

Mesaite, $\text{CaMn}_5^{2+}(\text{V}_2\text{O}_7)_3 \cdot 12\text{H}_2\text{O}$, a new vanadate mineral from the Packrat mine, near Gateway, Mesa County, Colorado, USA

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ABSTRACT

Mesaite (IMA2015-069), ideally $\text{CaMn}_5^{2+}(\text{V}_2\text{O}_7)_3 \cdot 12\text{H}_2\text{O}$, is a new mineral from the Packrat mine, Gateway district, Mesa County, Colorado, USA. Crystals of mesaite occur as orangish red blades up to 0.1 mm long and $\sim 10 \mu\text{m}$ thick. The streak is light pinkish orange and the lustre is vitreous, transparent. Mesaite has a brittle tenacity, {010} perfect cleavage; fracture is irregular, and no parting was observed. The mineral has a Mohs hardness ≈ 2 . The measured density of mesaite is $2.74(1) \text{ g cm}^{-3}$. Mesaite is biaxial (–), $\alpha = 1.760(\text{calc})$, $\beta = 1.780(5)$, $\gamma = 1.795(5)$ in white light; the measured 2V value = $81(2)^\circ$. Dispersion is strong, $r < v$, and pleochroism is present in shades of brownish orange. Mesaite is monoclinic, $P2_1/n$, with $a = 9.146(2)$, $b = 10.424(3)$, $c = 15.532(4) \text{ \AA}$, $\beta = 102.653(7)^\circ$ and $V = 1444.7(6) \text{ \AA}^3$. The strongest four diffraction lines in the powder diffraction pattern are [$(d_{\text{obs}}$ in $\text{\AA}$, (I_{obs}) , (hkl)]: $10.47(100)$ (010), $2.881(25)$ (132, $\bar{3}12$, 033, 310), $3.568(24)$ ($\bar{1}14$, $\bar{1}23$, $\bar{2}13$), $3.067(17)$ ($\bar{1}24$, $\bar{1}32$, $\bar{2}23$). The composition of mesaite was determined by electron microprobe, and yielded an empirical formula of $\text{Mn}_{5.32}\text{Ca}_{0.56}\text{Zn}_{0.31}\text{V}_{5.96}\text{As}_{0.04}\text{O}_{33}\text{H}_{23.61}$ on the basis of 33 O atoms per formula unit (apfu).

The atomic arrangement of mesaite was solved and refined to $R_1 = 0.0600$. The structure is formed of zigzag octahedral chains of edge-sharing Mn^{2+}O_6 octahedra. Oxygen atoms of the octahedra are shared with V_2O_7 groups, which link with adjacent octahedral chains to form {010} heteropolyhedral layers. The interlayer region contains Ca atoms and H_2O groups. Each Ca bonds to two O6 atoms in the heteropolyhedral layer and to two fully occupied and six partially occupied O (H_2O) sites in the interlayer, resulting in an effective Ca coordination of approximately seven. Similar zigzag chains of edge-sharing MnO_6 octahedra decorated with V_2O_7 groups are also found in the mineral fianelite. Mesaite has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2015-069). The name mesaite is conferred for Mesa County, Colorado, USA.

KEYWORDS: mesaite, new mineral, crystal structure, vanadate, Colorado, Packrat mine.

Introduction

THE Colorado Plateau is host to the Urvan Mineral belt, which has been a rich source of uranium and vanadium ores for more than a century. The Packrat

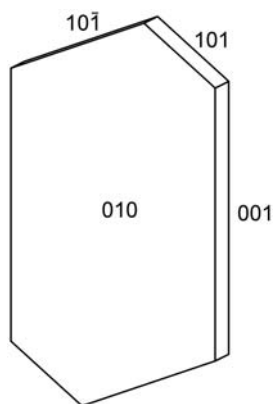
mine is located at the northern end of the belt near Gateway, Mesa County, Colorado ($38^\circ 38' 51.28''\text{N}$, $109^\circ 02' 49.77''\text{W}$), and its ores are uranium and vanadium minerals that occur together in bedded or roll-front deposits in the sandstone of the Salt Wash member of the Jurassic Morrison Formation (Carter and Gualtieri, 1965; Shawe, 2011). The original claims on the Packrat #1 and #2 were filed in 1943, but mining apparently did not commence until the

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FIG. 1. Mesaite blades; field of view: 0.3 mm.

