

# Piccoliite, $\text{NaCaMn}^{3+}_2(\text{AsO}_4)_2\text{O}(\text{OH})$ , a new arsenate from the manganese deposits of Montaldo di Mondovì and Valletta, Piedmont (Italy)

Fernando Cámara<sup>1,\*</sup>, Cristian Biagioni<sup>2</sup>, Marco E. Ciriotti<sup>3,4</sup>, Ferdinando Bosi<sup>5,6</sup>, Uwe Kolitsch<sup>7,8</sup>, Werner H. Paar<sup>9</sup>, Ulf Hålenius<sup>10</sup>, Giovanni Orazio Lepore<sup>11</sup>, Günter Blass<sup>12</sup> and Erica Bittarello<sup>13</sup>

<sup>1</sup>Dipartimento di Scienze della Terra Ardito “Ardito Desio”, Università degli Studi di Milano, via Luigi Mangiagalli 34, I-20133 Milano, Italy

<sup>2</sup>Dipartimento di Scienze della Terra, Università di Pisa, via Santa Maria 53, I-56126 Pisa, Italy

<sup>3</sup>Associazione Micromineralogica Italiana, via San Pietro 55, I-10073 Devesi-Cirié, Italy

<sup>4</sup>Dipartimento di Scienze della Terra, Università degli Studi di Torino, via Tommaso Valperga Caluso 35, 10125 Torino, Italy

<sup>5</sup>Dipartimento di Scienze della Terra, Sapienza Università di Roma, piazzale Aldo Moro 5, I-00185 Roma, Italy

<sup>6</sup>CNR, Istituto di Geologia Ambientale e Geoingegneria, U.O.S. di Roma, Roma, Italy

<sup>7</sup>Mineralogisch-Petrographische Abt., Naturhistorisches Museum, Burgring 7, A-1010 Wien, Austria

<sup>8</sup>Institut für Mineralogie und Kristallographie, Universität Wien, Josef-Holaubek-Platz 2, A-1090 Wien, Austria

<sup>9</sup>Pezoltgasse 46, A-5020 Salzburg, Austria

<sup>10</sup>Department of Geosciences, Swedish Museum of Natural History, Box 50007, SE-10405 Stockholm, Sweden

<sup>11</sup>Dipartimento di Scienze della Terra, Università degli Studi di Firenze, via La Pira 4, I-50121 Florence, Italy

<sup>12</sup>Merzbachstraße 6, D-55249 Eschweiler, Germany

<sup>13</sup>SpectraLab s.r.l. - Spin-off accademico dell'Università degli Studi di Torino, via Tommaso Valperga Caluso 35, 10125 Torino, Italy

\*E-mail: [fernando.camara@unimi.it](mailto:fernando.camara@unimi.it)



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## Abstract

Piccoliite, ideally  $\text{NaCaMn}^{3+}_2(\text{AsO}_4)_2\text{O}(\text{OH})$ , is a new mineral discovered in the Fe–Mn ore hosted in metaquartzites of the Montaldo di Mondovì mine, Corsaglia Valley, Cuneo Province, Piedmont, Italy. It occurs as small and rare black crystals and aggregates hosted by a matrix of quartz, associated with calcite and berzeliite/manganberzeliite. It has been also found in the Valletta mine near (Canosio, Maira Valley, Cuneo Province, Piedmont, Italy), where it occurs embedded in quartz associated with grandaite, hematite, tilasite/adelite and rarely thorianite. The mineral is opaque (thin splinters may be very dark red), with brown streak and has a resinous to vitreous lustre. It is brittle with irregular fracture. No cleavage has been observed. Measured Mohs hardness is  $\sim 5\text{--}5.5$ . Calculated density is  $4.08\text{ g}\cdot\text{cm}^{-3}$ . Piccoliite is non-fluorescent. Chemical spot analyses by WDS-EPMA resulted in the empirical formula (based on 10 anions pfu)  $(\text{Na}_{0.64}\text{Ca}_{0.35})_{\Sigma 0.99}(\text{Ca}_{0.75}\text{Na}_{0.24})_{\Sigma 0.99}(\text{Mn}^{3+}_{1.08}\text{Fe}^{3+}_{0.59}\text{Mg}_{0.20}\text{Ca}_{0.10})_{\Sigma 1.97}(\text{As}_{2.03}\text{V}_{0.03}\text{Si}_{0.01})_{\Sigma 2.07}\text{O}_9(\text{OH})$  and  $(\text{Na}_{0.53}\text{Ca}_{0.47})_{\Sigma 1.00}(\text{Ca}_{0.76}\text{Na}_{0.23}\text{Sr}_{0.01})_{\Sigma 1.00}(\text{Mn}^{3+}_{0.63}\text{Fe}^{3+}_{0.49}\text{Mg}_{0.48}\text{Mn}^{4+}_{0.34}\text{Ca}_{0.06})_{\Sigma 2.00}(\text{As}_{1.97}\text{P}_{0.01}\text{Si}_{0.01})_{\Sigma 1.99}\text{O}_9(\text{OH})$  for the Montaldo di Mondovì and Valletta samples, respectively. The mineral is orthorhombic, *Pbcm*, with single-crystal unit-cell parameters  $a = 8.8761(9)$ ,  $b = 7.5190(8)$ ,  $c = 11.689(1)\text{ \AA}$  and  $V = 780.1(1)\text{ \AA}^3$  (Montaldo di Mondovì sample) and  $a = 8.8889(2)$ ,  $b = 7.5269(1)$ ,  $c = 11.6795(2)\text{ \AA}$ ,  $V = 781.43(2)\text{ \AA}^3$  (Valletta sample) with  $Z = 4$ . The seven strongest X-ray powder diffraction lines for the sample from Montaldo di Mondovì are [ $d\text{ \AA}$  ( $I_{\text{rel}}$ ;  $hkl$ ): 4.85 (57; 102), 3.470 (59; 120, 113), 3.167 (100; 022), 2.742 (30; 310, 213), 2.683 (53; 311, 023), 2.580 (50; 222, 114) and 2.325 (19; 320, 214, 223)]. The crystal structure ( $R_1 = 0.0250$  for 1554 unique reflections for Montaldo di Mondovì sample and 0.0260 for 3242 unique reflections for Valletta sample) has  $\text{MnO}_5(\text{OH})$  octahedra forming edge-shared dimers; these dimers are connected through corner-sharing, forming two-up-two-down  $^{[6]}M_2(^{[4]}TO_4)_4\varphi_2$  chains [ $M = \text{Mn}$ ;  $T = \text{As}$ ;  $\varphi = \text{O}(\text{OH})$ ] running along [001]. These chains are bonded in the **a** and **b** directions by sharing corners with  $\text{AsO}_4$  tetrahedra, giving rise to a framework of tetrahedra and octahedra hosting seven-coordinated  $\text{Ca}^{2+}$  and  $\text{Na}^+$  cations. The crystal structure of piccoliite is closely related to that of pilawite-(Y) as well as to carminite-group minerals that also show the same type of chains but with different linkage. The mineral is named after the mineral collectors Gian Paolo Piccoli and Gian Carlo Piccoli (father and son) (1926–1996 and b.

