

Paseroite, $\text{PbMn}^{2+}(\text{Mn}^{2+}, \text{Fe}^{2+})_2(\text{V}^{5+}, \text{Ti}, \text{Fe}^{3+}, \square)_{18}\text{O}_{38}$, a new member of the crichtonite group

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Abstract: Paseroite, ideally $\text{PbMn}^{2+}(\text{Mn}^{2+}, \text{Fe}^{2+})_2(\text{V}^{5+}, \text{Ti}, \text{Fe}^{3+}, \square)_{18}\text{O}_{38}$, is a new mineral (IMA2011-069) from fossil wood in the upper part of the Molinello mine, Val Graveglia, Italy. Paseroite occurs in direct association with quartz, chalcocite, volborthite, metatyuyamunite and pyrophanite, and was also found as zones within V-rich senaite crystals with which it forms a solid-solution series. Paseroite forms as isolated submetallic, dark grey to black, elongated scalenohedral crystals between 50 and 100 μm in length, with the forms {001} and {102} present. The tenacity is brittle, the fracture conchoidal, and the streak is black. The Vickers hardness is 847 kg mm^{-2} (load 500g), which is equivalent to 6–6.5 on the Mohs scale. The calculated density is 4.315 g/cm^3 (on the basis of the empirical formula). In plane-polarised incident light, paseroite is greyish in colour, weakly bireflectant and non-pleochroic. Internal reflections are absent. Between crossed polars, paseroite is anisotropic, without characteristic rotation tints. Reflectance percentages (R_{min} and R_{max}) are: 18.4 %, 18.2 % (471.1 nm); 17.9 %, 17.7 % (548.3 nm); 17.6 %, 17.3 % (586.6 nm); and 17.0 %, 16.8 % (652.3 nm), respectively. The empirical formula, calculated on the basis of 38 O atoms *pfu* is: $(\text{Pb}_{0.61}\text{Sr}_{0.39})_{\Sigma 1.00}(\text{V}^{5+}_{7.78}\text{Ti}^{4+}_{7.03}\text{Mn}^{2+}_{1.86}\text{Fe}^{2+}_{0.67}\text{Fe}^{3+}_{0.37}\text{Zn}_{0.24}\text{Na}_{0.19}\text{U}_{0.02}\text{Mg}_{0.02}\square_{2.82})_{\Sigma 21.00}\text{O}_{38}$. According to the structural results, the simplified formula is: $\text{PbMn}^{2+}(\text{Mn}^{2+}, \text{Fe}^{2+})_2(\text{V}^{5+}, \text{Ti}, \text{Fe}^{3+}, \square)_{18}\text{O}_{38}$. Structurally, paseroite crystallises in the space group $R\bar{3}$, with the unit-cell parameters $a = 10.3894(5)$, $c = 20.8709(8)$ Å, $V = 1950.98(15)$ Å³ and $Z = 3$. The crystal structure was refined to $R = 0.0234$ for 632 reflections with $I_o > 2\sigma(I_o)$ and is isostructural with senaite and all other members of the crichtonite group. The eight strongest X-ray powder-diffraction lines [d in Å (hkl)] are: 3.417 (100) (024), 3.012 (21) (300), 2.896 (61) (2 $\bar{1}$ 6), 2.858 (36) (214), 2.765 (27) (303), 2.260 (85) ($\bar{1}$ 44), 2.149 (65) (4 $\bar{1}$ 5) and 1.809 (57) (4 $\bar{1}$ 8). The name is after Marco Pasero (b. 1958), Professor of Mineralogy at the University of Pisa.

Key-words: paseroite, senaite, crichtonite group, crystal structure, vanadium, new mineral, solid solution, Molinello, Val Graveglia, Italy.

1. Introduction

A sample of fossilised wood collected by S. Bottoni, S. Camarda and G. Sanguineti from the upper part of the Molinello mine (Val Graveglia, Italy), has yielded a remarkable association of minerals, including: chalcocite, hummerite, lenoblite, metatyuyamunite, pyrophanite, quartz, roscoelite, santafeite, tangeite and volborthite. Also found in this assemblage are two members of the crichtonite group, V-rich senaite and the new V-dominant member named paseroite; the latter is the subject of the present study. Both paseroite and V-rich senaite were first observed by Giuseppe Finello. Additional phases, including some potentially new minerals, are also part of this assemblage and are currently under investigation.