FIG. 2. Crystal drawing of mesaite; clinographic projection in nonstandard orientation, *a* vertical.

early 1950s. The mine remained in operation until 1990 and consists of several miles of drifts and numerous stopes. The mine site was reclaimed in 2002, but was reopened in 2007 for further exploration. It is currently inactive. The samples of the new mineral were collected by one of the authors (JM) on September 10, 2011, May 3, 2013 and October 18, 2013.

The Packrat mine has been a prolific source of new minerals. Four recently described minerals (vanarsite, packratite, morrisonite and gatewayite; Kampf *et al.*, 2016) are interesting in that they contain a novel polyoxometalate-like heteropoly-anion, $[\text{As}^{3+}\text{As}_6^{5+}\text{V}_{2+x}^{4+}\text{V}_{10-x}^{5+}\text{O}_{51}]^{(11+x)-}$ ($x = 0$ to 1.5), which is new to science. Another recently described mineral kegginite (Kampf *et al.*, 2017) contains a mono-capped Keggin ϵ -isomer. Mesaite is the sixth new mineral to be described from that locality, and its structural unit differs from that of the polyoxometalate phases. Mesaite has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2015-069), and the name mesaite (/ˈmeɪ sɑ ɪt/) is conferred for Mesa County, Colorado, USA, in which the Packrat mine is located. Five cotype specimens of mesaite are deposited in the collections of the Natural History Museum of Los Angeles County, Los Angeles, California, USA, with catalogue numbers 65595, 65596, 65597, 65598 and 65599.

Occurrence

Mesaite was found in the main tunnel level of the Packrat mine. The mineral is found on asphaltum blocks associated with montroseite-

TABLE 1. Analytical data (wt.%) for mesaite.

Constituent	wt.%	Range	S.D.	Probe standard
CaO	2.76	2.11–3.33	0.39	Diopside
MnO	33.41	32.04–34.35	0.70	Rhodonite
ZnO	2.26	1.30–2.85	0.53	Zn metal
V ₂ O ₅	47.91	46.95–49.11	0.69	Y vanadate (syn)
As ₂ O ₅	0.45	0.18–0.91	0.28	GaAs (syn)
H ₂ O*	18.82			
Total	105.58			

*Calculated based on structure determination.
S.D. – standard deviation.

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TABLE 2. Powder X-ray diffraction data (d in Å) for mesaite.

