Milanriederite, (Ca,*REE*)₁₉Fe³⁺Al₄(Mg,Al,Fe³⁺)₈Si₁₈O₆₈(OH,O)₁₀, a new vesuvianite-group mineral from the Kombat Mine, Namibia

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Abstract: Milanriederite, a new vesuvianite-group mineral, was discovered in the Kombat deposit, Grootfontein district, Otjozondjupa region, Namibia, in association with baryte, calcite, jacobsite, hausmannite, glaucochroite and native copper. The new mineral forms dark brownish-red dipyramidal crystals up to 3 mm across. The major crystal form is {111} and the minor forms are {001}, {110}, and {100}. Milanriederite is brittle, has a Mohs' hardness of six and an uneven fracture. Neither cleavage nor parting is observed. $D_{\text{meas}} = 3.53(2) \text{ g/cm}^3$, $D_{\text{calc}} = 3.547 \text{ g/cm}^3$. The new mineral is optically uniaxial (-), $\omega = 1.744(3)$, e = 1.737(3). The infrared (IR) spectrum of milanriederite significantly differs from IR spectra of other vesuvianite-group minerals. According to Mössbauer data, all iron in the mineral is trivalent. The chemical composition is (electron microprobe, H₂O determined by gas chromatography of ignition products, wt%): Na₂O 0.47, MgO 5.49, CaO 29.86, Mn₂O₃ 1.40, Al₂O₃ 9.75, Fe₂O₃ 6.03, Y₂O₃ 2.44, La₂O₃ 4.43, Ce₂O₃ 0.86, Pr₂O₃ 0.32, Nd₂O₃ 1.31, SiO₂ 34.84, H₂O 2.9, total 100.10. The empirical formula based on 78 O atoms is $[Ca_{16.48}(La_{0.84}Y_{0.67}Ce_{0.16}Nd_{0.24}Pr_{0.06})Na_{0.47}]_{\Sigma18.92}(Al_{5.92}Mg_{4.22}Fe_{2.34}^{3+}Mn_{0.55}^{3+})_{\Sigma13.03}Si_{17.95}O_{68.04}(OH)_{9.96}.$ The simplified formula is $(Ca, REE)_{19}Fe^{3+}Al_4(Mg, Al, Fe^{3+})_8Si_{18}O_{68}(OH, O)_{10}$. The crystal structure was refined to R = 0.027 for 1684 unique observed reflections with $|F_0| \ge 4\sigma_F$. The mineral is tetragonal, P4/nnc, a = 15.6578(4), c = 11.8597(5) Å, V = 2907.6(2) Å³, Z = 2. Milanriederite is the analogue of vesuvianite with Mg predominant at the Y3 site. The strongest lines of the powder X-ray diffraction pattern are [d, Å (I, %) (hkl)]: 2.970 (50) (511, 004), 2.774 (100) (204, 432, 440), 2.617 (87) (423, 531, 224, 522), 2.481 (30) (620), 2.143 (19) (315, 641), 1.676 (17) (921, 842, 436), 1.638 (38) (931, 526, 804, 922). The mineral is named in honour of Czech mineralogist Professor Milan Rieder (b. 1940), in recognition to his contributions to mineralogy and his service to the international mineralogical community.

Key-words: milanriederite; new mineral; vesuvianite group; crystal structure; Mössbauer; Kombat mine; Namibia.

1. Introduction

The vesuvianite group combines tetragonal neso-soro silicate minerals with the general formula $({}^{9}X3)_{8}({}^{8}X1)({}^{8}X4)_{2}$ $({}^{7}X2)_{8}({}^{6}Y2)_{4}({}^{6}Y3)_{8}({}^{5}Y1)_{1}({}^{4}T1)_{0-4}(SiO_{4})_{10}(Si_{2}O_{7})_{4}({}^{3}T2)_{0-1}$ $O_{0-2}(O10)_{2}(O11)_{8}$ where X1-4 = Ca, REE, Na, K, Bi³⁺, Sb³⁺, Th⁴⁺, U⁴⁺, H₂O; Y1 = Fe³⁺, Fe²⁺, Mg, Al, Mn³⁺, Cu²⁺, Mn²⁺, Cr; Y2 = Al (sometimes with subordinate Mg, Fe, Mn, Cr and/or Ti), Y3 = Al, Mg, Fe³⁺, Fe²⁺, Mn²⁺, Zn, Ti; T1 = \Box , B, Al; T2 = \Box , B, S; O10 = OH, O, F, CI; O11 = OH, O, F (the components that are known as dominant in corresponding sites are highlighted in bold; superscripts denote coordination numbers). The predominance of Al at Yl is more typical for ordered Fe-poor vesuvianite-group minerals (space groups *P*4/*n* and *P*4*nc*), whereas Mg usually occupies the Yl site in the *P*4/*nnc* modification (Giuseppetti & Mazzi, 1983; Fitzgerald *et al.*, 1987; Ohkawa *et al.*, 1992; Groat *et al.*, 1998; Armbruster *et al.*, 2002; Britvin *et al.*, 2003; Galuskin *et al.*, 2003; Aksenov *et al.*, 2016; Panikorovskii *et al.*, 2016a, b, 2017a–d; Xu *et al.*, 2017; Chukanov *et al.*, 2018). Rare-earth elements, Bi, Sb, Th, U concentrate at the X3 site; additional hydrogen atoms can be incorporated *via* a hydrogarnet-type substitution mechanism: $(H_4O_4)^{4-} \leftrightarrow (SiO_4)^{4-}$.