Paseroite is named for Marco Pasero (b. 1958), Professor of Mineralogy at the University of Pisa, Italy, in honour of his contributions to mineralogy and crystallography in general, and especially in recognition of his contributions to Italian mineralogy. Professor Pasero is a co-author of the book *Italian Type Minerals* (Ciriotti *et al.*, 2009) and has described 12 new minerals from Italy, including two new members of the crichtonite group, desauite-(Y) and gramaccioliite-(Y). He has also acted as the member for Italy on the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC) and is currently the Vice-Chairman. The mineral and name (IMA2011-069) were approved by the IMA–CNMNC prior to publication. Co-type material is deposited in the mineralogical collections of the Museo

di Storia Naturale, Sezione di Mineralogia e Litologia, Firenze, catalogue number 3111/I, and in the mineralogical collections of the Museo Regionale di Scienze Naturali, Torino, catalogue number 15900.

2. Occurrence, location and physical properties

The Molinello mine is located on the left bank of the Rio Novelli, Val Graveglia, Ne, Genoa Province, Liguria, Italy, and is the type locality for six other mineral species (Ciriotti *et al.*, 2009; Bindi *et al.*, 2011). Paseroite was found in microcavities and fractures in a piece of fossilised wood trunk (genus *Araucariaceae*; Cortesogno & Galli, 1974), measuring $\sim 50 \times 100$ cm, which was found partially embedded in grey chert. The new mineral is commonly found in direct association with quartz, chalcocite and volborthite, and more rarely with metatyuyamunite and pyrophanite. The presence of several V^{5+} minerals in association with paseroite, and the presence of uranium, indicates oxidising conditions of formation (*e.g.* Drever, 1997). We note that volborthite can be synthetically prepared at room temperature with a pH of ~ 3 (Melghit *et al.*, 2003), or at a pH ~ 6 if the temperature is 100°C (Melghit, 2006) and thus this may give insight into the formation conditions needed to produce paseroite.

Paseroite occurs as submetallic, dark grey to black, elongated scalenohedral crystals between 50 and $100\ \mu\text{m}$ in length. Crystals are usually isolated and may be zoned between paseroite and V-rich senaite. The main forms observed are $\{001\}$ and $\{102\}$. The tenacity is brittle, the fracture conchoidal, and the streak is black. The Vickers hardness of paseroite is $847\ \text{kg mm}^{-2}$ (load 500 g), with a range (10 measurements) of $834\text{--}865\ \text{kg mm}^{-2}$, which is equivalent to 6–6.5 on the Mohs scale.

The density of paseroite could not be measured because of small grain size and the strong zoning observed in most of the crystals. The calculated density (on the basis of the empirical formula and single-crystal unit cell) is $4.315\ \text{g/cm}^3$.

3. Optical properties

In plane-polarised incident light, paseroite is greyish in colour, weakly bireflectant and non-pleochroic. Internal reflections are absent. Between crossed polars, paseroite is anisotropic, without characteristic rotation tints. The reflectance was measured in air by means of an MPM-200 Zeiss microphotometer equipped with a MSP-20 system processor on a Zeiss Axioplan ore microscope. The filament temperature was approximately 3350 K. Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. Reflectance percentages (R_{min} and R_{max}) are: 18.4 %, 18.2 % (471.1 nm); 17.9 %, 17.7 % (548.3 nm); 17.6 %, 17.3 % (586.6 nm); and 17.0 %, 16.8 % (652.3 nm), respectively. By analogy with senaite, paseroite may be uniaxial (–).

4. Chemical composition

The chemical composition of the paseroite crystal used for the structural study was determined by WDS methods using a JEOL JXA-8200 electron microprobe. Major and minor elements were determined at an accelerating voltage of 20 kV, a 30 nA beam current, a beam size of $2\ \mu\text{m}$, and with 40 and 20 s counting time on the peak and background, respectively. The crystal fragment was found to be relatively homogeneous (Fig. 1, Table 1); however,