I_{obs}	d_{obs}		d_{calc}	I_{calc}	hkl	I_{obs}	d_{obs}		d_{calc}	I_{calc}	hkl
100	10.47		10.4240	100	0 1 0						
10	8.60	{	8.5885	7	0 1 1	6	2.773	{	2.8051	2	3 0 1
5	7.55		8.5523	3	$\bar{1}$ 0 1				2.7651	2	$\bar{2}$ 2 4
6	6.69	{	7.5774	3	0 0 2				2.7525	2	1 2 4
4	6.20		6.7790	1	1 1 0				2.7498	1	$\bar{3}$ 1 3
3	5.22		6.6118	2	$\bar{1}$ 1 1	5	2.717	{	2.7127	1	$\bar{2}$ 1 5
6	4.55		6.1291	2	0 1 2				2.7087	2	3 1 1
			5.2120	1	0 2 0				2.6958	1	1 0 5
			4.5459	3	0 1 3				2.6362	1	2 3 1
			4.4182	1	$\bar{1}$ 1 3				2.6201	3	2 2 3
11	4.30	{	4.2942	6	0 2 2	11	2.615	{	2.6099	5	1 1 5
4	4.11		4.2762	3	$\bar{2}$ 0 2				2.6060	1	0 4 0
			4.0721	2	$\bar{1}$ 2 2				2.6011	1	$\bar{3}$ 2 2
			3.7887	1	0 0 4				2.5835	1	3 2 0
			3.7618	1	1 1 3				2.5683	1	0 4 1
			3.6945	1	1 2 2				2.5608	1	0 3 4
			3.6274	2	0 2 3				2.5582	1	$\bar{2}$ 3 3
24	3.568	{	3.5699	3	$\bar{1}$ 1 4	2	2.505		2.5073	2	3 1 2
			3.5615	6	$\bar{1}$ 2 3	2	2.464	{	2.4736	1	2 3 2
			3.5537	9	$\bar{2}$ 1 3				2.4643	1	0 4 2
			3.4747	2	0 3 0				2.4390	1	$\bar{2}$ 0 6
			3.3868	1	0 3 1				2.3944	1	1 2 5
			3.3059	1	$\bar{2}$ 2 2	2	2.372		2.3702	1	1 3 4
11	3.132	{	3.1584	3	0 3 2				2.3332	1	1 4 2
			3.0952	6	1 1 4	5	2.313	{	2.3160	2	0 4 3
17	3.067	{	3.0704	1	$\bar{1}$ 2 4				2.3145	1	$\bar{3}$ 2 2
			3.0668	1	$\bar{1}$ 3 2				2.3061	1	$\bar{1}$ 3 5
			3.0601	8	$\bar{2}$ 2 3				2.2841	1	2 3 3
			3.0478	2	$\bar{3}$ 0 1				2.2797	1	4 0 2
			2.9254	3	$\bar{3}$ 1 1	3	2.239	{	2.2476	1	1 1 6
			2.9104	1	2 1 3				2.2271	1	4 1 2
25	2.881	{	2.8955	4	1 3 2				2.1826	1	3 3 1
			2.8844	4	$\bar{3}$ 1 2				2.1471	1	0 4 4
			2.8628	8	0 3 3	2	2.135	{	2.1381	1	4 0 4
			2.8604	3	3 1 0				2.1288	1	$\bar{3}$ 1 6
			2.8301	1	$\bar{1}$ 3 3				2.1056	1	1 2 6
									2.0969	1	$\bar{2}$ 1 7
						5	2.087	{	2.0887	1	4 2 2
									2.0730	2	3 3 2

and corvusite-bearing sandstone. Other secondary minerals found in close association with mesaite are ansermetite, kegginitite, martyite, morrisonite, rossite/metarossite and sherwoodite. Other secondary minerals found in the mine include andersonite, calcite, dickthomssenite, gatewayite, gypsum, hewettite, hummerite, lasalite, magnesiopascoite, martyite, munirite, navajoite, packratite, pascoite, pharmacolite, picropharmacolite, postite, selenium, uranopilite, vanarsite and other potentially new minerals, currently under study.

The new mineral forms 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 conditions, water reacts with pyrite and an unknown As-bearing phase (perhaps arsenopyrite) to form aqueous solutions with relatively low pH. The various secondary vanadate phases that form depend upon prevailing Eh-pH conditions and the presence of other cations (e.g. Na^+ , Ca^{2+} , Mn^{2+}).

TABLE 3. Data collection and structure refinement details for mesaite.

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation/power	MoK α ($\lambda = 0.71075$ Å)/50 kV, 40 mA
Temperature	293(2) K
Structural Formula	(Ca _{0.80} Mn _{0.20})Mn ₅ ²⁺ (V ₂ O ₇) ₃ ·12H ₂ O
Space group	<i>P2</i> / <i>n</i>
Unit-cell dimensions	<i>a</i> = 9.146(2) Å <i>b</i> = 10.424(3) Å <i>c</i> = 15.532(4) Å β = 102.653(7)°
<i>V</i>	1444.7(6) Å ³
<i>Z</i>	2
Density (for above formula)	2.702 g cm ⁻³
Absorption coefficient	4.295 mm ⁻¹
<i>F</i> (000)	1144
Crystal size (μm)	80 × 40 × 10
θ range	3.01 to 19.97°
Index ranges	$-8 \leq h \leq 8, -9 \leq k \leq 9, -14 \leq l \leq 14$
Refls collected/unique	5353/1323; <i>R</i> _{int} = 0.115
Reflections with <i>F</i> > 4 σ (<i>F</i>)	883
Completeness to $\theta = 19.97^\circ$	98.1%
Max. and min. transmission	0.958 and 0.725
Refinement method	Full-matrix least-squares on <i>F</i> ²
Parameters/restraints	206/0
Goof	1.019
Final <i>R</i> indices [<i>F</i> _o > 4 σ (<i>F</i>)]	<i>R</i> ₁ = 0.0600, <i>wR</i> ₂ = 0.1350
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1023, <i>wR</i> ₂ = 0.1581
Largest diff. peak/hole	+0.71/−0.58 e/Å ³