Table 1. Dominant components in some structure sites of vesuvianite-group minerals.

Mineral	<i>X</i> 1–4	<i>Y</i> 1	<i>Y</i> 2	<i>Y</i> 3	<i>T</i> 1	<i>T</i> 2	010	011	012	References
Vesuvianite s.s.	Ca	Fe ³⁺	Al	Al			OH	OH		Giuseppetti & Mazzi (1983), Panikorovskii et al. (2017d)
Fluorvesuvianite	Ca	Fe ²⁺	Al	Al			F	F		Britvin et al. (2003)
Manganvesuvianite	Ca	Mn ³⁺	Al	Al			OH	OH		Armbruster et al. (2002)
Cyprine	Ca	Cu	Al	Al			OH	OH		Panikorovskii et al. (2017b)
Magnesiovesuvianite	Ca	Mg	Al	Al			OH	OH		Panikorovskii et al. (2017c)
Alumovesuvianite	Ca	AĬ	Al	Al			OH	OH		Panikorovskii et al. (2017a)
Wiluite	Ca	Mg	Al	Al	В	В	0	0	0	Groat <i>et al.</i> (1998)
Hongheite	Ca	Fe ²⁺	Al	Fe ³⁺		В	0	0		Xu et al. (2017)
Milanriederite	Ca	Fe ³⁺	Al	Mg			OH	OH		This work

The new mineral milanriederite described here is the second representative of the vesuvianite group in which Mg is the predominant component at the Y3 site, after the recently discovered manaevite-(Ce), $[Ca_{13}Ce_4(H_2O)_2]_{19}Mg(Mg_4Al_3)$ $Ti_3Fe_2^{3+})[Si_2O_7]_4[(SiO_4)_8(H_4O_4)_2](OH)_9O$ (IMA no. 2018-046, Moiseev *et al.*, 2018). In contrast to manaevite-(Ce), milanriederite has no *REE*-dominant site and is Fe³⁺-dominant at the Y1 site (Table 1).

Milanriederite occurs in a jacobsite–hausmannite ore of the Kombat deposit, situated in the Grootfontein district, Otjozondjupa region, northern Namibia. The mineral assemblage that contains milanriederite was formed by hydrothermal and metasomatic replacement and fracture-filling of dolostones of the Upper Proterozoic Hüttenberg Formation by polymineralic aggregates consisting of Mn-rich spinels, calcite, dolomite, baryte, as well as various subordinate components including several lead oxychlorides (Innes & Chaplin, 1986). According to the author's data based on the statistics of the number of reflections violating spacegroup symmetry (see below), the estimated temperature of milanriederite crystallization is in the range 400–550 °C.

The new mineral is named in honour of the well-known Czech mineralogist Professor Milan Rieder (b. 1940), who worked in the Geological Survey of Czechoslovakia (now Czech Geological Survey), at Charles University (Faculty of Science) in Prague and VŠB-Technical University of Ostrava. A significant part of his publications is related to rock-forming silicates. In particular, Prof. Rieder is the senior author of the nomenclature of the micas. Milan-riederite description and name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA no. 2018-041). The type specimen is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the registration number 5224/1.

2. General appearance and physical properties

Milanriederite occurs as dark brownish red dipyramidal crystals up to 3 mm across embedded in granular baryte–calcite–jacobsite–hausmannite aggregates with minor glau-cochroite and native copper (Figs. 1a and b). The major crystal form is {111} and the minor forms (observed on

some crystals) are {001}, {110}, and {100}. Based on morphological features, one can conclude that milanriederite is the earliest mineral in this association, whereas native copper belongs to a later stage of mineral formation.

Milanriederite is brittle, has a Mohs' hardness of six and an uneven fracture. Neither cleavage nor parting is observed. The density measured by hydrostatic weighing is 3.53(2) g/ cm³. Density calculated using the empirical formula and the unit-cell dimensions obtained from single-crystal X-ray diffraction data is 3.547 g/cm³. The new mineral is nonfluorescent under short- and long-wave UV light.