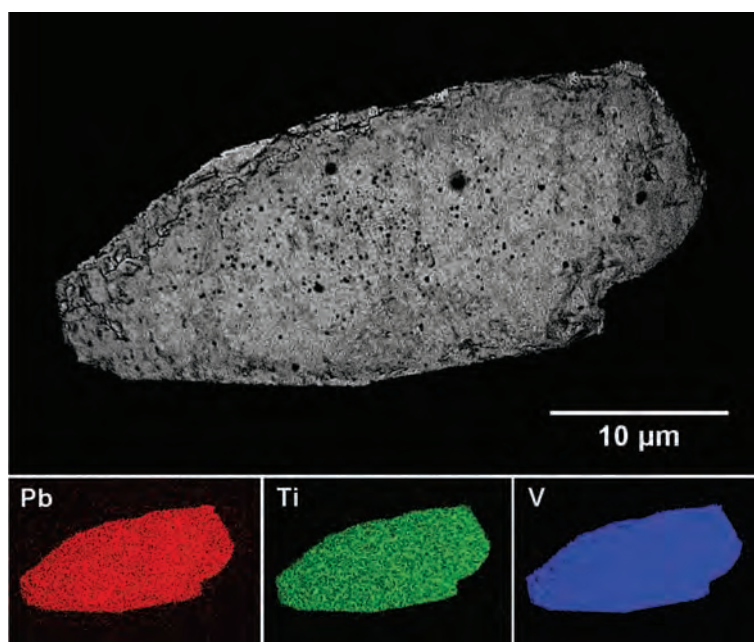


Fig. 1. Backscattered electron (top) and elemental X-ray maps (bottom) for the paseroite crystal used in the chemical and crystal structure studies.

Table 1. EMPA WDS analyses of paseroite (11 analyses).

Oxide	wt%	Range	SD	Probe standard (line)
Na ₂ O	0.35	0.28–0.42	0.05	Albite (<i>Kα</i>)
MgO	0.05	0.02–0.08	0.02	Diopside (<i>Kα</i>)
MnO	7.70	7.55–7.81	0.25	Bustamite (<i>Kα</i>)
ZnO	1.15	1.07–1.21	0.07	Willemite (<i>Kα</i>)
SrO	2.36	2.20–2.45	0.11	Strontianite (<i>Kα</i>)
PbO	8.01	7.88–8.19	0.31	PbSO ₄ (<i>Lα</i>)
FeO ^a	2.80			Hematite (<i>Kα</i>)
Fe ₂ O ₃ ^a	1.71			Hematite (<i>Kα</i>)
La ₂ O ₃	0.02	0.00–0.04	0.01	La ₃ ReO ₈ (<i>Lα</i>)
Ce ₂ O ₃	0.03	0.00–0.07	0.02	Monazite (<i>Lα</i>)
TiO ₂	32.78	32.13–32.98	0.52	Rutile (<i>Kα</i>)
ThO ₂	0.05	0.01–0.08	0.01	Thorianite (<i>Mα</i>)
UO ₃	0.36	0.27–0.46	0.04	Uraninite (<i>Mα</i>)
V ₂ O ₅	41.27	40.90–41.60	0.47	LaVO ₄ (<i>Kα</i>)
Total	98.64			

^aAllocated based on site distributions. FeO_{tot} = 5.13 wt%.

other crystals examined ranged between V-rich senaite and paseroite. Nb, Y, Cr and Ba were analysed for, but were below the detection limits. The mean results of 11 analyses are given in Table 1. Vanadium was assumed to be pentavalent and Mn divalent based on the association with other V⁵⁺ and Mn²⁺ minerals and because of the presence of a stoichiometric formula and a total which approaches 100 wt%. If V was assumed to be trivalent, the average analytical total would be ~92.57 wt%. The structure confirms the lack of water in the structure (see below), and thus we can be quite confident of the site assignments. Unfortunately due to lack of material we were unable to undertake advanced spectroscopic methods on paseroite. We were also unable to obtain a spectrum using Raman spectroscopy.

The empirical formula, calculated on the basis of 38 O atoms *pfu* (consistent with members of the crichtonite group) is: (Pb_{0.61}Sr_{0.39})Σ1.00(V⁵⁺_{7.78}Ti⁴⁺_{7.03}Mn²⁺_{1.86}Fe²⁺_{0.67}Fe³⁺_{0.37}Zn_{0.24}Na_{0.19}U_{0.02}Mg_{0.02}□_{2.82})Σ21.00O₃₈ (with +0.02 charge due to rounding errors). Taking into account the crystal structure, the simplified formula is: PbMn²⁺(Mn²⁺,Fe²⁺)₂(V⁵⁺,Ti,Fe³⁺,□)₁₈O₃₈.