**R*_{int} = $\sum [F_o^2 - F_o^2(\text{mean})] / \sum [F_o^2]$. Goof = $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$. *R*₁ = $\sum [|F_o| - |F_c|] / \sum |F_o|$. *wR*₂ = $\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]\}^{1/2}$; *w* = $1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where *a* is 0.085, *b* is 0 and *P* is $[2F_o^2 + \text{Max}(F_o^2, 0)] / 3$.

Appearance and physical properties

Mesaite crystals occur as blades up to 0.1 mm long and ~10 μm thick in divergent sprays (Figs 1, 2). The crystals are orangish red and brownish orange in transmitted light. The streak is light pinkish orange and the lustre is vitreous, transparent. Mesaite has a brittle tenacity, {010} perfect cleavage; fracture is irregular and no parting was observed. The mineral is non-fluorescent and has a Mohs hardness ≈ 2, estimated from the behaviour

of crystals when broken. No twinning was observed in mesaite.

The measured density of mesaite is 2.74(1) g cm⁻³, obtained by flotation in a mixture of methylene iodide and toluene. The calculated density is 2.744 g cm⁻³ using the empirical formula and 2.695 g cm⁻³ using the ideal formula.

Mesaite is biaxial (−), $\alpha = 1.760(\text{calc})$, $\beta = 1.780(5)$, $\gamma = 1.795(5)$ in white light. The thinness of the blades made it impossible to measure α ; consequently, α was calculated based on β , γ and 2*V* (Gunter *et al.*, 2004). The measured 2*V* is 81(2)°, obtained using direct conoscopic observation on a spindle stage. Dispersion is strong, $r < v$, and pleochroism is present in shades of brownish orange, $X < Y < Z$. Orientation is $X = b$, $Z \wedge a = 58^\circ$ in obtuse angle β .

Chemistry of mesaite

Analyses of mesaite (11 points over 4 crystals) were performed at the University of Utah using a Cameca SX-50 electron microprobe with four wavelength dispersive spectrometers utilizing 'Probe for EPMA' software, v. 9.6.4 (Probe Software, Inc.). Analytical conditions were 15 keV accelerating voltage, 10 nA beam current and a beam diameter of 5 μm. Counting times were 20 s on peak and 20 s on background for each element. Raw X-ray intensities were corrected for matrix effects with a $\phi\rho(z)$ (PAP) algorithm (Pouchou and Pichoir, 1991).

Mesaite is difficult to polish well, and surface roughness necessitated the relatively small beam diameter. Nonetheless, no visible damage from the electron beam was observed. However, as is typical of highly hydrated phases with weakly held H₂O, mesaite partially dehydrates under vacuum either during carbon coating or in the microprobe chamber. This H₂O loss results in higher concentrations for the remaining constituents than are to be expected for the fully hydrated phase. The water content has been calculated based on the structure determination because insufficient material is available for a direct determination of H₂O. Analytical data are given in Table 1. Mesaite is insoluble in H₂O; the mineral is easily soluble in dilute HCl at room temperature.

The empirical formula based on 33 O atoms per formula unit (apfu) is Mn_{5.32}Ca_{0.56}Zn_{0.31}V_{5.96}As_{0.04}O₃₃H_{23.61}. The simplified structural formula is CaMn₅²⁺(V₂O₇)₃·12H₂O, which requires CaO 4.78, MnO 30.25, V₂O₅ 46.53, H₂O 18.44, total 100.00 wt.%.