Milanriederite is optically uniaxial (–), $\omega = 1.744(3)$, e = 1.737(3) (589 nm). The extinction is straight. Inspected with the polarizing microscope, the mineral is pleochroic from brownish-pink (*O*) to nearly colourless (*E*).

3. Infrared spectroscopy

In order to obtain infrared (IR) absorption spectrum, powdered sample of milanriederite was mixed with dried KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) with a resolution of 4 cm⁻¹ and 16 scans. The IR spectrum of a pellet of pure KBr was used as a reference.

The IR spectrum of a milanriederite (Fig. 2) contains bands of O–H-stretching vibrations (in the range 3000– 3700 cm⁻¹), strong bands of Si–O-stretching vibrations of the groups SiO₄ and Si₂O₇ (in the range 860–1080 cm⁻¹), as well as mixed lattice modes involving Si–O–Si and O–Si–O bending and *M*–O-stretching (M = AI, Mg, Fe³⁺) vibrations (below 660 cm⁻¹). The shoulder at 805 cm⁻¹ is assigned to $M \cdots O$ –H bending vibrations. The absence of absorption bands in the range 1100–1500 cm⁻¹ indicates the absence of boron-bearing groups.

The bands of O–H-stretching vibrations at 3670, 3629, 3567 and 3200 cm⁻¹ correspond to the bands *A*, *B*, *D* and *J*, respectively, which are predominantly polarized along *c* and correspond to differently coordinated OH groups at the O11 (the bands *A*, *B* and *D*) and O10 (the band *J*) sites (Groat *et al.*, 1995). The band at 3320 cm⁻¹ does not have analogues among the O–H-stretching bands discussed by Groat *et al.* (1995) and is a specific feature of milanriederite. The assignment of this band is ambiguous. The shoulder at



Fig. 1. (a) Crystal of milanriederite in hausmannite-jacobsite ore and (b) separate crystal of milanriederite; field of view 4 mm for both pictures.



Fig. 2. Powder IR absorption spectrum of milanriederite.

3670 cm⁻¹ corresponds to the weak hydrogen bond O11–H1···O7 and indicates the presence of domains with P4/n or P4nc symmetry (Chukanov *et al.*, 2018).

A specific feature of the IR spectrum of milanriederite, which distinguishes it from the IR spectra of all other approved vesuvianite-group minerals (Britvin *et al.*, 2003; Panikorovskii *et al.*, 2017a–d; Chukanov *et al.*, 2018), is the unusually high intensity of the band at 953 cm⁻¹. Based on available IR spectra of a restricted set of vesuvianite-group minerals, Kurazhkovskaya & Borovikova (2003) concluded that for low-symmetry samples the band of Si–O-stretching vibrations in the range 960–990 cm⁻¹ is shifted by 10–15 cm⁻¹ towards lower frequencies as compared to high-symmetry samples. Our data confirm this conclusion only partially (Chukanov *et al.*, 2018). Indeed, among nine samples with the space group P4/n, eight show strong IR bands in the range 962–968 cm⁻¹, whereas a band at 973 cm⁻¹ is observed in the remaining sample. Among

21 boron-poor samples with the space group *P4/nnc*, for 16 samples bands in the range 976–986 cm⁻¹ are observed, but five samples show bands between 962 and 968 cm⁻¹. The band at 953 cm⁻¹ in the IR spectrum of milanriederite is beyond the range 960–990 cm⁻¹ indicated by Kurazh-kovskaya & Borovikova (2003). Consequently, this criterion cannot be applied.

Another specific feature of low-symmetry vesuvianitegroup minerals indicated by Kurazhkovskaya & Borovikova (2003) and Borovikova & Kurazhkovskaya (2006) is the doublet at ~575 + 615 cm⁻¹ corresponding to O–Si–O bending vibrations. This observation was confirmed as a general trend; however, among 21 boron-poor samples with the space group *P4/nnc*, three samples show doublets in the range ~575–615 cm⁻¹ with components of approximately equal intensity (Chukanov *et al.*, 2018). The absence of splitting of the band at 606 cm⁻¹ in the IR spectrum of milanriederite is in agreement with this general trend and confirms the *P4/nnc* space group.

4. Mössbauer spectroscopy

The Fe valence state in milanriederite was determined using a SM-1201 Mössbauer spectrometer (IAI RAS) at room temperature in a constant-acceleration mode over the velocity range of ± 10 mm/s with a nominal 50 mCi ⁵⁷Co source in a Rh matrix (Ritverc). The spectrometer was calibrated relative to metallic iron at room temperature. The iron density in the absorber was about 5 mg/cm³. The spectrum was approximated by a sum of Lorentzian lines using the MOSSFIT[©] software.