1953, respectively), the latter having discovered the type material at the Montaldo di Mondovì mine.

**Keywords:** piccolite, new-mineral, manganese arsenate, crystal structure, Raman, Montaldo mine, Piedmont, Italy.

## Introduction

The north of Italy is rather rich in manganese deposits. Among the 391 species described so far in Italy, sixteen species contain  $Mn^{3+}$  and all of them are from a Ligurian or Piedmontese (*s.l.*) manganese type-locality deposit (Table 1). Piccolite,  $NaCaMn^{3+}_2(AsO_4)_2O(OH)$ , was first recognised on a specimen found in 2007 by Gian Carlo Piccoli in the dumps of the Montaldo di Mondovì mine (latitude  $44^{\circ}19'08.9''$ , longitude  $7^{\circ}51.09'5''$ ), Borgata Oberti, Montaldo di Mondovì, Corsaglia Valley, Piedmont, Italy (Figure 1). A preliminary characterisation of the crystal structure of the mineral was provided by Kolitsch (2008). A second occurrence, which helped to improve the understanding of the mineral's crystal chemistry, was recognised in 2015 on specimens from the dumps of the Valletta mine (latitude  $44^{\circ}23'42''N$ , longitude  $7^{\circ}5'42''E$ , 2536 m above sea level), Canosio, Maira Valley, Piedmont, Italy.

The name of the new mineral honours the mineral collectors Gian Carlo Piccoli (b. 1953) and his father Gian Paolo Piccoli (1928–1996) for their contribution to the knowledge of the regional mineralogy of Piedmont and Aosta Valley. Since the 1970s, father and son carried out mineralogical researches in the Western Alps (Maritime and Cottian Alps, in the province of Cuneo, Piedmont), leading to the discovery of gramaccioliite-(Y) (Orlandi *et al.*, 2004) and grandaite (Cámara *et al.*, 2014) and to the creation of the mineralogical collection of the province of Cuneo, kept in the “Federico Eusebio” civic museum in Alba, Cuneo Province, Piedmont. After his father's death, Gian Carlo Piccoli devoted himself to the writing of the books “*Minerali delle Alpi Marittime e Cozie – Provincia di Cuneo*” (Piccoli, 2002) and “*Minerali del Piemonte e della Valle d'Aosta*” (Piccoli *et al.*, 2007b). In this latter work, more than 570 different mineral species found in Piedmont and Aosta Valley are described. Finally, Gian Carlo Piccoli is co-author of the book “*Minerali in Val d'Ala*” (Maletto and Piccoli, 2014).

The mineral and its name were approved by the International Mineralogical Association's Commission on New Minerals, Nomenclature and Classification (IMA2017-

016). Cotype material from Montaldo di Mondovì is deposited in the Mineralogical Collection of the Museo di Storia Naturale, Università di Pisa, Via Roma 79, Calci (Pisa, Italy), under catalogue number 19906 as well as in the mineralogical collection of the Museo civico archeologico e di scienze naturali "Federico Eusebio" di Alba (Cuneo, Italy), with catalogue numbers M00673 (Montaldo di Mondovì specimen) and M00674 (Valletta specimen).

## Occurrence

The Fe-Mn ores of the Montaldo di Mondovì mine were exploited for iron (Sismonda, 1841a, b; Conti, 1873) from 1838 until its closure in the mid-1950s. The deposit is hosted within the 'Klippen of Deviglia' Unit (Vanossi, 1980) belonging to the Mesozoic sequence of the innermost Brianzonese Zone (Dalla Giovanna and Vanossi, 1991; Vanossi *et al.*, 1986). Metaquartzites and quartz-bearing marbles host the Fe-Mn ores that occur as layers, boudins, and, subordinately, in mineralised veins. Late-stage hematite-bearing veinlets crosscut both quartz arenites and marbles (Cabella *et al.*, 1992, 1995, 1999). The mineralisation consists of hollandite-supergroup minerals  $\pm$  hematite  $\pm$  braunite, with variable amounts of quartz, calcite, Mn- and Fe-rich muscovite and aegirine (Cabella *et al.*, 1999; Kolitsch *et al.*, 2011; Giai, 2020). Further details on the geological setting are reported in Cámara *et al.* (2021a) and references therein, which describe armellinoite-(Ce),  $\text{Ca}_4\text{Ce}^{4+}(\text{AsO}_4)_4 \cdot \text{H}_2\text{O}$ , another arsenate for which the Montaldo di Mondovì mine is also the type locality. Other associated minerals include aegirine, anatase, armellinoite-(Ce), arsenogoyazite, berzeliite/manganberzeliite, braunite, calcite, chernovite-(Y), dolomite, cinnabar, cryptomelane, As-rich fluorapatite, gasparite-(Ce), gasparite-(La), goethite, hausmannite(?), hematite, hollandite, monazite-(Ce), montmorillonite, muscovite, orthoclase, pyrolusite(?), quartz, ramsdellite, ranciéite, romanèchite, rutile, spessartine, svabite, talmessite, tilasite, titanite wakefieldite-(Ce), wakefieldite-(Y), zircon, and three potential new minerals, *i.e.* the unnamed La-, Nd- and (Ca,Y,REE)-dominant analogues of chernovite-(Y) (Piccoli, 2002, 2007; Piccoli *et al.*, 2007a,b; Ciriotti, 2007; Kolitsch *et al.*, 2011; Giai, 2020). Piccoliite at this locality always occurs in quartz-calcite veins (Figure 2a), associated with calcite, berzeliite/manganberzeliite and, very rarely, with chernovite and the aforementioned unnamed REE analogues of chernovite-(Y).