5. Powder X-ray diffraction

Powder X-ray diffraction data for paseroite were obtained on a Rigaku R-Axis Rapid II curved-imaging-plate micro-diffractometer utilising monochromatised Mo*Kα* radiation. Observed *d* spacings and intensities were derived by profile fitting using JADE 9.3 software (Materials Data Inc.). Data (in Å) are given in Table 2. Hexagonal unit-cell parameters refined from the powder data using JADE 9.3 with whole-pattern fitting are *a* = 10.434(1), *c* = 20.895(2) Å, *V* = 1970.29(2) Å³ and *Z* = 3, which are in good agreement with those obtained from the single-crystal study (see Section 6).

Table 2. Powder X-ray diffraction data for paseroite^a.

<i>d</i> _{obs}	<i>I</i> _{obs}	<i>I</i> _{calc}	<i>d</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>
5.215	7	15	5.195	1	1	0
4.415	9	17	4.398	0	2	1
4.146	9	23	4.131	2	0	2
3.792	13	19	3.787	0	1	5
3.417	100	100	3.407	0	2	4
3.068	19	20	3.060	2	0	5
3.012	21	46	2.999	3	0	0
		49	2.890	1	1	6
2.896	61	51	2.890	2	1	6
2.858	36	62	2.849	2	1	4
2.834	7	13	2.830	1	0	7
		35	2.754	0	3	3
2.765	27	27	2.754	3	0	3
		17	2.637	1	3	5
2.644	15	16	2.637	1	2	5
2.608	8	15	2.597	2	2	0
		16	2.478	1	3	1
2.488	4	6	2.478	1	4	1
		17	2.433	4	2	3
2.443	16	14	2.433	2	2	3
2.437	4	14	2.427	4	1	2
		39	2.251	1	3	4
2.260	85	22	2.251	1	4	4
		6	2.142	3	1	5
2.149	65	59	2.142	4	1	5
2.121	7	12	2.118	2	1	9
1.972	7	10	1.963	4	1	0
1.927	8	14	1.919	3	2	4
1.919	5	11	1.914	1	3	7
1.809	57	54	1.803	4	1	8
1.783	6	9	1.779	3	1	10
		9	1.710	1	5	6
1.716	17	14	1.710	4	1	6

^aOnly reflections with *I*_{calc} > 5σ(*I*_{calc}) are listed.

6. Single-crystal X-ray diffraction

The X-ray data collection was performed on the same crystal used for the electron-microprobe study using an

Oxford Diffraction Xcalibur 3 CCD diffractometer, utilising graphite-monochromatised MoK α radiation ($\lambda = 0.71073$ Å). Experimental details of the data collection are reported in Table 3. The structure was solved by direct methods using SHELXS-97 (Sheldrick, 2008) and the location of all atoms was straightforward. SHELXL-97 (Sheldrick, 2008) was used for the refinement of the structure. The hexagonal setting was used for the refinement of the data. We note that several refinements are reported in the rhombohedral setting for members of the crichtonite group; however, the ICSD database has transposed these to the standard hexagonal setting. We refined the dominant atomic species versus vacancy at each structural site to obtain a mean electron number. The final solution was checked by PLATON (Spek, 2009).

The crichtonite structure (see below) has six cation sites. From the crystal-structure refinement and the electron-microprobe data (above), a tentative site-distribution scheme can be proposed (Table 4), which takes into account the common elements found on each of these sites and which is consistent with that reported for crichtonite and senaite (Grey *et al.*, 1976). A summary of these elements, modified from Wülser *et al.* (2005), can be found in Table 5. It is only possible to give a definitive scheme for the M0, M1 and M2 structural sites, while the M3, M4 and

Table 4. Tentative site-distribution scheme for paseroite.

Sites	e ⁻ EPMA	e ⁻ X-ray
M0: (Pb _{0.61} Sr _{0.39})	64.8	63.9
M1: (Mn ²⁺ _{0.79} Zn _{0.19} U _{0.02})	27.3	27.3
M2: (Mn ²⁺ _{0.54} Fe ²⁺ _{0.34} Na _{0.09} Zn _{0.03} Mg _{0.01})	23.2	20.8
M3+M4+M5: (V ⁵⁺ _{7.78} Ti ⁴⁺ _{7.03} Fe ³⁺ _{0.37} □ _{2.82})	343.2	351.6

M5 octahedral sites were considered together because of the close scattering powers of Ti and V.