The milanriederite spectrum can be approximated by a symmetric QS doublet with IS = 0.363(3) mm/s, QS = 0.513(4) mm/s and FWHM = 0.461(8) mm/s (Fig. 3), which corresponds to trivalent iron. Unfortunately, a correct and unambiguous deconvolution of the Mössbauer spectrum into individual doublets is impossible because of their proximity.

 $\begin{array}{c} 100.0 \\ 99.5 \\ 99.0 \\ 98.5 \\ 98.0 \\ -10 \\ -10 \\ -5 \\ 0 \\ 0 \\ 5 \\ 10 \\ \end{array}$

Fig. 3. Mössbauer spectrum of milanriederite.

5. Chemical data

Seven spot analyses were carried out using a digital scanning electron microscope Tescan VEGA-II XMU equipped by an Oxford INCA Wave 700 spectrometer (wavelength-dispersive mode, accelerating voltage of 20 kV, electron beam current of 20 nA, beam diameter of 3 μ m). The H₂O content was determined by gas chromatography of products of ignition at 1200 °C with a Vario Micro cube-analyser (Elementar GmbH, Germany). CO₂ was not determined because the bands of CO₃^{2–} groups are absent in the IR spectrum.

Analytical data are given in Table 2. Contents of other elements with atomic numbers >8 are below the detection limits.

The empirical formula of milanriederite (based on 78 O *apfu, i.e.* Z = 2) is $[Ca_{16.48}(La_{0.84}Y_{0.67}Ce_{0.16}Nd_{0.24}Pr_{0.06})$ $Na_{0.47}]_{\Sigma 18.92}(Al_{5.92}Mg_{4.22}Fe_{2.34}^{3+}Mn_{0.55}^{3+})_{\Sigma 13.03}Si_{17.95}O_{68.04}$ (OH)_{9.96}.

The simplified formula written in accordance with the structural data is $(Ca, REE)_{19}Fe^{3+}Al_4(Mg, Al, Fe^{3+})_8Si_{18}O_{68}$ $(OH, O)_{10}$.

The Gladstone-Dale compatibility index (Mandarino, 1981) is: $1 - (K_p/K_c) = -0.010$ ("superior").

6. X-ray diffraction data and crystal structure

Powder X-ray diffraction data were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with a cylindrical image-plate detector (d = 127.4 mm), using Debye-Scherrer geometry and CoK α radiation. The data were integrated using the software package OSC2XRD (Britvin *et al.*, 2017) and are provided in Table S1 of the Supplementary Material, linked to this article and freely available at https://pubs.geoscienceworld.org/eurjmin/. The unit-cell parameters refined from the powder data are a = 15.679(2), c = 11.888(3) Å, V = 2922(2) Å³.

For the single-crystal X-ray diffraction experiment, a crystal of milanriederite was fixed on a micromount and placed

Table 2. Chemical composition (wt%) of milanriederite.

Oxide	Mean	Range	Probe standard
Na ₂ O	0.47	0.42-0.57	Albite
MgO	5.49	5.07-6.72	Diopside
CaO	29.86	28.34-31.08	Wollastonite
Mn_2O_3	1.40	1.09-1.43	Mn
Al_2O_3	9.75	8.26-10.65	Albite
Fe_2O_3	6.03	5.47-7.22	Fe
Y_2O_3	2.44	1.79-3.03	YPO_4
La_2O_3	4.43	3.43-5.30	LaPO ₄
Ce_2O_3	0.86	0.64-1.05	CePO ₄
Pr_2O_3	0.32	0.27-0.42	PrPO ₄
Nd_2O_3	1.31	0.98-1.46	NdPO ₄
SiO ₂	34.84	34.33-35.41	SiO_2
H ₂ O	2.9(3)		
Total	100.10		

Note: Iron is considered as Fe^{3+} in accordance with Mössbauer data. Considering the deep brownish-red color of the mineral, we assume that Mn is also trivalent.

Table 3. Crystal parameters, data collection and structure refinement details for milanriederite.

