at similarly short wavelengths assigned to Mn^{3+} (Platonov et al. 1995). The 415 feature of the Pajsberg spectrum resembles the 424 nm dominant features in the spectra of the pink vesuvianite from Naslawice, Poland, and a similar spectrum from yellow vesuvianite from Jordanow, Poland. Each of these spectra adds credence to the possibility that the Pajsberg vesuvianite is dominated by Mn^{3+}.

Some uncertainties in the assignment remain. The full-width at half-height of the 415 nm band is about 3350 cm^{-1}, which is about halfway between the widths commonly seen for crystal-field transitions of individual cations and the widths of intervalence charge-transfer bands (Mattson & Rossman 1987). One possible explanation is that Mn occupies multiple crystal sites. The chemical analyses above show that the dominant transition metal ion in the Pajsberg vesuvianite is Fe, and charge-balance considerations and optical spectra strongly suggest that it is dominantly present as Fe^{3+}. This raises the possibility

that Mn^{2+}–Fe^{3+} interactions of the type discussed by Smith et al. (1983) may contribute to the spectrum. Smith et al. (1983) considered the interaction between pairs of $Mn^{2+}(VI)$ and $Fe^{3+}(IV)$ ions, each with a d^5 electron configuration, and thus with only spin-forbidden bands, which produce high-intensity absorption when the two ions interact with incident light in concert. Although the alternate case of interactions between octahedrally coordinated Mn^{2+} and Fe^{3+} pairs has not been experimentally demonstrated, interactions between pairs of octahedrally coordinated Fe^{3+} ions in minerals has been well documented (Rossman 1975). Interactions between cations at the T2 site with the Y3 site could contribute to the spectrum in the E\\c direction, but the information at hand does not establish that possibility.

Optics

The sample is optically negative and faintly biaxial, with $2V < 5°$. Indices are $\varepsilon = 1.733(0.002)$, $\omega = 1.738(0.002)$; pleochroism is E pale orange brown, O orange brown. This is in contrast to the much stronger pleochroism from colorless-yellowish to dark red-lilac observed in manganvesuvianite from the Kalahari manganese fields, South Africa (Armbruster et al. 2002), which contains 15.96 wt.% Mn_2O_3 at Y1 and Y3. Wiluite, the vesuvianite-group mineral with the T site at least one-half occupied by B, is optically positive.

DISCUSSION

Site occupancy

Some differences between this refinement and those of Groat et al. (1994b) should be mentioned: there is no indication of an O12 position in this structure, despite the indicated small occupancy of T2. Also, despite the fairly large thermal parameters of O7 and O10, a satisfactory refinement was attained without splitting these sites into a and b positions.

X1, X2, and X3 refine as only Ca. X4, on the four-fold axis, is close to Y1. Both are sites of occupancy 2, but because of their proximity, adjacent X4 and Y1 sites cannot both be occupied. The two sites are typically both one-half occupied. In this structure X4 refined as 0.53Ca (1.06 atoms) and Y1 as 0.47Fe (0.94 atoms). These values may reflect actual site occupancy, or some heavier atom may substitute for Ca at X4, raising its apparent occupancy. The substitution of Pb or Mn for Ca at X4 would raise the electron density and apparent occupancy of the site. In particular, the amount of lead from the LA-ICP-MS analysis gives 0.02 atoms of Pb in the formula, equivalent in electron density to 0.10 Ca, enough to increase the apparent

proportion of Ca at X4 by more than the required amount. However, X3 has longer bond lengths than X4 and Pb^{2+} ($r = 1.20$ Å) would be expected to favor the larger site, although X3 refined as solely Ca. Overall, bond-length considerations, the chemical analysis, and the structural refinement are compatible with X4 containing enough lead (0.014 atom) to account for the higher apparent occupancy, with the balance being at X3, and that is the interpretation adopted here.