TABLE 4. Atom coordinates and displacement parameters ($\text{\AA}^2$) for mesaite.*

	x/a	y/b	z/c	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ca**	0.7500	0.6026(5)	0.2500	0.081(3)	0.164(7)	0.045(5)	0.029(4)	0	0.012(3)	0
Mn1	0.7500	0.9387(4)	0.2500	0.0352(11)	0.031(2)	0.055(3)	0.019(2)	0	0.0051(15)	0
Mn2	0.0742(2)	0.0534(3)	0.36196(15)	0.0385(9)	0.0394(17)	0.058(2)	0.0183(17)	-0.0042(13)	0.0074(12)	-0.0013(13)
Mn3	0.3984(2)	0.1308(3)	0.47583(15)	0.0358(8)	0.0375(15)	0.053(2)	0.0165(16)	-0.0008(13)	0.0055(11)	0.0008(13)
V1	0.3961(3)	0.8962(3)	0.32016(17)	0.0349(9)	0.0361(16)	0.054(2)	0.0153(17)	-0.0034(15)	0.0069(13)	-0.0013(15)
V2	0.9187(3)	0.7794(3)	0.44368(17)	0.0353(9)	0.0415(17)	0.045(2)	0.0193(18)	-0.0004(15)	0.0072(13)	0.0036(15)
V3	0.2350(3)	0.8697(3)	0.55541(17)	0.0353(9)	0.0366(16)	0.052(2)	0.0179(17)	0.0003(15)	0.0064(12)	0.0036(15)
O1	0.5169(9)	0.2006(11)	0.5990(6)	0.037(3)	0.040(6)	0.059(8)	0.010(6)	0.003(6)	0.001(5)	0.001(6)
O2	0.5123(10)	0.9491(10)	0.2572(6)	0.038(3)	0.044(6)	0.055(9)	0.016(6)	0.002(5)	0.012(5)	0.003(6)
O3	0.3049(10)	0.0197(10)	0.3563(6)	0.041(3)	0.042(6)	0.052(8)	0.025(7)	-0.005(6)	0.003(5)	-0.004(6)
O4	0.2500	0.8011(15)	0.2500	0.041(4)	0.039(8)	0.056(12)	0.021(9)	0	-0.006(7)	0
O5	0.9634(10)	0.6346(11)	0.4707(7)	0.046(3)	0.057(7)	0.051(9)	0.033(7)	-0.002(6)	0.014(6)	-0.001(6)
O6	0.8111(10)	0.7783(10)	0.3408(6)	0.040(3)	0.047(6)	0.057(9)	0.013(6)	0.005(6)	0.001(5)	0.002(6)
O7	0.8290(10)	0.8442(11)	0.5206(6)	0.039(3)	0.034(6)	0.068(9)	0.016(6)	-0.008(6)	0.008(5)	0.012(6)
O8	0.0898(9)	0.8729(10)	0.4523(6)	0.032(3)	0.032(6)	0.050(8)	0.015(6)	0.002(5)	0.006(5)	-0.003(5)
O9	0.2768(11)	0.7195(11)	0.5775(7)	0.048(3)	0.058(7)	0.048(9)	0.038(8)	-0.002(6)	0.011(5)	0.006(6)
O10	0.3922(10)	0.9480(10)	0.5448(6)	0.035(3)	0.041(6)	0.046(8)	0.024(7)	-0.004(5)	0.020(5)	-0.006(5)
O11	0.8411(10)	0.0624(10)	0.3625(6)	0.039(3)	0.039(6)	0.068(9)	0.012(6)	-0.003(6)	0.009(5)	0.002(6)
O12	0.4187(11)	0.3047(11)	0.4029(7)	0.050(3)	0.060(7)	0.055(9)	0.033(8)	0.001(6)	0.005(5)	-0.005(6)
O13	0.0711(11)	0.2333(11)	0.2851(8)	0.061(4)	0.081(8)	0.057(9)	0.052(9)	0.023(7)	0.028(7)	-0.003(7)
O14	0.6194(12)	0.4362(12)	0.1609(7)	0.064(4)	0.059(8)	0.088(11)	0.052(9)	-0.011(7)	0.028(7)	0.002(7)
O15	0.2555(14)	0.5080(14)	0.4522(9)	0.086(4)	0.094(10)	0.092(12)	0.077(11)	-0.021(9)	0.028(8)	0.012(9)
O16A*	0.931(2)	0.581(2)	0.182(2)	0.062(10)						
O16B*	0.902(4)	0.554(4)	0.124(4)	0.072(19)						
O17A*	0.214(4)	0.531(3)	0.274(3)	0.15(2)						
O17B*	0.073(3)	0.616(4)	0.294(2)	0.123(18)						