Temperature (K)	100(2)
Crystal system	Tetragonal
Space group	P4/nnc
a = b (Å)	15.6578(4)
<i>c</i> (Å)	11.8597(5)
$\alpha = \beta = \gamma (^{\circ})$	90
Volume/Å ³	2907.6(2)
Ζ	2
ρ_{calc} (g/cm ³)	3.523
$\mu (mm^{-1})$	3.659
<i>F</i> (000)	3026.0
Crystal size (mm)	$0.17 \times 0.15 \times 0.12$
Radiation	Mo <i>K</i> α ($\lambda = 0.71073$ Å)
2θ range for data collection (°)	6.76-55.00
Index ranges	$-9 \le h \le 20, -17 \le k \le 19,$
	$-15 \le l \le 13$
Reflections collected	6807
Independent reflections	1684 [$R_{\rm int} = 0.0231$,
	$R_{\rm sigma} = 0.0194$]
Data/restraints/parameters	1684/0/157
Goodness-of-fit on F^2	1.247
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0268, wR_2 = 0.0644$
Final <i>R</i> indexes [all data]	$R_1 = 0.0291, wR_2 = 0.0652$
Largest diff. peak/hole ($e^{-} Å^{-3}$)	0.76/-0.50

onto an Agilent Technologies Xcalibur Eos diffractometer. The X-ray diffraction data were measured at 100 K in order to improve accuracy of the experiment, using monochromated MoK α radiation. The unit-cell parameters were refined by least-square techniques using 1684 reflections in the 2 θ range 6.76–55.00°. The details of data collection and structure refinement are given in Table 3.

The crystal structure of milanriederite (Fig. 4) was solved and refined to R = 0.027 by means of the *SHELX* program (Sheldrick, 2008). Empirical absorption correction was

Site	Occupancy	$e_{\rm ref}$ (obs.)	x	у	Z	Multiplicity	$U_{\rm eq}$ (Å ²)
X1	Ca _{0.75} Na _{0.15} REE _{0.10}	21.55	3/4	1/4	1/4	4 <i>c</i>	0.0082(4)
X2	Ca	20	0.68883(3)	0.45368(4)	0.37840(5)	16k	0.0066(2)
X3	Ca _{0.78} <i>REE</i> _{0.22}	26.82	0.67999(3)	0.60096(3)	0.60991(4)	16k	0.0113(2)
X4	$Ca_{0.40}Na_{0.10}$	10	3/4	3/4	0.1488(2)	4e	0.0088(4)
Z1	Si	14	3/4	1/4	1/2	4d	0.0057(3)
Z2	Si	14	0.54011(5)	0.31972(5)	0.37228(6)	16k	0.0056(2)
Z3	Si	14	0.58469(5)	0.65077(5)	0.36374(6)	16k	0.0067(2)
<i>Y</i> 1	$Fe_{0.47}^{3+}Mg_{0.03}$	12.58	3/4	3/4	0.45710(17)	4e	0.0113(6)
Y2	Al	13	1/2	1/2	1/2	8f	0.0053(2)
Y3	$Mg_{0.56}Al_{0.25}Fe_{0.19}^{3+}$	14.94	0.61226(4)	0.37875(5)	0.12579(6)	16k	0.0041(3)
01	0		0.77764(12)	0.32717(12)	0.41466(17)	16k	0.0084(4)
02	0		0.61724(13)	0.33854(13)	0.28190(17)	16k	0.0094(4)
O3	0		0.72385(12)	0.45512(13)	0.57275(17)	16k	0.0084(4)
04	0		0.55946(13)	0.39512(12)	0.46861(17)	16k	0.0085(4)
05	0		0.82775(13)	0.48875(13)	0.32029(18)	16k	0.0108(4)
06	0		0.62260(14)	0.72498(13)	0.44363(18)	16k	0.0138(5)
07	0		0.44361(13)	0.32642(13)	0.32055(18)	16k	0.0123(4)
08	0		0.59201(12)	0.56043(12)	0.43082(17)	16k	0.0085(4)
09	0		0.64674(12)	0.64674(12)	1/4	8h	0.0104(6)
O10	(OH,O)		3/4	3/4	0.6356(4)	4e	0.023(1)
011	(OH,O)		0.56081(13)	0.49866(13)	0.63510(17)	16k	0.0090(4)

Table 4. Atom coordinates, equivalent displacement parameters $(U_{eq}, Å^2)$ and site occupancies in the structure of milanriederite.

Table 5. Selected bond distances (Å) in the crystal structure of milanriederite.