The Valletta mine was mined for iron in the 15<sup>th</sup> century and probably hastily abandoned both due the uneconomic mixture of hematite with manganese ores and because it is located at very high altitude (2536 m above sea level). The Fe-Mn deposit is

located in the Briançonnais Zone of the Cottian Alps. Specifically, the Mn-bearing minerals are hosted in Permian quartzites overlying quartzitic conglomerates (Verrucano formation) and quartz-feldspar fine-grained schists derived from Permian rhyolitic volcanism of the so-called Axial Permian-Carboniferous Zone (Franchi and Stella, 1930). A major subvertical tectonic contact, Faille de Ceillac (Gidon *et al.*, 1994), separates the rocks found at the Valletta mine from the Middle Triassic carbonate sequence of the Becco Grande to the north and from the Rocca La Meja ridge to the south. The rocks found at the Valletta mine are part of the Bande de Marinet, the southernmost tectonic zone of the Axial Permian-Carboniferous Zone; specifically, it is part of Unit M3, the structurally highest unit defined in the Bande de Marinet by Lefèvre (1982). During the Alpine tectonometamorphic cycle, the rocks now exposed in the Bande de Marinet were affected by high-*P*, low-*T* metamorphism of blueschist facies, the effects of which are more evident in the metabasites interlayered in the metavolcanic quartz-feldspar schists that often display the characteristic lawsonite-glaucophane assemblage (Franchi and Stella, 1930; Gidon *et al.*, 1994). Here, piccolite is also always embedded in quartz matrix, associated with hematite, grandaite (Figure 2b), tilasite/adelite, and, rarely, with thorianite. Other minerals that have been observed in the Valletta mine dump include aegirine, albite, aldomarinoite, azurite, baryte, bariopharmacosiderite, berzeliite, bosiiite, braccoite, braunite, calcite, canosioite, castellarite, coralloite, cryptomelane, diopside, fianelite, gamagarite, ganophyllite, gypsum, hollandite, ilmenite, lombardoite, magnesio-arfvedsonite, magnesio-riebeckite, magnetite, malachite, manganberzeliite, mimetite, muscovite (Mn-bearing), neotocite, opal, orthoclase, oxy-dravite (Fe<sup>3+</sup>-Mn<sup>3+</sup>-V<sup>3+</sup>-rich), palenzonaite, phlogopite, pyrobelonite, ranciéite, rhodochrosite, rhodonite, richterite, rüdlingerite, rutile, saneroite, talc, tetrahedrite series minerals, tinnunculite, tiragalloite, titanite, tokyoite, wallkilldellite, arsenate members of the alluaudite group as well as other possible uncharacterised amphiboles (Cámara *et al.* 2022 and references therein). It is worth noting that many Mn-bearing phases at the Valletta mine contain iron exclusively as Fe<sup>3+</sup> and manganese as Mn<sup>3+</sup>.

### **Appearance and physical properties**

Piccolite occurs rarely at the Montaldo di Mondovì locality as black well-developed prismatic crystals within calcite-quartz veins (Figure 2a), whereas it forms aggregates of anhedral crystals, embedded in the quartz matrix at the Valletta locality (Figure 2b). Splinters may be very dark red. Streak is brown and lustre is resinous to vitreous. The

mineral is non fluorescent and opaque, but transparent in thin section. Hardness was measured with Vickers indentation: four measurements were performed, with two different loads, obtaining VHN<sub>15</sub> (two measurements) = 654 and 656 kg/mm<sup>2</sup> and VHN<sub>25</sub> (two measurements) = 584 and 657 kg/mm<sup>2</sup>, which corresponds to a Mohs hardness of 5 – 5½. Piccoliite is brittle, with no cleavage or parting observed. Fracture is irregular. Density was not measured because of the lack of heavy liquids of sufficient density. Calculated density is 4.084 g·cm<sup>-3</sup> (based on the empirical formula and unit-cell volume refined from single-crystal X-ray diffraction (XRD) data of the Montaldo di Mondovì specimen) and 4.011 g·cm<sup>-3</sup> (Valletta sample).

Owing to the small amount of material available for the mineralogical study, the optical properties of piccoliite were determined in plane-polarised reflected light on a crystal fragment embedded in epoxy. Piccoliite is grey in colour. Under crossed polars, it is distinctly anisotropic, with rotation tints in shades of grey. Internal reflections in brownish tints are commonly observed. Reflectance was measured in air using a LEITZ microphotometer. Readings were taken for specimen and standard (Zeiss SiC Standard 079) maintained under the same focus conditions for the standard wavelengths recommended by the Commission on Ore Mineralogy of the IMA. The edge of the square-like measuring area was ~0.1 mm. Reflectance percentages ( $R_{\min}$  and  $R_{\max}$ ) are:

$\lambda$ (nm)	$R_1$ (%)	$R_2$ (%)
470	7.7	9.8
546	7.7	9.5
589	7.4	9.3
650	7.4	9.2

The mean refractive index, calculated using the Gladstone-Dale relationship (Mandarino, 1979, 1981), and the calculated density of the Montaldo di Mondovì material, is 1.878.

## Raman spectroscopy

Unpolarised micro-Raman spectra were obtained on an unpolished sample from Montaldo di Mondovì locality in nearly back-scattered geometry with a Jobin-Yvon Horiba XploRA Plus apparatus, equipped with a motorised x-y stage and an Olympus BX41 microscope with a 10× objective. The 532 nm line of a solid-state laser was used. The minimum lateral and depth resolution was set to a few  $\mu\text{m}$ . The system was calibrated using

the 520.6  $\text{cm}^{-1}$  Raman band of silicon before each experimental session. Spectra were collected through multiple acquisition with single counting times of 180 s. Backscattered radiation was analyzed with a 1200  $\text{mm}^{-1}$  grating monochromator. Peak deconvolution was performed through the software Fityk (Wojdyr, 2010).

In the range between 100 and 1200  $\text{cm}^{-1}$  (Figure 3a), the observed Raman spectrum in piccolite from Montaldo di Mondovì is dominated by a band at  $\sim 850 \text{ cm}^{-1}$ . Other bands are observed at (in  $\text{cm}^{-1}$ ) 160, 191 (lattice vibrations), 342, 441, 488 (bending of As–O bonds), 745 (hydroxyl deformation band) and 803 (As–O stretching vibrations, along with the band at 894  $\text{cm}^{-1}$ ); band assignment is in agreement with Frost and Klopogge (2003). The Raman spectrum of piccolite from Valletta (Figure 3a) shows the same bands at slightly different values due to the small difference in chemical composition (in  $\text{cm}^{-1}$ ): 200, 318, 445, 518, 730, 800, 852, and 890. Differences in the intensity are probably due to the different crystallographic orientation of the studied grains.

In both spectra there are two bands at  $\sim 1650$  and  $1770 \text{ cm}^{-1}$  that may correspond to overtones or combination modes of As–O-stretching vibrations, as no structural evidence in support of the presence of  $\text{H}_2\text{O}$  groups was found (see later).