The Y sites are more complicated than the X sites. When the Y1 site along the four-fold axis of the structure contains Cu^{2+} (Fitzgerald *et al.* 1986a) or Mn^{3+} (Armbruster *et al.* 2002) it shows Jahn-Teller distortion, with a relative lengthening of the Y1–O(10) distance. This site is five-coordinated, essentially an octahedral site missing one apex ligand. In manganvesuvianite the difference between the Y1–O10 distance and the Y1–O6 distance O(10)–O(6) is +0.150 for the more distorted of the two Y1 sites, and for Cu-rich vesuvianite it is +0.235. The Pajsberg sample has a O(10)–O(6) bond-length difference of (2.094–2.057 = +0.037), and does not show Jahn-Teller distortion; therefore, we conclude that Y1 does not contain Mn^{3+}. The site refined as Fe, and the average bond length, 2.0575 Å, is more compatible with Fe^{3+} than Fe^{2+} or Mn^{2+}. When Y1 is occupied by a trivalent cation, the adjoining O10 site is occupied by oxygen, not hydroxyl (Fitzgerald *et al.* 1986b); thus O10 is O(OH) rather than 2O. The Y2 and Y3 sites form an edge-sharing trimer Y3–Y2–Y3, cross-linked to adjacent trimers by Si2, through O2 and O4. The tetrahedrally coordinated T1 site lies between adjacent bands. The Y2 site is occupied exclusively by Al in almost all known vesuvianites, but Groat *et al.* (2013) found a small amount (4.6%) occupied by As. In the Pajsberg vesuvianite, refinement of Y2 as Al + As shows 2% occupancy by As (0.08As) at Y2.

Y3, the general site in vesuvianite, contains a wide variety of di- and tri-valent cations; in Pajsberg vesuvianite Mg^{2+}, Al^{3+}, Mn, and Fe are all assigned to Y3. The site was refined as Mg + Fe, with the total constrained to 1, which gave Mg 0.64 and Fe 0.36 or $Mg_{5.12}Fe_{2.88}$. In interpreting the actual contents of Y3, all Mg was assigned to the site, with enough Al to make up the "Mg" portion, and all Mn was assigned to the site, with enough Fe to make up the "Fe" portion. The derived chemistry of the site is Mg 2.83, Al 2.29, Mn 0.90, Fe 1.98. If Mn is regarded as trivalent, the indicated charge at Y3 is lower (21.17) at the site than in ideal vesuvianite (22), and if Mn is regarded as divalent, the charge is significantly lower (20.27).

The average bond length around the Y3 site is 2.011 Å, and the bond range is 0.147 Å; for comparison, the Al-rich, Fe-free vesuvianite studied by Fitzgerald *et al.* (1986b) has average bond length

1.950 Å and range 0.122 Å for the same site, suggesting relatively little polyhedral distortion. The bond angles around Y3 (Table 6) also show relatively little distortion.

The Z1 site, of multiplicity 2, is occupied exclusively by Si; the Z2 site (multiplicity 8) refined to $Si_{0.96}As_{0.04}$; and the Z3 site (also multiplicity 8, forming Si_2O_7 groups) also refined to exclusively Si. The refined amounts of As at Y2 and Z2 account for all the arsenic determined by electron microprobe analysis; thus, no As was assigned to any other position. The formula on the basis of 50 cations has a Si + As total of $17.37 + 0.32 = 17.71$, suggesting substitution of 0.29 Al for Si. The three Si sites have similar bond lengths (1.64, 1.65, and 1.63 Å, respectively); however, the Si2 site is bonded to Y2, Y3, and T1, which provide a number of possible balancing substitutions, discussed below, so 0.29 Al is assigned to Z2.