Bond	Bond distance	Bond	Bond distance	Bond	Bond distance
X1–O1 ×4	2.337(2)	X3–O8	2.610(2)	Z3–O9	1.6636(13)
X1–O2 ×4	2.527(2)	X3–O10	2.5962(8)	<z3–o></z3–o>	1.6314
<x1–o></x1–o>	2.432	X3–O11	2.477(2)		
		<x3–o></x3–o>	2.593	<i>Y</i> 1–O6 ×4	2.039(2)
X2O1	2.458(2)			Y1–O10	2.117(6)
X2–O2	2.412(2)	<i>X</i> 4 O6 ×4	2.310(2)	<y1–o></y1–o>	2.055
X2–O3	2.369(2)	<i>X</i> 4 O9 ×4	2.582(3)		
X2–O4	2.468(2)	<x4–o></x4–o>	2.446	Y2–O4 ×2	1.9241(19)
X2–O5	2.347(2)			Y2–O8 ×2	1.9089(19)
X2–O5	2.433(2)	Z101 ×4	1.635(2)	<i>Y2</i> –O11 ×2	1.864(2)
X206	3.068(2)			<y2–o></y2–o>	1.899
X2–O8	2.341(2)	Z2-O2	1.641(2)		
<x2–o></x2–o>	2.487	Z2-O3	1.638(2)	Y3-O1	1.963(2)
		Z2-04	1.671(2)	Y3-O2	1.957(2)
X3–O3	2.425(2)	Z2-07	1.634(2)	Y3–O3	2.022(2)
X3–O6	2.494(2)	<z2–o></z2–o>	1.646	<i>Y</i> 3–O4	2.103(2)
X3–O6	2.910(2)			Y3–O5	2.063(2)
X3–O7	2.391(2)	Z3–O5	1.623(2)	Y3–O11	1.981(2)
X3–O7	2.596(2)	Z3-06	1.612(2)	<y3–o></y3–o>	2.015
X3–O7	2.534(2)	Z3–O8	1.627(2)		

applied in the CrysAlisPro (Agilent Technologies, 2014) program complex using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. Final atom coordinates and site occupancies are given in Table 4, anisotropic displacement parameters in Table S2 of the Supplementary Material. Selected interatomic distances are reported in Table 5. The space group *P4/nnc* was chosen because only 49 weak reflections were observed violating absence conditions for this space group. Refinement in the *P4/n* space group shows no deviations from the equal occupancies of the channel sites *X*4A,B and *Y*1A,B. Refinement

in the *P4nc* space group led to a large number of atoms with unrealistic anisotropic displacement parameters. The bond-valence sums (BVS) are given in Table 6. Hydrogen sites could not be located. According to the chemical data, milanriederite contains significant amounts of *REE* (both Ln and Y), and during the structure refinement their mean atomic number was taken as 51.

In milanriederite, tetrahedrally coordinated sites are occupied by Si atoms only, with mean \langle Si–O> distances in the range 1.631–1.646 Å. The bond-valence sums (BVS) for the Z-sites are 3.88, 3.77 and 3.99 valence units

Site	<i>X</i> 1	<i>X</i> 2	<i>X</i> 3	Half-pop	ulated sites	Y2	Y3	Z1	Z2	Z3	\sum_{a}
				<i>X</i> 4	<i>Y</i> 1						
01	$0.34^{\times 4\downarrow}$	0.27					0.48**	$0.97^{ imes 4 \downarrow}$			2.06**
	0.34^{\rightarrow}						0.43***	0.97→			2.01***
O2	$0.20^{ imes 4\downarrow}$	0.30					0.49**		0.96		1.95**
	0.20^{\rightarrow}						0.44***				1.90***
O3		0.34	0.33				0.41**		0.96		2.04**
							0.37***				2.00***
O4		0.26				$0.48^{\times 2\downarrow}$	0.33**		0.88		1.95**
						0.48^{\rightarrow}	0.29***				1.91***
05		0.36					0.37**			0.97	1.98**
		+0.28					0.33***				1.94***
06		0.07	0.27 + 0.09	$0.37^{\times 4\downarrow}$	$0.46^{\times 4\downarrow}$					1.00	1.85
				0.37^{\rightarrow}	0.46^{\rightarrow}						
O7			0.36 + 0.21						0.97		1.79
			+0.25								
08		0.36	0.20			$0.50^{ imes 2\downarrow}$				1.03	2.09
						0.50^{\rightarrow}					
09				$0.18^{\times 4\downarrow}$						0.99↓	2.16
				0.18^{\rightarrow}						$0.99^{\times 2 \rightarrow}$	
010*			0.21^{\downarrow}		0.38						1.22
			$0.21^{\times 4}$								
011*			0.28			$0.56^{\times 2\downarrow}$	0.46**				1.30**
						0.56^{\rightarrow}	0.41***				1.25***
\sum_{c}	2.16	2.24	2.20	1.10	1.11	3.04	2.54**	3.88	3.77	3.99	
							2.27***				

Table 6. Bond-valence calculation for milanriederite (v.u.). Bond-valence parameters are taken from Brese & O'Keefe (1991).

Note: BVS contribution of each cation was calculated according to its occupancy. The superscripts indicate the multiplying of the corresponding valence contributions due to symmetry.*Sites populated by OH. **For Y3 fully occupied by Mg.