*The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

**Occupancies: Ca/Mn 0.80/0.20(6), O16A/O16B 0.63/0.37(6), O17A/O17B 0.53/0.47(3)

TABLE 5. Selected bond distances (Å) in mesaite.

Mn1–O6(×2)	2.179(10)	V1–O1	1.670(10)	Ca–O16A(×2)	2.16(2)
Mn1–O11(×2)	2.185(10)	V1–O2	1.687(9)	Ca–O6(×2)	2.304(0)
Mn1–O2(×2)	2.204(9)	V1–O3	1.695(10)	Ca–O14(×2)	2.372(13)
<Mn1–O>	2.189	V1–O4	1.821(9)	Ca–O16B(×2)	2.69(5)
		<V1–O>	1.718	Ca–O17B(×2)	2.89(3)
				<Ca–O>	2.42
Mn2–O7	2.131(10)				
Mn2–O11	2.136(9)	V2–O5	1.596(11)		
Mn2–O2	2.143(10)	V2–O6	1.684(10)	Hydrogen bonds	
Mn2–O3	2.159(9)	V2–O7	1.728(9)	O12–O9	2.746(16)
Mn2–O13	2.220(11)	V2–O8	1.823(9)	O12–O15	2.793(17)
Mn2–O8	2.333(10)	<V2–O>	1.708	O13–O12	3.034(15)
<Mn2–O>	2.187			O13–O14	2.976(15)
		V3–O9	1.631(11)	O14–O5	2.890(15)
Mn3–O7	2.108(9)	V3–O10	1.692(9)	O14–O9	2.683(14)
Mn3–O1	2.111(9)	V3–O11	1.732(9)	O15–O5	2.950(16)
Mn3–O12	2.167(11)	V3–O11	1.843(9)	O15–O9	2.919(17)
Mn3–O10	2.172(9)	<V3–O>	1.725	O16A–O1	2.81(3)
Mn3–O10	2.193(10)			O16A–O6	2.99(3)
Mn3–O3	2.196(10)			O16B–O1	2.82(5)
<Mn3–O>	2.158			O16B–O15	2.78(4)
				O17A–O4	2.87(4)
				O17A–O15	2.73(4)
				O17B–O4	2.70(4)
				O17B–O15	2.88(4)

Crystal structure

Powder X-ray diffraction data were recorded using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromatized MoK α radiation. Observed d values (Å) and intensities were derived by profile fitting using *JADE 2010* software (MDI Materials Data, California, USA). Data are given in Table 2. Unit-cell parameters refined from the powder data using *JADE 2010* with whole pattern fitting are $a = 9.135(2)$, $b = 10.427(2)$, $c = 15.530(2)$ Å, $\beta = 102.650(6)^\circ$ and $V = 1443.3(5)$ Å³.