Finally, in the (O–H)-stretching region (2800–3800  $\text{cm}^{-1}$ ), a broad band at 3140  $\text{cm}^{-1}$  has been observed in the spectrum of piccolite from Montaldo di Mondovì (Figure 3b). The same spectral feature occurs in the spectrum collected on the sample from the Valletta mine but it shows a lower intensity. By using the relation of Libowitzky (1999), a donor-acceptor  $\text{O}\cdots\text{O}$  distance of approximately 2.685 Å was calculated, in good agreement with the observed  $\text{O7}\cdots\text{O1}$  distance of 2.660(3) Å (see below). Similar bands are also found in the structurally related mineral carminite (Frost and Klopogge, 2003).

## Chemical composition

Preliminary EDS chemical analysis of piccolite showed Na, Mg, Ca, Mn, Fe and As being the only elements present with atomic number  $> 8$ . Quantitative chemical analyses were carried out on the crystal used for the crystal-structure refinement using a CAMECA SX50 electron microprobe (WDS mode, 15 kV, 15 nA, nominal beam diameter 1  $\mu\text{m}$ ). The elements Al, S, K, Ti, Cr, Ni, Cu and Ba were sought but found to be below detection limit. Counting times were 20 s on the peak and 10 s on the backgrounds for Na and 30 s on the peak and 15 s on the background for all the other elements. Direct  $\text{H}_2\text{O}$  determination was

not performed because of the very small amount of material available. Chemical data are given in Table 2.

The empirical formula of piccolite, based on 10 (O,OH) anions per formula unit (*pfu*) and 6 cations *pfu*, is  $(\text{Na}_{0.64}\text{Ca}_{0.35})_{\Sigma 0.99}(\text{Ca}_{0.75}\text{Na}_{0.24})_{\Sigma 0.99}(\text{Mn}^{3+}_{1.08}\text{Fe}^{3+}_{0.59}\text{Mg}_{0.20}\text{Ca}_{0.10})_{\Sigma 1.97}(\text{As}_{2.03}\text{V}_{0.03}\text{Si}_{0.01})_{\Sigma 2.07}\text{O}_9(\text{OH})$  (Montaldo di Mondovì) and  $(\text{Na}_{0.53}\text{Ca}_{0.47})_{\Sigma 1.00}(\text{Ca}_{0.76}\text{Na}_{0.23}\text{Sr}_{0.01})_{\Sigma 1.00}(\text{Mn}^{3+}_{0.63}\text{Fe}^{3+}_{0.49}\text{Mg}_{0.48}\text{Mn}^{4+}_{0.34}\text{Ca}_{0.06})_{\Sigma 2.00}(\text{As}_{1.97}\text{P}_{0.01}\text{Si}_{0.01})_{\Sigma 1.99}\text{O}_9(\text{OH})$  (Valletta mine). All Fe is given as  $\text{Fe}^{3+}$ , whereas  $\text{H}_2\text{O}$  was calculated from stoichiometry to correspond to 1 (OH) pfu. See later for discussion on oxidation state of Mn in the studied material from both localities. The ideal formula of piccolite is  $\text{NaCaMn}^{3+}_2(\text{AsO}_4)_2\text{O}(\text{OH})$ , corresponding to  $\text{Na}_2\text{O}$  6.41,  $\text{CaO}$  11.59,  $\text{Mn}_2\text{O}_3$  32.63,  $\text{As}_2\text{O}_5$  47.51,  $\text{H}_2\text{O}$  1.86, total 100.00 wt%.

## X-ray crystallography

Powder X-ray diffraction data were collected on Montaldo di Mondovì material using a 114.6 mm Gandolfi camera. Data (in Å, for  $\text{CuK}\alpha$ ) are listed in Table 3. Unit-cell parameters were refined from the X-ray powder data using the method of Holland and Redfern (1997) based on 14 unequivocally indexed reflections. Refined unit-cell parameters are  $a = 8.879(2)$ ,  $b = 7.509(2)$ ,  $c = 11.707(2)$  Å and  $V = 779.7(2)$  Å<sup>3</sup>,  $Z = 4$ .

Single-crystal X-ray diffraction intensity data were collected on a  $0.080 \times 0.040 \times 0.035$  mm crystal from Montaldo di Mondovì using a Bruker Smart Breeze diffractometer equipped with an air-cooled CCD detector, and graphite-monochromatised  $\text{MoK}\alpha$  radiation (Dipartimento di Scienze della Terra, Università di Pisa). The detector-to-crystal distance was 50 mm. Data were collected using  $\omega$  and  $\phi$  scans, in  $0.5^\circ$  slices, with an exposure time of 45 s per frame and corrected for Lorentz and polarisation factors and absorption using the software package *Apex2* (Bruker AXS Inc., 2004). Data were obtained on a  $0.243 \times 0.194 \times 0.119$  mm crystal from Valletta mine using an Oxford Gemini R Ultra diffractometer equipped with a CCD area detector at CrisDi (Università di Torino), with graphite-monochromatised  $\text{MoK}\alpha$  radiation. The detector-to-crystal distance was 54.8 mm. Data were collected using  $\omega$  scan modes, in  $1^\circ$  slices, with an exposure time of 17 s per frame and corrected for Lorentz and polarisation factors and absorption using the software package *CrysAlisPro* (Agilent Technologies, 2019).

Observed unit-cell parameters (Table 4) are consistent with orthorhombic symmetry. The statistical tests on the distribution of  $|E|$  values ( $|E^2 - 1| = 0.872$ ) and the systematic



absences suggested the space group symmetry *Pbcm*. The crystal from Valletta showed significant systematic absences violations of the *c*-glide but further examination of structural models having a lower symmetry led to models that were equivalent to a *Pbcm* structure. The violations of systematic absences may be due to double diffraction phenomena. The crystal structure was solved through direct methods using *SHELXS-97*. After locating the heavier atoms, the structure solution was completed through successive difference-Fourier syntheses and refined using *SHELXL-2014* (Sheldrick, 2015). Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). The following curves were used: Ca vs Na at the A1 and A2 sites, Mn vs Mg at the Mn site, As at the As1 and As2 sites; and O at the O1-O7 sites. The As1, As2 and O sites were found to be fully occupied by As and O, respectively. The A1 and A2 sites have a mixed (Na,Ca) and (Ca,Na) occupancy, respectively. Owing to the similar scattering factors of Mn and Fe, the occupancy of the Mn site was refined based on the chemical-analytical data: mixed (Mn,Fe) occupancy with minor Mg and Ca. The H atom bonded to the oxygen atom hosted at the O7 site was found in the difference-Fourier map. After several cycles of anisotropic refinement (only H was refined isotropically), the  $R_1$  factor converged to 0.0250 for 1554 reflections with  $F_o > 4\sigma(F_o)$  for the crystal from the Montaldo di Mondovì mine, and 0.0260 for 3242 reflections with  $F_o > 4\sigma(F_o)$  for the crystal from the Valletta mine. Details of data collection and refinement are given in Table 4. Fractional atom coordinates, site occupancies and equivalent isotropic or isotropic displacement parameters are reported in Table 5. The crystallographic information file has been deposited with the **Principal Editor of Mineralogical Magazine and is available as Supplementary material**. Table 6 reports selected bond distances. Table 7 shows the comparison between observed site scattering and that calculated from the proposed site population. Finally, Table 8 provides a bond-valence analysis carried out using the bond-valence parameters of Gagné and Hawthorne (2015).