The tentative site-distribution scheme gives the following structural formula for paseroite: $\sum_{\Sigma 1.00}^{M0}(\text{Pb}_{0.61}\text{Sr}_{0.39}) \sum_{\Sigma 1.00}^{M1}(\text{Mn}^{2+}_{0.79}\text{Zn}_{0.19}\text{U}_{0.02}) \sum_{\Sigma 1.00}^{M2}(\text{Mn}^{2+}_{0.54}\text{Fe}^{2+}_{0.34}\text{Na}_{0.09}\text{Zn}_{0.03}\text{Mg}_{0.01}) \sum_{\Sigma 1.00}^{M3,M4,M5}(\text{V}^{5+}_{7.78}\text{Ti}^{4+}_{7.03}\text{Fe}^{3+}_{0.37}\square_{2.82}) \sum_{\Sigma 18.00} \text{O}_{38}$.

The final refinement converged to $R_1 = 0.0234$ [632 reflections with $I_o > 2\sigma(I_o)$] and the resulting atomic parameters and displacement factors are listed in Tables 6 and 7, and bond lengths in Table 8. The residual highest peak and deepest hole are: 1.23 and $-1.27 \text{ e}/\text{Å}^{-3}$; both are close to M0 and likely are related to some disorder in the position of Pb and Sr, *i.e.* the two cations are not likely to be in exactly the same position.

7. Description of the crystal structure and discussion

The minerals of the crichtonite group crystallise in the space group $R\bar{3}$. Their chemical composition is represented by the general formula $\sum_{\Sigma 18}^{XII}A \sum_{\Sigma 18}^{VI}B \sum_{\Sigma 18}^{IV}T_2 \sum_{\Sigma 18}^{VI}C_{18}\text{O}_{38}$, where the Roman numerals preceding each component indicate the coordination numbers of their sites and: $A = \text{Ba, K, Pb, Sr, La, Ce, Na or Ca}$; $B = \text{Mn, Y, U, Fe, Zr or Sc}$; $T = \text{Fe, Mn, Mg or Zn}$; and $C = \text{Ti}^{4+}, \text{Fe}^{3+}, \text{Cr, Nb, V}^{5+}, \text{Mn}^{3+}$ or Al (e.g. Grey & Lloyd, 1976; Grey *et al.*, 1976; Orlandi *et al.*, 1997; Wülser *et al.*, 2005; Table 5). The cation sites are denoted as follows: $A = \text{M0}$, $B = \text{M1}$, $C = \text{M3} + \text{M4} + \text{M5} + \text{M6}$ and $T = \text{M2}$. The four sites M3–M6 are grouped together under C , because the cations which occupy them have very similar ionic radii ($r\text{V}^{5+} = 0.54$ vs. $r\text{Ti}^{4+} = 0.605$ Å; Shannon, 1976).

The structure is defined by layers of close-packed octahedra (M1, M3, M4, M5 and M6) and tetrahedra (M2) and containing large 12-coordinated M0 sites (Fig. 2). The octahedral site M6 shares a face with the tetrahedral site M2, so that adjacent M2 and M6 sites cannot both be occupied at the same time. The M2 site has been reported as having a low occupancy in mathiasite (Gatehouse *et al.*, 1983) and dessauite-(Y) (Orlandi *et al.*, 1997). In the dessauite-(Y) structure, additional low-occupancy sites, labelled M7, M8 and M9, have also been reported. The dominant A , B , C and T cations in the different sites determine the mineral species. The following species have been described thus far (*cf.* Theye *et al.*, 2010 and Table 5): cleusonite, crichtonite, davidite-(La), davidite-(Ce),

Table 3. Crystal data and structure refinement for paseroite.