***For *Y*3 fully occupied by Al.



Fig. 4. Projections of the milanriederite structure along the **b** axis (left) and along the **c** axis (right). Small ellipsoids represent oxygen atoms. Larger circles represent *REE*-containing (X3, X1) and calcium-occupied (X2, X4) sites. The unit cell is outlined.

(v.u.), indicating the absence of a hydrogarnet-type substitution. The X2 and X4 sites are occupied by Ca atoms only, while the X1 (BVS = 2.16 v.u.) and X3 (BVS = 2.20 v.u.) sites contain admixtures of REE^{3+} , which is typical for

vesuvianite-group minerals (see Fitzgerald *et al.*, 1987). The refined number of electrons (e_{ref}) at the X3 site (Fig. 5) is 26.82, and the mean $\langle X3-O \rangle$ distance is 2.593 Å, in accordance with the refined occupancy



Fig. 5. Arrangement of the nine-coordinated *REE*-bearing X3 sites around channels along the fourfold axis in the structure of milanriederite.



Fig. 6. Local coordination of the Mg-dominant *Y*3 site in the crystal structure of milanriederite.

 $Ca_{0.78}REE_{0.22}$. Rare-earth elements and sodium also occur at the X1 site with the total occupancy $Ca_{0.75}Na_{0.15}REE_{0.10}$.

In the crystal structure of milanriederite, Mg prevails over Al at the Y3 site, which is confirmed by the mean $\langle Y3-O \rangle$ distance of 2.015 Å. For comparison, corresponding mean distances for two samples of vesuvianite from its type locality, the Vesuvius volcano in Campania, Italy, are 1.966 and 1.961 Å (Panikorovskii *et al.*, 2017d).

The total scattering of the Y2 (BVS = 3.04 v.u.) and Y3 sites are 13.00 and 14.94, which is in agreement with their refined occupancies [Al]_{1.00} and $[Mg_{0.56}Al_{0.25}Fe_{0.19}^{3+}]_{1.00}$, respectively (Fig. 6). The refined populations of the Y2 and Y3 sites are also in agreement with the total chemical

composition of milanriederite and the BVS values for the mixed *Y*3 site (2.54 v.u. for Mg at *Y*3 and 2.27 v.u. for Al at *Y*3). The low BVS values of 1.79, 1.22 and 1.31 observed for the O7, O10 and O11 sites, respectively, indicate their involvement in the hydrogen bonding system. The refined crystal-chemical formula of milanriederite is $[^{X2,4}(Ca_{8.80} Na_{0.20})_{\Sigma9.00} \ ^{X3}(Ca_{6.24}REE_{1.76})_{\Sigma8.00} \ ^{X1}(Ca_{1.50}Na_{0.30} REE_{0.20})_{\Sigma2.00}] \ ^{Y1}(Fe_{0.94} Mg_{0.06})_{\Sigma1.00} \ ^{Y2}Al_{4.00} \ ^{Y3} [Mg_{4.48}Al_{2.00} (Fe,Mn)_{1.52}]_{\Sigma8.00} [SiO_4]_{10.00} [Si_2O_7]_{4.00}(OH,O)_{10}.$

7. Discussion

Milanriederite is the Mg-dominant (at the Y3 site) analogue of the mineral species vesuvianite, *i.e.* vesuvianite *s.s.* (Panikorovskii *et al.*, 2017d). In both minerals the Y1 site is predominantly occupied by Fe³⁺. The high *REE* content is a characteristic feature of milanriederite. Despite the fact that rare earth elements do not dominate at any structural site of this mineral, they play an important charge-balancing role, ensuring the possibility of divalent cations entering the Y3 site, in accordance with the major substitution scheme Ca²⁺ + Al³⁺ \leftrightarrow *REE*³⁺ + Mg²⁺. This mechanism of heterovalent isomorphism is predominant also in manaevite-(Ce) and, very likely, also active in other *REE*-rich vesuvianite-group minerals involving Mg and other divalent cations (Fe²⁺, Mn²⁺, Zn²⁺).

Heterovalent substitutions at the Y1 site, in accordance with the scheme $^{(Y1)}M1^{2+} + {}^{(Y3)}A1 \leftrightarrow {}^{(Y1)}M2^{3+} + {}^{(Y3)}M1^{2+}$ (M1 = Mg, Fe, Mn, Zn; M2 = Al, Fe, Mn), play a subordinate charge-balancing role in vesuvianite-group minerals. The presence of Fe³⁺ at the Y1 site of milanriederite contributes to the enrichment of the Y3 site by divalent cations as well.