### **X-ray Absorption Spectroscopy (XAS)**

X-ray Absorption Spectroscopy (XAS) measurements at the *K*-edge of Mn were performed at the LISA beamline (BM-08) (d'Acapito *et al.*, 2019) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Samples were measured using a pair of Si (111) flat crystals; Si-coated focusing mirrors ( $E_{\text{cutoff}} \approx 16$  KeV) were used for harmonic rejection. Measurements were performed on a single crystal in the fluorescence

mode using a four-channel Silicon Drift Detector (SDD) ARDESIA (Hafizh *et al.*, 2019); Mn model compounds (rhodochrosite, bixbyite-(Mn), pyrolusite) were measured in transmission mode. The spectra were acquired with a fixed  $k$  step of  $0.05 \text{ \AA}^{-1}$  up to a maximum value of  $12 \text{ \AA}^{-1}$ . Samples were measured at room temperature. Standard procedures (Lee *et al.*, 1981) were followed to extract the structural EXAFS signal ( $k \cdot \chi(k)$ ): pre-edge background removal, spline modelling of bare atomic background, edge step normalisation using a region far above the edge, and energy calibration using the software ATHENA (Ravel and Newville, 2005). Model atomic clusters centred on the absorber atom were obtained by ATOMS (Ravel, 2001), using atomic coordinates taken from the crystal-structure determination reported in this study; theoretical amplitude and phase functions were generated using the FEFF8 code (Ankudinov *et al.*, 1998). EXAFS spectra were fitted through the ARTEMIS software (Ravel and Newville, 2005) in the Fourier-Transform (FT) space.

Figure 4 reports the XAS spectrum in the X-ray absorption near edge structure (XANES) region of piccolite, together with those of rhodochrosite, bixbyite-(Mn), pyrolusite and hollandite. An accurate quantification of Mn valence state is rather difficult, especially without the comparison with well-known model compounds belonging to the same structural family, because different octahedral arrangements and distortions, especially related to Jahn-Teller effects, may affect the pre-edge peak intensity and the overall XANES shape, i.e. the features commonly used to evaluate Mn valence (see Farges, 2005 and Manceau *et al.*, 2012 for a detailed discussion). It is, therefore, safer to limit the discussion to a purely qualitative point of view. The position of the main absorption edge of piccolite (main inflection point at 6548.4 eV), although lying close to that of bixbyite-(Mn) (6547.4 eV), is shifted towards higher energy values, clearly indicating the presence of a moderate quantity of  $\text{Mn}^{4+}$ . As a comparison, the edge position of hollandite (6551.4 eV, data from Manceau *et al.*, 2012), where the average Mn valence is close to 4+, lies much closer to that of pyrolusite (6552.4 eV).

The Mn  $K$ -edge EXAFS spectrum and Fourier transform of piccolite are shown in Figure 5a and b, respectively; results of the EXAFS multiparameter fit are reported in Table 9. Attempts to fit the first shell using an average Mn–O distance calculated from the starting model were unsuccessful, leading to a poor fit and an extremely high Debye-Waller factor ( $\sigma^2$ ) [ $0.02(1) \text{ \AA}^{-2}$ ]; only the use of six different Mn–O paths, as suggested by the crystal-structure data, allowed to suitably fit the data and resulted in a drop of  $\sigma^2$  of a factor 5, thus confirming that Mn is hosted in a very distorted site. The set of six distances is in excellent

agreement with the crystal-structure model (Table 6), resulting in a value of  $\langle \text{Mn-O} \rangle = 2.03$  Å. The second shell signal is dominated by the contribution of the four closest Mn-As scattering paths. Resulting Mn-As distances are in good agreement with those obtained by the crystal-structure refinement. Neither the contribution of the Mn-Mn/Mg scattering paths nor that of the Mn-Ca/Na ones was observable during the fit procedure. The lack of these contributions is probably due to destructive interferences occurring between the signals corresponding to the aforementioned paths as suggested in ESM-2. It is possible to notice, on the other hand, how Mn-As paths are not affected by this interference, showing higher amplitude at higher  $k$  values.

## Structure description

The crystal structure of piccolite (Figure 6a) is characterised by  $\text{MnO}_5(\text{OH})$  octahedra forming edge-shared  $[M\phi_{10}]$  dimers; these dimers are connected through corner-sharing, forming two-up-two-down  $^{[6]}M_2(^{[4]}TO_4)_4\phi_2$  chains [ $M = \text{Mn}$ ;  $T = \text{As}$ ;  $\phi = \text{O}(\text{OH})$ ] running along  $c$  (Figure 6b and 6c). These chains are bonded in the  $a$  and  $b$  directions by sharing corners with  $\text{AsO}_4$  tetrahedra, giving rise to a framework of tetrahedra and octahedra hosting  $\text{Ca}^{2+}$  and  $\text{Na}^+$  cations.

Arsenic is tetrahedrally coordinated by oxygen atoms, with  $\langle \text{As-O} \rangle = 1.690$  and  $1.683$  Å for the  $\text{As1}$  and  $\text{As2}$  sites, respectively (Montaldo di Mondovì data). The observed  $\langle T\text{-O} \rangle$  value is in good agreement with the grand mean value reported for arsenates in the literature [ $1.687(27)$  Å, Gagné and Hawthorne, 2018]. The bond-valence sum (BVS) values at  $\text{As1}$  and  $\text{As2}$  are 4.96 and 5.06 valence units (v.u.), respectively. Trivalent Mn at the  $Mn$  site, partially replaced by  $\text{Fe}^{3+}$  and minor  $\text{Mg}^{2+}$  and possibly  $\text{Ca}^{2+}$ , is hosted within a Jahn-Teller distorted octahedra, with bond distances ranging from  $1.804(1)$  to  $2.172(1)$  Å, and a  $\langle \text{Mn-O} \rangle$  distance of  $2.023$  Å. Calculated BVS at the  $Mn$  site is 3.03 v.u. (Table 8a), slightly larger than the expected atomic valence from site population (2.82 v.u.; Table 7). Finally, Ca and Na are hosted in the cavities of the framework of octahedra and tetrahedra. Calcium is preferentially partitioned at the seven-fold coordinated  $A2$  site, with average bond distance of  $2.479$  Å, whereas Na occurs at the seven-fold coordinated  $A1$  site, having a slightly larger average bond distance ( $2.501$  Å). The BVSs at the  $A1$  and  $A2$  sites are 1.33 and 1.71 v.u., respectively, in agreement with mixed (Na,Ca) and (Ca,Na) site populations, respectively (Table 8a). The hydrogen atom is bonded to the oxygen hosted at the  $\text{O7}$  site, forming a

O7–H  $\cdots$  O1 hydrogen bond. Its bond strength, calculated from the relation of Ferraris and Ivaldi (1988), is 0.25 v.u.