Simplified formula	PbMn ²⁺ (Mn ²⁺ ,Fe ²⁺) ₂ (V ⁵⁺ ,Ti,Fe ³⁺ ,□) ₁₈ O ₃₈
Temperature	296(2) K
Wavelength	0.71073 Å
Space group	$R\bar{3}$
Unit-cell dimensions	$a = 10.3894(5)$ Å $c = 20.8709(8)$ Å
Volume	$1950.98(15)$ Å ³
Z	3
Density (calculated)	4.297 g/cm^3
Absorption coefficient	3.388 mm^{-1}
$F(000)$	590
Crystal size	$65 \times 45 \times 30 \mu\text{m}^3$
Theta range for data collection	$8.15\text{--}34.98^\circ$
Index ranges	$-16 \leq h \leq 16, -16 \leq k \leq 16, -33 \leq l \leq 33$
Independent reflections	632 [$R_{\text{int}} = 0.070$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	632/0/99
Goodness-of-fit on F^2	0.908
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0234, wR_2 = 0.0268$
R indices (all data)	$R_1 = 0.0502, wR_2 = 0.0505$
Extinction coefficient	$0.00107(5)$
Largest diff. peak and hole	1.23 and $-1.27 \text{ e}/\text{Å}^{-3}$

Table 5. Distribution of cations in the metal sites of crichtonite-group minerals (after Wülser *et al.*, 2005).

	M0	M1	M2	M3–5	Reference
Landauite	Na,Pb	Mn,Y	Zn ₂	Ti,Fe,Nb	Grey and Gatehouse (1978)
Loveringite	Ca,LREE	Zr,Fe	(Mg,Fe) ₂	Ti,Fe,Cr,Al	Gatehouse <i>et al.</i> (1978)
Lindsleyite	Ba,K	Zr,Fe	(Mg,Fe) ₂	Ti,Cr,Fe	Zhang <i>et al.</i> (1988)
Mathiasite	K,Ba,Sr	Zr,Fe	(Mg,Fe) ₂	Ti,Cr,Fe	Gatehouse <i>et al.</i> (1983)
Davidite-(La)	La,Ce,Ca	Y,HREE,U	(Fe,Mg) ₂	Ti,Fe,Cr,V	Gatehouse <i>et al.</i> (1979)
Davidite-(Ce)	Ce,La	Y,HREE,U	(Fe,Mg) ₂	Ti,Fe,Cr,V	Gatehouse <i>et al.</i> (1979)
Crichtonite	Sr,Ba,Pb	Mn	(Fe,Zn) ₂	Ti,Fe	Grey <i>et al.</i> (1976)
Dessauite-(Y)	Sr,Pb	Y,U	(Fe,Zn) ₂	Ti,Fe	Orlandi <i>et al.</i> (1997)
Senaite	Pb,Sr	Mn	(Fe,Zn) ₂	Ti,Fe	Grey <i>et al.</i> (1976)
Gramaccioliite-(Y)	Pb,Sr	Y,Mn	(Fe,Zn) ₂	Ti,Fe	Orlandi <i>et al.</i> (2004)
Cleusonite	Pb,Sr	U	(Fe,Zn) ₂	Ti,Fe	Wülster <i>et al.</i> (2005)
Paseroite	Pb,Sr	Mn	(Mn,Fe) ₂	V,Ti,Fe	This paper

Table 6. Atoms, multiplicity and Wyckoff letter, fractional atom coordinates and equivalent isotropic displacement parameters (\AA^2) for paseroite.

Atom	Wyckoff	x	y	z	U_{iso}
M0	3a	0	0	0	0.0240(1)
M1	3b	0	0	½	0.0167(3)
M2	6c	0	0	0.31037(4)	0.0171(3)
M3	18f	0.18510(7)	0.04422(7)	0.16498(3)	0.0149(2)
M4	18f	0.08385(7)	0.33987(7)	0.60882(3)	0.0165(2)
M5	18f	0.07595(8)	0.31544(7)	0.38897(3)	0.0166(2)
O1	18f	0.1333(3)	0.1888(3)	0.5585(1)	0.0208(4)
O2	18f	0.7109(3)	0.2050(3)	0.4465(1)	0.0199(4)
O3	18f	0.3616(3)	0.1020(3)	0.5572(1)	0.0221(5)
O4	18f	0.5930(3)	0.0332(3)	0.5480(1)	0.0206(4)
O5	18f	0.0525(3)	0.8531(3)	0.3363(1)	0.0214(5)
O6	18f	0.3653(3)	0.0985(3)	0.3386(1)	0.0200(4)
O7	6c	0	0	0.2133(2)	0.0158(6)