Vesuvianites with significant content of rare earth elements are known for almost seventy years. For instance, vesuvianite with 4.31 wt% REE and the unit-cell dimensions a = 15.66 and c = 11.85 Å was described from pegmatoid syenites of the Ayakhta intrusion in Enisey ridge (Siberia, Russia) by Orlov & Mart'yanov (1960). The empirical formula recalculated from their data (on the basis of O + OH = 78 apfu, with the assumption that all H₂O corresponds to OH groups; REE are formally calculated as Ce) is: $(Ca_{17.02}REE_{0.95}Na_{0.52}K_{0.10}Th_{0.01})_{\Sigma 18.60}(Al_{7.41}Fe_{2.42}^{2+}Ti_{1.50})$ $\operatorname{Fe}_{1.19}^{3+}\operatorname{Mg}_{1.09}\operatorname{Mn}_{0.14}^{2+})_{\Sigma13.75}(\operatorname{Si}_{17.83}\operatorname{Al}_{0.17})_{\Sigma18.00}\operatorname{O}_{70.48}(\operatorname{OH})_{7.52}.$ Semenov (1963) reported a metamict vesuvianite-group mineral with 4.03 wt% REE (unfortunately, full chemical data for this material were not published) from a pegmatite related to ijolites of the Khunchol alkaline complex in Tuva (Siberia, Russia) and suggested for vesuvianite the following substitution schemes: $Ce^{3+} + Fe^{2+} \rightarrow Ca^{2+} +$ Al^{3+} and $Ce^{3+} + Na^+ \rightarrow 2Ca^{2+}$. In both cases *LREE* with a distinct Ce maximum strongly prevail over (Y + HREE) (Semenov, 1963).

A *REE*-rich vesuvianite-related mineral containing 14.74–20.57 wt% *REE*₂O₃ was reported from San Benito Co., California, USA (Murdoch & Ingram, 1966; Crook & Oswald, 1979; Groat *et al.*, 1992a). Fitzgerald *et al.* (1987) refined its crystal structure and found selective



Fig. 7. Relationships between unit-cell parameters and compositional features of vesuvianite-group minerals.

incorporation of *REE* into the *X*3 site. The mineral occurs in fractures of extremely altered greenstones of Franciscan age and forms gold-coloured to brown-black prismatic crystals. The empirical formula of a *REE*-rich sample (Crook & Oswald, 1979) based on electron-microprobe analyses and calculated on the basis of 18 Si atoms is $(Ca_{12.90}Ln_{4.15} Na_{0.13}K_{0.13})_{\Sigma 17.31}(Al_{6.88}Mg_{3.13}Fe_{1.23}Ti_{1.00}Mn_{0.13})_{\Sigma 12.37}$ Si_{18.00}(O,OH)₇₈. This formula may correspond to milan-riederite (provided that *Y*2 is fully occupied by Al) but shows some deficiency of the *X*- and *Y*-cations. The deficit of *X*-cations can be explained by the presence of vacancies or H₂O molecules at the *X*-sites as observed for manaevite-(Ce) (Moiseev *et al.*, 2018).

The relationship between the cell parameters and chemical composition of vesuvianite-group minerals shows two main trends, illustrated in Fig. 7 and based upon available data (Warren & Modell, 1931; Coda *et al.*, 1970; Rucklidge *et al.*, 1975; Giuseppetti & Mazzi, 1983; Fitzgerald *et al.*, 1986, 1987; Groat *et al.*, 1992a, 1994a, b, 1996; Ohkawa *et al.*, 1992; Ohkawa, 1994; Pavese *et al.*, 1998; Lager *et al.*, 1999; Armbruster & Gnos, 2000a, b; Britvin *et al.*, 2003; Galuskin *et al.*, 2003, 2007; Kurazhkovskaya *et al.*, 2005; Balassone *et al.*, 2011; Hålenius *et al.*, 2013). The first thend is related to boron incorporation in accordance with the substitutions schemes ${}^{T1}B + {}^{Y}Mg + 2{}^{W}O \leftrightarrow {}^{T1}\Box + {}^{Y}Al + 2{}^{W}(OH)$ and ${}^{T2}B + 2{}^{W}O \leftrightarrow {}^{T2}\Box + {}^{W}(OH)$ (Groat *et al.*, 1992b). The second trend reflects heterovalent substitutions, first of all Ca $\leftrightarrow REE$.

In milanriederite, La not only prevails among *REE* but strongly dominates over Ce: the La:Ce ratio is 5.25. We believe that this can be explained by the highly oxidizing conditions of the mineral-forming system in which a large proportion of cerium was oxidized to Ce^{4+} and, thus,

separated from REE^{3+} . We did not find Ce⁴⁺-bearing minerals in this assemblage, but the idea of highly oxidizing conditions is in agreement with the presence of exclusively trivalent iron in milanriederite, which is very unusual for vesuvianite-group minerals.

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