The blackish colouration of the mineral suggests the presence of both Mn<sup>3+</sup> and Mn<sup>4+</sup> and XANES data indicate the presence of Mn<sup>4+</sup> in piccolite from the Valletta mine. Both mineralisations have a strongly oxidised character, with Fe always occurring as Fe<sup>3+</sup> (e.g., hematite) and Mn as Mn<sup>3+</sup> and Mn<sup>4+</sup> (e.g., members of the hollandite supergroup). In agreement with this, the calculated bond valence incident at the *Mn* site for the Valletta specimen is larger than the expected from a formula without Mn<sup>4+</sup> (2.89 v.u. vs 2.73 v.u., respectively), thus supporting a partial amount of more highly charged cations ordered at that site. The presence of Mn<sup>4+</sup> is needed to charge balance the presence of Mg<sup>2+</sup> at the *M* sites. It could be also balanced either by dehydroxylation at the O7 anion site or by an increase of Na (> 1 apfu) at the A1,2 sites. If we assume that part of the Mn is present as Mn<sup>4+</sup> also in the Montaldo of Mondovì sample, and we calculate 41% of Mn<sup>4+</sup> in the bulk Mn, the average charge turns +3.025, closer to the corresponding BVS calculated at the *M* sites (3.035 v.u.). Moreover, the calculated bond length would be 2.015 Å, closer to the observed value (2.023 Å) than the value calculated if all Mn is considered Mn<sup>3+</sup> (2.041 Å). Besides, if all the Mn is considered as Mn<sup>3+</sup> there is an O site with a relatively high BVS of  $\sim$ 2.33 v.u. (see Table 8a). The assumed presence of 41% of Mn<sup>4+</sup> would reduce the BVS to 2.24 v.u., still high and thus showing a weakness of this topology. This remanent high BVS is due to the presence of a very short distance (*M*–O6 = 1.804 Å) compared to the average equatorial bond distance of the MO<sub>6</sub> octahedron (2.093 Å). This distance is even shorter than the one observed by Gagnè and Hawthorne (2020) for both six-fold coordinated Mn<sup>3+</sup> and Mn<sup>4+</sup>, 1.843 and 1.841 Å, respectively. The BVS values reported in Table 8a for the crystal from Valletta when considering 35% of Mn<sup>4+</sup> reduces the BVS at O6 to 2.145 v.u. and yields a calculated averaged bond length of 2.024 Å, very close to the one observed (2.029 Å); moreover, the observed BVS at the *M* site (2.897 v.u.) is almost coincident with the average charge (+2.900). In any case, both XANES data and crystal-chemical considerations indicate that Mn in the Valletta specimen is mainly present at its trivalent state, thus Mn<sup>3+</sup> is the dominant cation of the dominant charge (+3). The ideal-charge cation formula is thus A1<sup>1+</sup> A2<sup>2+</sup> M<sup>3+</sup>(T<sup>5+</sup>O<sub>4</sub>)O(OH).

The hydrogen-bonding topology is rather constrained and shows a O–H $\cdots$ O angle of 175(5)°. The donor-acceptor (O7 $\cdots$ O1) distance is short (2.67 Å) but, using that donor-acceptor distance, the corresponding wavenumber value calculated using the relation of Libowitzky (1999), 3066 cm<sup>-1</sup>, is in good agreement with the observed (OH) stretching

Raman shifts (3124 and 3252  $\text{cm}^{-1}$ ). The presence of two bands could agree with two local arrangements with two  $\text{Mn}^{3+}$  or one  $\text{Mg}^{2+}$  and  $\text{Mn}^{4+}$  in agreement with the proposed presence of  $\text{Mn}^{4+}$  at the *M* sites, as the O7 site is shared by two edge-sharing  $\text{MO}_6$  octahedra. Further shifts can be attributed to the mixed valence at the A1 site, also coordinating the O7 anion site.

## Relation to other species

The topology of the piccolite structure is not new. The mineral pilawite-(Y), ideally  $\text{CaYAl}_2(\text{SiO}_4)_2\text{O}(\text{OH})$  (Pieczka *et al.*, 2015), has the same topology (see Figure 7b), although its symmetry is monoclinic ( $P2_1/c$ ), with a  $\beta$  angle of  $90.61(4)^\circ$ . Consequently, pilawite-(Y) has two symmetrically independent *M* sites and two anions split in two non-symmetrically equivalent positions (O1 and O2 and O7 and O8, corresponding, respectively, to O5 and O2 in the piccolite structure).

A particularity of the structure of piccolite is the high  $U_{\text{eq}}$  value observed in both crystals for the anion at the O1 site (Table 5), coordinating the  $\text{As1O}_4$  tetrahedron, which receives further bonding from the H bonded to O7. The observed value is three times the mean value observed for the other anion sites. The anisotropic displacement values also show a dynamic disordering of this anion site along [001] in the (010) plane. This is a particularly striking feature considering the stressed nature of the topology of hydrogen bond and could be related to a particular instability of the structure that could relax at lower temperature lowering the symmetry to monoclinic by a shear in the (010) plane. Interestingly, the  $U_{\text{eq}}$  value of the corresponding O6 site in the pilawite-(Y) structure is still 50% higher than the average anion-site value, but much lower, in agreement with a monoclinic relaxation of a possible high-*T* orthorhombic structure, as suggested by Pieczka *et al.* (2015). Likewise, no anion site has a BVS > 2.1 v.u. in pilawite-(Y) (see Table 8b). Both facts, along with the possible charge partitioning of Mn at the *M* site, may explain the weak violations of the *c*-glide observed in piccolite from the Valletta Mine.