Table 7. Anisotropic displacement parameters (\AA^2) for paseroite.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M0	0.0239(2)	0.0239(2)	0.0241(2)	0.01194(8)	0	0
M1	0.0169(4)	0.0169(4)	0.0164(5)	0.0085(2)	0	0
M2	0.0170(3)	0.0170(3)	0.0174(5)	0.0085(2)	0	0
M3	0.0151(3)	0.0152(3)	0.0148(3)	0.0079(2)	-0.0003(2)	-0.0005(2)
M4	0.0174(3)	0.0164(3)	0.0164(3)	0.0090(2)	-0.0002(2)	-0.0002(2)
M5	0.0169(3)	0.0164(3)	0.0168(3)	0.0084(2)	0.0001(2)	-0.0001(2)
O1	0.019(1)	0.024(1)	0.0184(9)	0.0103(9)	-0.0007(8)	-0.0008(7)
O2	0.020(1)	0.019(1)	0.0212(9)	0.0105(8)	-0.0006(7)	-0.0016(7)
O3	0.021(1)	0.022(1)	0.0230(9)	0.011(1)	-0.0014(8)	-0.0003(8)
O4	0.021(1)	0.018(1)	0.0208(9)	0.0083(9)	0.0003(7)	0.0001(8)
O5	0.020(1)	0.017(1)	0.026(1)	0.0077(9)	0.0009(8)	0.0021(8)
O6	0.022(1)	0.020(1)	0.0198(8)	0.011(1)	-0.0015(8)	-0.0003(7)
O7	0.016(1)	0.016(1)	0.015(1)	0.0081(5)	0	0

dessauite-(Y), gramaccioliite-(Y), landauite, lindsleyite, loveringite, mathiasite and senaite.

The crystal structure of paseroite is consistent with that reported for senaite and crichtonite by Grey *et al.* (1976) and Grey & Lloyd (1976) and senaite by Armbruster &

Kunz (1990). Its structure is dominated by a close-packed anion framework with a nine-layer *chhchh...* stacking sequence (Fig. 3). Large cations (Pb^{2+} , Sr^{2+}) replace O at the origin of the unit cell and perturb this layer sequence (*e.g.* Fig. 2a and j). In the structure of paseroite, no extra

Table 8. Main interatomic distances (Å) and geometric parameters for paseroite.

M0-O6 (×6)	2.851(2)	M4-O6	1.858(3)
M0-O2 (×6)	2.860(2)	M4-O2	1.862(3)
		M4-O3	1.994(3)
M1-O1 (×6)	2.131(2)	M4-O6	2.094(3)
V_{oct}	12.90	M4-O5	2.121(3)
σ^2	0.20	M4-O1	2.153(3)
λ	1.0001	Mean	2.014
		V_{oct}	10.63
M2-O5 (×3)	1.937(2)	σ^2	56.45
M2-O7	2.026(3)	λ	1.0198
Mean	1.959	M5-O5	1.868(3)
V_{tet}	3.85	M5-O6	1.931(3)
σ^2	11.89	M5-O1	2.016(3)
λ	1.0029	M5-O5	2.023(3)
M3-O4	1.919(2)	M5-O4	2.045(3)
M3-O4	1.956(2)	M5-O3	2.054(3)
M3-O3	1.957(2)	Mean	1.990
M3-O2	1.975(2)	V_{oct}	10.40
M3-O7	2.011(2)	σ^2	21.41
M3-O2	2.020(3)	λ	1.0075
Mean	1.973		
V_{oct}	10.10		
σ^2	32.37		
λ	1.0095		

Note: The mean quadratic elongation (λ) and the angle variance (σ^2) were computed according to Robinson *et al.* (1971).

metal sites were observed, analogous to Grey & Lloyd's structure, and M6 was found to be unoccupied, therefore requiring full occupancy of M2. In Armbruster & Kunz's U-rich senaite, extra metal sites M6–M9 were found,

which resulted in an extra octahedrally-packed unit within the cell.