Single-crystal X-ray studies were also carried out using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromatized MoK α radiation. The *Crystal Clear* (Rigaku Corporation, Tokyo) software package was used for processing the structure data, including the application of numerical and empirical absorption corrections. The structure was solved by direct methods using *SIR2004* (Burla *et al.*, 2005). *SHELXL-2013* (Sheldrick, 2008) was used for the refinement of the structure. Because of the lack of high-angle data, the positions of hydrogen atoms could not be determined. In addition, during

refinement two oxygen atoms (O16, O17) were found to occupy split sites, and those split sites were successfully modelled with isotropic displacement parameters for the split atoms. Chemical analysis and structure refinement demonstrated that a small amount of Mn substituted in the Ca site, and this substitution was successfully modelled in the refinement with the constraint (Mn + Ca = 1). Data collection and refinement details are given in Table 3, atom coordinates and displacement parameters in Table 4, selected bond distances in Table 5 and bond-valence sums in Table 6.

Mesaite contains zigzag chains of edge-sharing Mn²⁺O₆ octahedra along [301] and pairs of corner-sharing VO₄ tetrahedra forming V₂O₇ (divanadate) groups (Fig. 3). The divanadate groups link the chains of octahedra into heteropolyhedral layers parallel to {010}. The interlayer region contains Ca atoms and H₂O groups. Each Ca bonds to two O6 atoms in the heteropolyhedral layer and to two fully occupied and six partially occupied O (H₂O) sites in the interlayer, resulting in an effective Ca coordination of approximately seven. One fully occupied O site in the interlayer is an isolated H₂O group. The only direct linkages between heteropolyhedral layers are *via* hydrogen bonds.

MESAITE, A NEW VANADATE MINERAL

TABLE 6. Bond-valence sums for mesaite.

	Ca	Mn1	Mn2	Mn3	V1	V2	V3	H-bonds	Σ_a	
O1				0.42	1.43			+0.11,+0.07	2.03	O
O2		0.33	0.39		1.37				2.09	O
O3			0.37	0.33	1.34				2.04	O
O4					0.95 $\times 2 \rightarrow$			+0.10,+0.09	2.09	O
O5						1.75		+0.15,+0.12	2.02	O
O6	0.37 $\times 2 \downarrow$	0.35				1.38		+0.06	2.16	O
O7			0.40	0.42		1.22			2.04	O
O8			0.23			0.95	0.90		2.08	O
O9							1.59	+0.19,+0.21,+0.14	2.13	O
O10				0.36 0.34			1.35		2.05	O
O11		0.34	0.39				1.21		1.94	O
O12				0.36				+0.08,-0.19,-0.18	0.07	H ₂ O
O13			0.31					-0.08,-0.11	0.12	H ₂ O
O14	0.31 $\times 2 \downarrow$							0.11,-0.15,-0.21	0.06	H ₂ O
O15								+0.18,+0.07,+0.11 +0.07,-0.12,-0.14	0.17	H ₂ O
O16A	0.35 $\times 2 \downarrow$									
O16B	0.05 $\times 2 \downarrow$									
O17A										
O17B	0.04 $\times 2 \downarrow$									
Σ_c	2.24	2.04	2.09	2.23	5.09	5.30	5.05			

Multiplicities indicated by $\times 2 \downarrow$; bond strengths based upon refined site occupancies; bond-valence parameters from Brown and Altermatt (1985); hydrogen-bond strengths based on O...O bond lengths from Brown and Altermatt (1985). Bond-valence balance for partially occupied O16A, O16B, O17A and O17B have not been included.

Similar structural components are found in the structure of fianelite, $\text{Mn}_2^{2+}(\text{V}_2\text{O}_7) \cdot 2\text{H}_2\text{O}$ (Brugger and Berlepsch, 1996). Fianelite also has zigzag chains of edge-sharing Mn^{2+}O_6 octahedra and divanadate groups. The divanadate groups link the chains to one another; however, the linkages in the fianelite structure result in a heteropolyhedral framework, rather than a layer. The chains and connected divanadate groups in mesaite and fianelite are compared in Fig. 4. Despite the structural similarities between the two minerals, they occur in distinctly different environments. Fianelite occurs in late fractures within metamorphosed As-V-rich Mn deposits under mild hydrothermal conditions based on the association with quartz and aegerine (Brugger and Gieré, 2000).