Other minerals related to piccolite are reported in Table 10. The structure of carminite, palermoite and attakolite are reported in Figure 7c, d and e, respectively, for comparison. These structures are not topologically congruent, as the  $[\text{M}_2^{[6]}(\text{TO}_4)_4\phi_2]$  chains cross-link in different ways in the **a** direction (Pieczka *et al.*, 2015), or in the **b** direction for palermoite (different cell setting; see Table 10). There is also a relative  $\frac{1}{2}$  shift of the chains along the chain direction between palermoite (and attakolite) and carminite. Palermoite and

attakolite keep the same topology; attakolite relaxes to monoclinic due to the presence of  $\text{HSiO}_4$  groups that point to an empty site alternating with Mn along [001]. This allows for the ordering of Si in 1 out of 4 sites with tetrahedral coordination, whereas high-charge cations (P in this case) order in tetrahedra without (OH) groups. While these structures can be considered as having different polytypic stacking of the  $[\text{M}_2(\text{TO}_4)_4\phi_2]$  chains, the extra framework cavities are occupied by large cations (Sr, Pb, Y, Ca, Na) or smaller cations ( $\text{Mn}^{2+}$ , Li, H) with different bonding topologies, leading to different stoichiometries (from 4 to 3 apfu) and may not be strictly considered polytypes.

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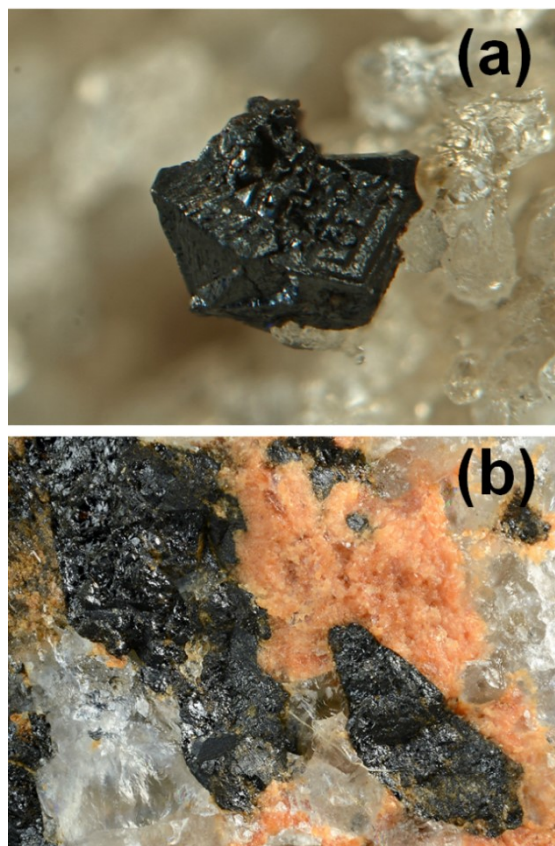
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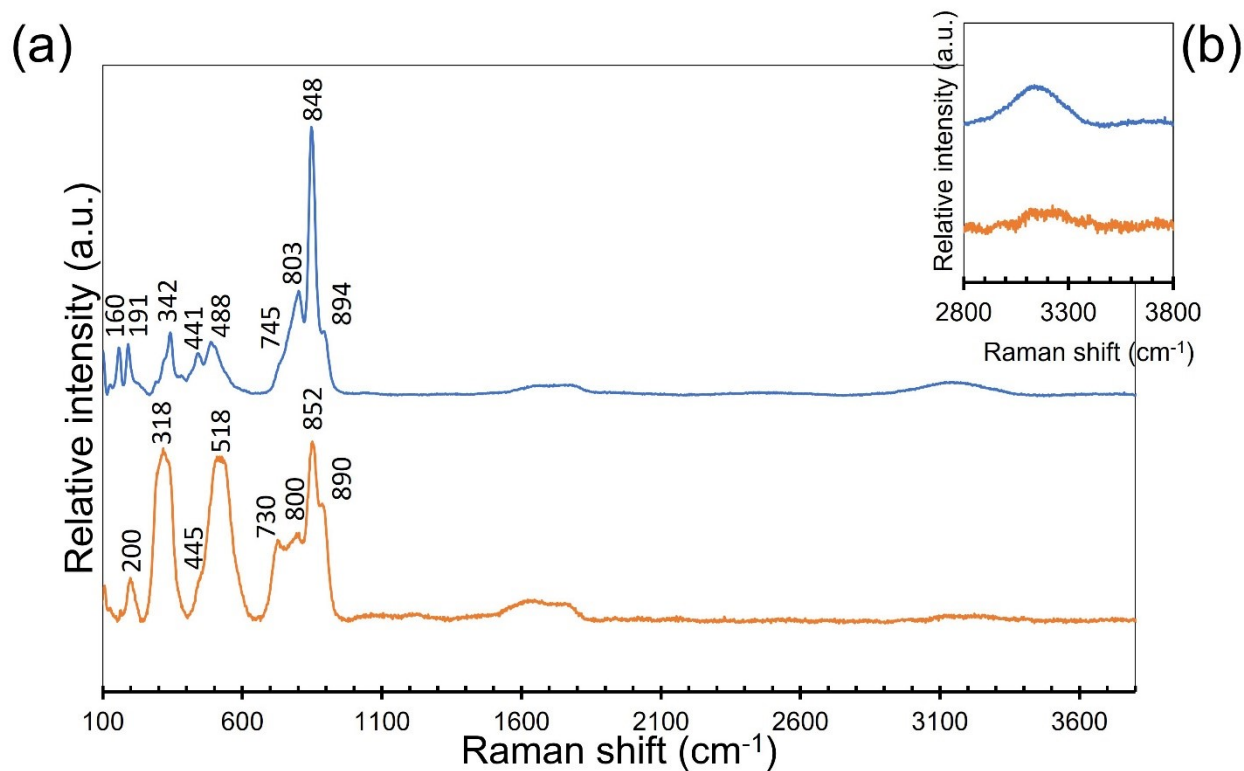


**Figure 1.** Manganese ore cropping out along the Corsaglia river (Montaldo di Mondovì mine). In the photo mineral collector Pierluigi Ambrino. Photo Marco E. Ciriotti.