For paseroite, both the EMPA and structure refinement show the sum of $A + B + T + C$ cations to be substantially lower than the ideal value of 22 *pfu* required by the formula $\text{XII}^{\text{A}}\text{VI}^{\text{B}}\text{IV}^{\text{T}}\text{VI}^{\text{C}}\text{C}_{18}\text{O}_{38}$. Indeed, the structure refinement leads to the crystal-chemical formula: $\text{PbMn}^{2+}(\text{Mn}^{2+}, \text{Fe}^{2+})_2(\text{V}^{5+}, \text{Ti}, \text{Fe}^{3+}, \square)_{18}\text{O}_{38}$, which can be generalised to $\text{XII}^{\text{A}}\text{VI}^{\text{B}}\text{IV}^{\text{T}}\text{VI}^{\text{C}}\text{C}_{18-x}\text{O}_{38}$, allowing for the flexibility needed to accommodate greater amounts of V^{5+} . Assuming only pentavalent cations in C, and $\text{Mn}^{2+} > \text{Fe}^{2+}$ in T, the paseroite stoichiometric end-member would thus be: $\text{PbMn}^{2+}\text{Mn}^{2+}\text{V}^{5+}_{14}\text{O}_{38}$.

Since substantial Sr also exists within paseroite, it is conceivable that a new Sr- and V^{5+} -dominant member of the crichtonite group may also be found at Molinello. The combination of Sr and V has been recently reported by Bindi *et al.* (2011) in the new mineral bassoite, $\text{SrV}_3\text{O}_7 \cdot 4\text{H}_2\text{O}$, also from the same Molinello fossil wood.

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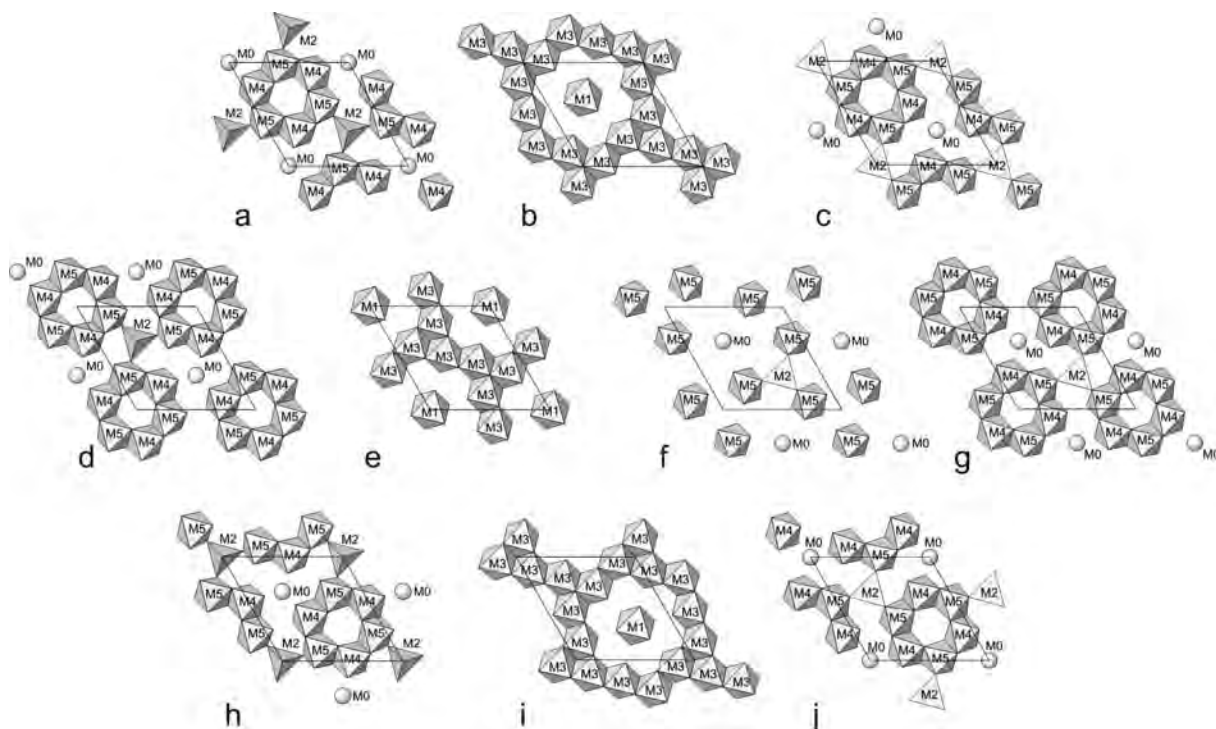


Fig. 2. A view of each of the polyhedral layers in paseroite, looking down c ; from (a) where $x = 0$, to (j) where $x = 1$.