The formula derived from the LA-ICP-MS analysis gave 0.82 Be and 0.35 B, or 1.0306 B equivalent structurally. The structural analysis gave 0.31 B occupancy at $T1_4$ (1.24 B atoms equivalent). If all Be and B are assigned to T1, there is an excess of electron density at the site equivalent to 0.21 B. If a small amount of some heavier cation is present at the site as per Groat *et al.* (1994a), it would account for the discrepancy; 0.037 Fe could make up the difference and involves the least incompatibility with the chemical analysis. Because of its smaller size and preference for distorted environments, we assumed that it is present as Fe^{3+}. Having Fe^{3+} at the site rather than Fe^{2+}, Mg, or Al would also be compatible with the optical absorption spectrum if at least some Mn at Y3 were divalent, although that is not the interpretation adopted here. However, the attempt to refine T1 as partly Fe resulted in a significantly higher *R* factor.

The T2 site refined as 0.04B with two T2–O10 bond lengths of 1.381 Å; similar very short bond lengths were determined by Groat *et al.* (1994b). As there is no additional oxygen site (O12 of Groat *et al.* 1994b) to help balance T2, it seems more likely that the site represents a disordered H position forming an OH group with O10 (Groat *et al.* 1994b). Table 8 gives the cation site contents derived from this interpretation, and Table 9 gives the average core value from EMP analysis and the composition calculated from the structural analysis.

Charge balance

Groat *et al.* (1994b) showed that B at $T1_4$ is balanced mostly by the exchange $BMgH_{-2}Al_{-1}$, that is, by removing 2H from $O11_8$, which is typically OH, and substituting Mg (or Fe^{2+}, Mn^{2+}) for Al (or Fe^{3+}) at

TABLE 8. SITE CONTENTS FOR PAJSBERG VESUVIANITE B20761 FROM STRUCTURAL ANALYSIS

Site	Contents
$X1_2$	Ca_8
$X2_8$	Ca_8
$X3_8$	$Ca_{7.96}Pb_{0.01}$
$X4_1$	$Ca_{0.99}Pb_{0.01}$
$Y1_1$	Fe^{3+}_1
$Y2_4$	$Al_{3.92}As_{0.08}$
$Y3_8$	$Mg_{2.83}Al_{2.29}Mn^{3+}_{0.90}Fe^{3+}_{1.98}$
$Z1_2$	Si_2
$Z2_8$	$Si_{7.37}As_{0.32}Al_{0.31}$
$Z3_8$	Si_8
$T1_4$	$Be_{0.82}B_{0.35}Fe^{3+}_{0.037}$

TABLE 9. AVERAGE CORE COMPOSITION OF PAJSBERG VESUVIANITE B50761 FROM TABLE 2, AND COMPOSITION CALCULATED FROM STRUCTURAL ANALYSIS, WITH ATOMIC PROPORTIONS CALCULATED ON THE BASIS OF 50 CATIONS PER FORMULA UNIT EXCLUDING THOSE AT THE T1 SITE

	B20761 Av.core	B20761 from struct.
SiO_2	34.74	35.19
As_2O_5	1.33	1.52
Al_2O_3	11.21	11.00
Mn_2O_3	2.63	2.35
Fe_2O_3	8.04	7.96
MgO	3.81	3.78
CaO	35.57	34.56
PbO		0.18
BeO		0.67
B_2O_3		0.41
H_2O		1.27
F		1.40
$F=O$		−0.59
Total	97.13	99.70
Ca	18.96	18.98
Pb	0.02	0.02
Al	6.57	6.53
Fe	2.99	3.017
Mg	2.83	2.83
Mn	0.90	0.90
Si	17.37	17.36
As	0.34	0.40
Be	0.82	0.82
B	0.35	0.35
F		2.23
Charge	148.88	149.081