Synthetic compounds also contain zigzag octahedral chains decorated with divanadate groups. In

a comparison of the atomic arrangement of $\gamma\text{-Cu}_2\text{V}_2\text{O}_7$ and the minerals blossite ($\alpha\text{-Cu}_2\text{V}_2\text{O}_7$) and ziesite ($\beta\text{-Cu}_2\text{V}_2\text{O}_7$), Krivovichev *et al.* (2005) illustrated a zigzag chain of CuO_6 octahedra that has attached V_2O_7 groups that link the octahedral chain to other structural elements. Blossite and ziesite also contain zigzag structural chains decorated by divanadate groups, but the copper in blossite and ziesite is five-coordinated to oxygen in an apically elongate square pyramid.

Such zigzag chains decorated with ditetrahedral groups are not limited to vanadates, either. The compound $(\text{NH}_4)_2[\text{Fe}_3(\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_2]$ (Liu *et al.*, 2012), reportedly isostructural with its Mn and Ni analogues, displays zigzag octahedral chains of Fe^{2+}O_6 octahedra decorated by P_2O_7 pyrophosphate groups that link to adjacent chains to form a layer structure.

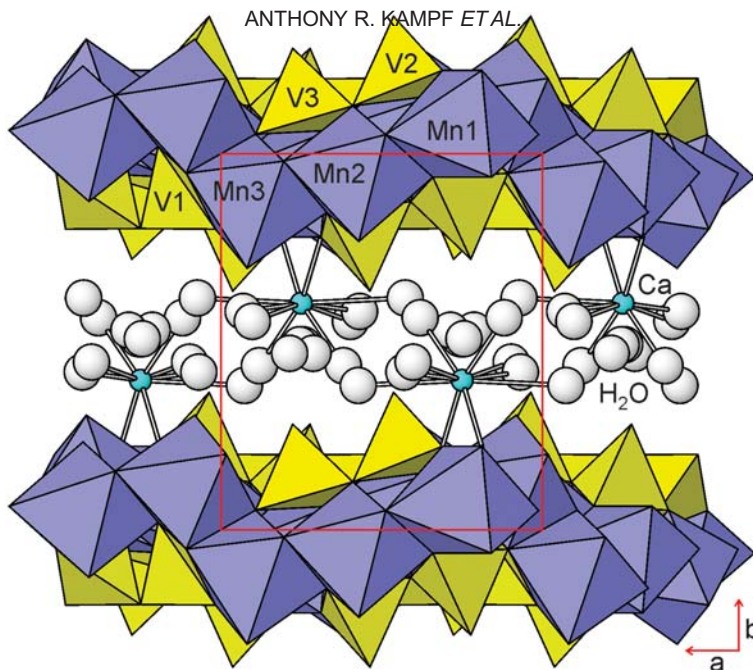


FIG. 3. Structure of mesaite viewed down c . The unit cell is outlined in red.

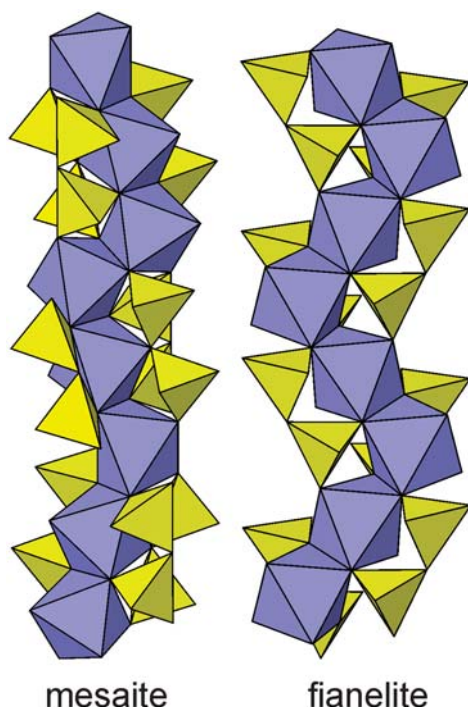


FIG. 4. Zig-zag chains of edge-sharing Mn^{2+}O_6 octahedra with pairs of linked VO_4 tetrahedra in the structures of mesaite and fianelite.

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