Y3. If Be is at T1, both H atoms bonded to O11 must be absent, and their removal balances Be without any cation exchange at Y3. If As is at Y2, it requires an additional −2 charge in the adjoining anions, or a decrease of +2 charge at the adjoining Y3 or Si2 sites. The Y2 site is bonded to 2O11, and loss of both the H atoms bonded to them ($AsAl_{-1}H_{-2}$) balances the As without any other substitution. The Y2 position is also bonded to 2Y3 through O4 and O11, and substitution of Mg for two Al at Y3 would balance As at Y2 ($AsMgAl_{-1}Al_{-2}$). Finally, Y2 is bonded to two Si2 through O4, and the substitution of Al for Si at two adjoining Si2 would also balance As substituting for Al at Y2 ($AsAl_2Al_{-1}Si_{-2}$). Because Y3 shows an unusually low charge total and there appears to be considerable Al for Si substitution, most likely at Si2, either of the second two substitutions are plausible. If the first substitution is predominant, the T1 site adjacent to a Y2 site containing As could not contain Be or B, as these ions are also balanced by loss of H from O11.

The majority of As in the structure is at the Z2 site, substituting for Si. The Si atom is bonded to O2, O3, O4, and O7 with bonds through O2 and O4 to Y3. Substitution of Mg for Al at Y3 would compensate for the As at Z2 ($AsMgSi_{-1}Al_{-1}$).

Incorporation of Be at T1 involves loss of 2H from O11, as does incorporation of B or Fe^{3+} at T1. Together, these substitutions require loss of $1.64 + 0.70 + 0.04 = 2.38$H per formula from O11, resulting in a formula content of $O_{2.38}OH_{5.62}$ for O11. Finally, the substitution of 2.23F for OH at O11, indicated by the structural analysis, would yield $O_{2.46}OH_{3.31}F_{2.23}$ and a negative charge of 10.46. [Fitzgerald et al. (1992) found only 0.35F in their analysis of Pajsberg vesuvianite, substantially less than indicated by the current structural analysis.] Both B or Fe^{3+} at T1 and

As at Z2 require the substitution of Mg for Al at Y3; together, these substitutions require $0.35 + 0.02 + 0.32 = 0.69$ charge deficiency at the Y3 site, close to the 0.83 deficiency indicated by the interpretation of the contents of the Y3 site given above if Mn is trivalent, but substantially less than the 1.73 deficiency indicated if Mn is divalent. Overall, the negative charge total from the structure, including the substitutions discussed above, is 149.46; the positive charge total from the analysis is 148.181 if Mn is divalent and 149.081 if Mn is trivalent. Local charge-balance calculations (Brown 1981, Brese & O'Keeffe 1991) suggest that Mn is largely trivalent: Mn at Y3 would receive 3.335 charges from neighboring O if Mn is modeled as divalent or 3.076 charges if it is modeled as trivalent. Likewise, Fe^{2+} would receive 2.867 charges and Fe^{3+}

TABLE 10. POSITIVE AND NEGATIVE CHARGE-
BALANCE COMPARISON FROM DERIVED
COMPOSITION OF THE PAJSBERG VESUVIANITE
B20761

	# Atoms	Charges
Ca	18.95	37.90
Pb	0.02	0.04
Mg	2.83	5.66
Al	6.52	19.56
Fe^{3+}	2.98 (3.017)	9.051
Mn^{3+}	0.90	2.70
Si	17.37	69.48
As	0.40	2.00
Be	0.82	1.64
B	0.35	1.05
Σ-T	50	
Total positive charges		149.081
68 O bonded to Si		136
1.00 O at O10		2
1.00 OH at O10		1
2.46 O at O11		4.92
3.31 OH at O11		3.31
2.23 F at O11		2.23
Total negative charges		149.46

would receive 3.067 charges. Table 10 gives a charge-balance comparison, based on all Mn and Fe being trivalent; the difference between total anion and total cation charges is $149.46 - 149.08 = 0.33$.

The optical absorption spectrum of the Pajsberg vesuvianite appears more compatible with Mn being trivalent, as do the charge total, overall charge-balance, and charge-balance considerations for Y3 discussed above. We consider Mn in the Pajsberg vesuvianite to be trivalent. However, the absence of trivalent Mn at the Y1 site and the lesser distortion of the Y3 site compared to the vesuvianite from Asbestos, Quebec (Fitzgerald *et al.* 1986b) favor Mn as divalent. Armbruster & Gnos (2000) reported a low-temperature, acentric vesuvianite from South Africa containing 14.34 MnO, and posited both Mn^{2+} and Mn^{3+} at Y1 and Y3 sites. That Mn^{3+} may be present at Y1 (Armbruster & Gnos 2002) or Y3 (this paper), or both (Armbruster & Gnos 2002) speaks to the crystal-chemical complexity of this mineral.

Final note

In environments which contain sufficient Be to form some Be mineral, any associated vesuvianite should be expected to contain Be. Beryllium is not detectable by EDS analysis, and it may be more widely present in vesuvianite than currently appreciated. A separate Be-vesuvianite species would require half occupancy of the $T1_4$ site, or 2Be in the structural formula. This would require about 2.2 wt.% BeO or 0.79 wt.% Be. Analyses of Franklin vesuvianite reported by Hurlbut (1961) do not exceed this amount and the "beryllium vesuvianite" from Franklin is not a separate species. Further investigation might reveal such a species, however.

REFERENCES

ARMBRUSTER, T. & GNOS, E. (2000) Tetrahedral vaciences and cation ordering in low-temperature vesuvianites. *Acta American Mineralogist* **85**, 570–577.

ARMBRUSTER, T. & GNOS, E. (2002) Tetrahedral vacancies and cation ordering in low-temperature Mn-bearing vesuvianites: Indication of a hydrogarnet-like substitution. *American Mineralogist* **85**, 570–577.

ARMBRUSTER, T., GNOS, E., DIXON, R., GUTZMER, J., HEINY, C., DOBELIN, N., & MEDENBACH, O. (2002) Manganvesuvianite and tweddillite, two new Mn^{3+}-silicate minerals from the Kalahari manganese fields, South Africa. *Mineralogical Magazine* **661**, 137–150.

BRESE, N.E. & O'KEEFFE, M. (1991) Bond valence parameters for solids. *Acta Crystallogaphica* **B47**, 192–197.

BROWN (1981) The bond-valence method: an empirical approach to chemical structure and bonding. *In* Structure and Bonding in Crystals II (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York City, New York, United States (1–30).

BRUKER (2007) *Apex2*. Bruker AXS Inc., Madison, Wisconsin, United States.

DANA, E.S. (1893) *The System of Mineralogy*. John Wiley & Sons, New York City, New York, United States (p. 481).

FITZGERALD, S.F., RHEINGOLD, A.R., & LEAVENS, P.B. (1986a) Crystal structure of a cuprian vesuvianite. *American Mineralogist* **71**, 1011–1014.

FITZGERALD, S.F., RHEINGOLD, A.R., & LEAVENS, P.B. (1986b) Crystal structure of a P4/n vesuvianite. *American Mineralogist* **71**, 1483–1488.

FITZGERALD, S.F., RHEINGOLD, A.R., LEAVENS, P.B., & NELEN, J.A. (1987) Crystal structure of a REE-bearing vesuvianite from San Benito County, California. *American Mineralogist* **72**, 625–628.

FITZGERALD, S.F., LEAVENS, P.B., & NELEN, J.A. (1992) Chemical variation in vesuvianite. *Mineralogy and Petrology* **46**, 163–178.

GLASS, J.J., JAHNS, R.H., & STEVENS R.E. (1944) Helvite and danalite from New Mexico and the helvite group. *American Mineralogist* **29**, 163–191.

GROAT, L.A. & EVANS, R.J. (2012) Crystal Chemistry of Bi- and Mn-bearing vesuvianite from Langbån, Sweden. *American Mineralogist* **97**, 1627–1634.

GROAT, L.A. & HAWTHORNE, F.C. (1992) The chemistry of vesuvianite. *Canadian Mineralogist* **30**, 19–48.

GROAT, L.A., HAWTHORNE, F.C., & ERCIT, T.S. (1994a) 'Excess' Y-group cations in the crystal structure of vesuvianite. *Canadian Mineralogist* **32**, 497–504.

GROAT, L.A., HAWTHORNE, F.C., & ERCIT, T.S. (1994b) The incorporation of boron into the vesuvianite structure. *Canadian Mineralogist* **32**, 505–523.

GROAT, L.A., EVANS, R.J., CEMPIREK, J., McCAMMON, C., & HOUZAR, S. (2013) Fe-rich and As-bearing vesuvianite and wiluite from Kozlov, Czech Republic. *American Mineralogist* **98**, 1330–1337.

HURLBUT, C.S., JR. (1955) Beryllian idocrase from Franklin, New Jersey. *American Mineralogist* **40**, 118–120

MANNING, P.G. (1968) Optical absorption spectra of octahedrally bonded Fe^{3+} in vesuvianite. *Canadian Journal of Earth Sciences* **5**, 89–92.

MANNING, P.G. & TRICKER, M.J. (1975) Optical-absorption and Mössbauer spectral studies of iron and titanium site-populations in vesuvianites. *Canadian Mineralogist* **13**, 259–265.

MATTSON, S.M. & ROSSMAN, G.R. (1987) Identifying characteristics of charge transfer transitions in minerals. *Physics and Chemistry of Minerals* **14**, 94–99.

MEEN, V.B. (1939) *Vesuvianite from Great Slave Lake region, Canada.* University of Toronto Studies, Geologic Series **42**, 269.

MOORE, P.B. (1970) Mineralogy and chemistry of Langban-type deposits in Bergslagen, Sweden. *Mineralogical Record* **1**, 154–172.

PALACHE, C. (1935) *The Minerals of Franklin and Sterling hill, Sussex County, New Jersey.* United States Geological Survey Professional Paper **180**, 161 pp.

PALACHE, C. & BAUER, L.H. (1930) On the occurrence of beryllium in the zinc deposits of Franklin, New Jersey. *American Mineralogist* **15**, 30–33.

PLATONOV, A.N., ZABINSKI, W., & SACHABINSKI, M. (1995) Optical absorption spectra of Mn^{3+} ions in vesuvianites from Lower Silesia, Poland. *European Journal of Mineralogy* **7**, 1345–1352; *Mineralogicheskii Zhurnal* **17**, 38–47 (in Russian).

PAN, Y. & FLEET, M.E. (1992) Mineral Chemistry and Geochemistry of vanadian silicates in the Hemlo gold deposit, Ontario, Canada. *Contributions to Mineralogy and Pertology* **109**, 511–525.

ROSSMAN, G.R. (1975) Spectroscopic and magnetic studies of ferric iron hydroxy sulfates: intensification of color in ferric iron clusters bridged by a single hydroxide ion. *American Mineralogist* **60**, 698–704.

ROSSMAN, G.R. (2015) Vesuvianite Visible Spectra. http://minerals.gps.caltech.edu/FILES/Visible/vesuvianite/Index.html [date accessed: July 2015]

RUCKLIDGE, J.C., KLOCKMAN, V., WHITLOW, S.H., & GABE, E.J. (1975) The crystal structures of three Canadian vesuvianites. *Canadian Mineralogist* **13**, 15–21.

SHELDRICK, G.M. (2008), A short history of *SHELX. Acta Crystallographica* **A64**, 112–122, doi: 10.1107/S0108767307043930

SMITH, G., HALENIUS, U., ANNERSTEN, H., & ACKERMANN, L. (1983) Optical and Mossbauer spectra of manganese-bearing phlogopites: $Fe^{3+}_{IV}–Mn^{2+}_{Vi}$ pair absorption as the origin of reverse pleochroism. *American Mineralogist* **68**, 759–768.

SRIVASTAVA, K. & MEHRA, A. (1972) Optical absorption of $NaMnF_3$. *Journal of Chemical Physics* **57**, 1587–1591.