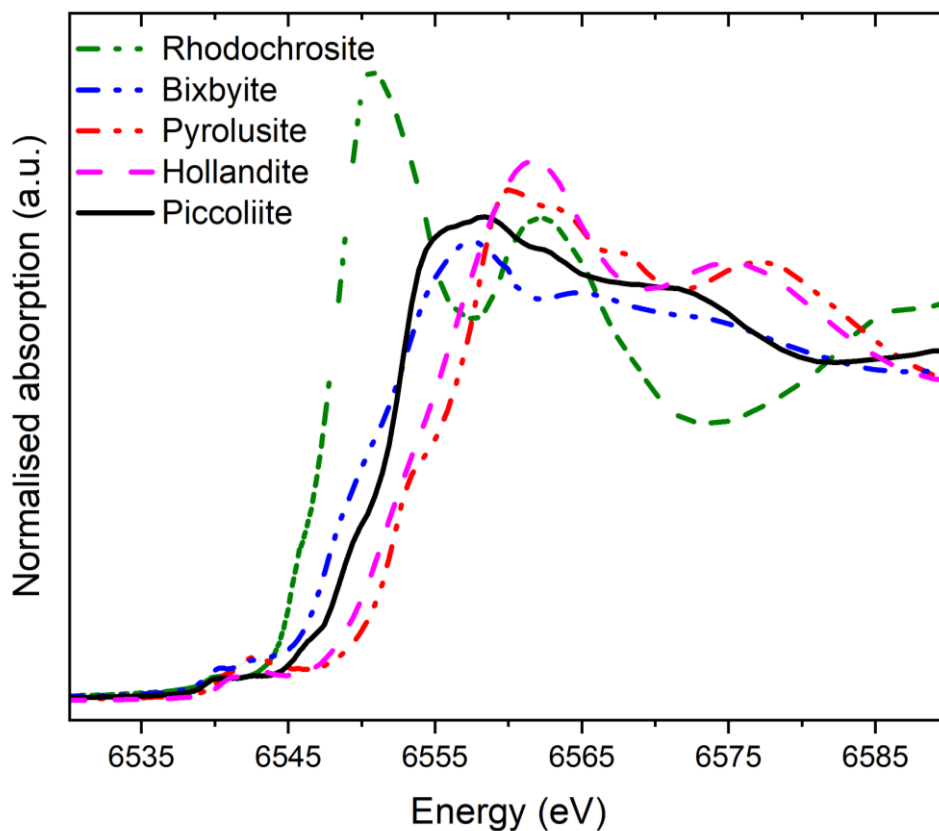
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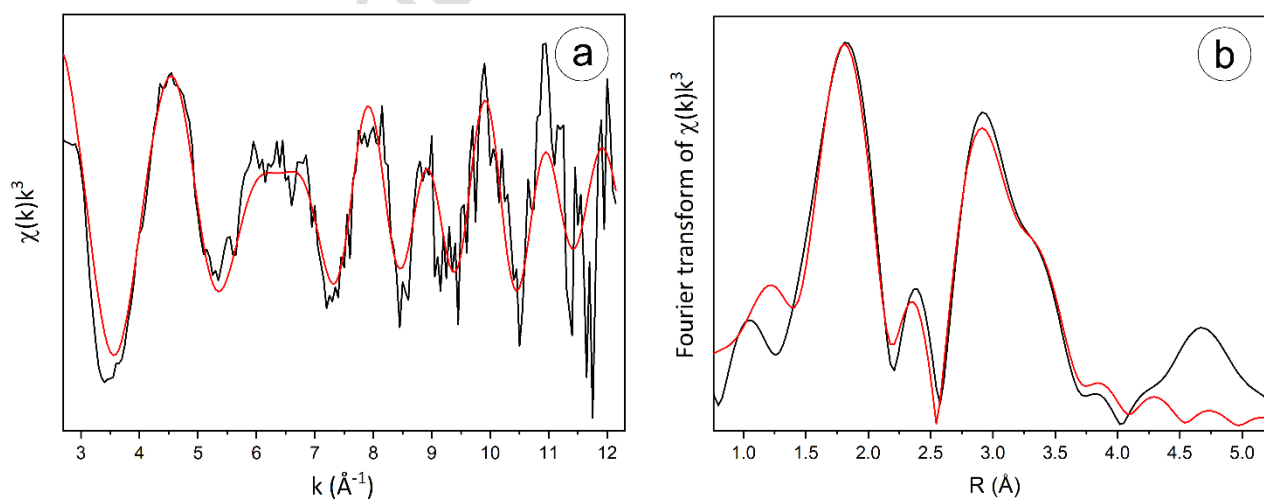
**Figure 2.** Piccoliite from the two Italian occurrences. (a) A well-developed black crystal (1 mm) on quartz from the dump of the Montaldo di Mondovì mine. Collection Gianluca Armellino, photo Pierluigi Ambrino. (b) Black crystals of piccoliite associated with grandaite from the Valletta mine dump. Field of view 5 mm. Collection and photo Roberto Bracco.



**Figure 3.** Raman spectrum of piccolite from Montaldo di Mondovì (upper, in blue) and from Valletta (lower, in orange) in the region 100-1200 cm<sup>-1</sup> (a) and 2800-3800 cm<sup>-1</sup> (b).

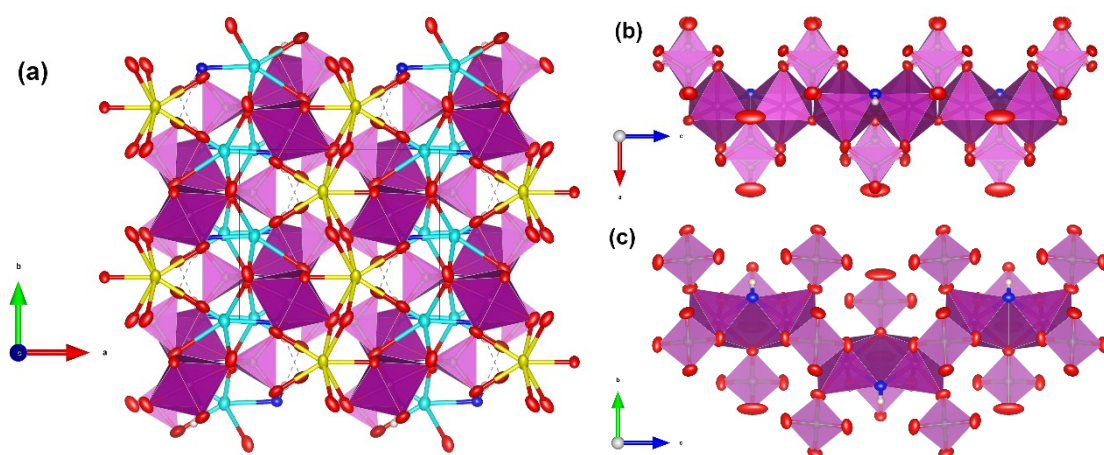


**Figure 4.** Mn *K*-edge XANES of piccoliite from Valletta mine, together with rhodochrosite, bixbyite-(Mn), pyrolusite and hollandite (hollandite spectrum from Manceau *et al.*, 2012)

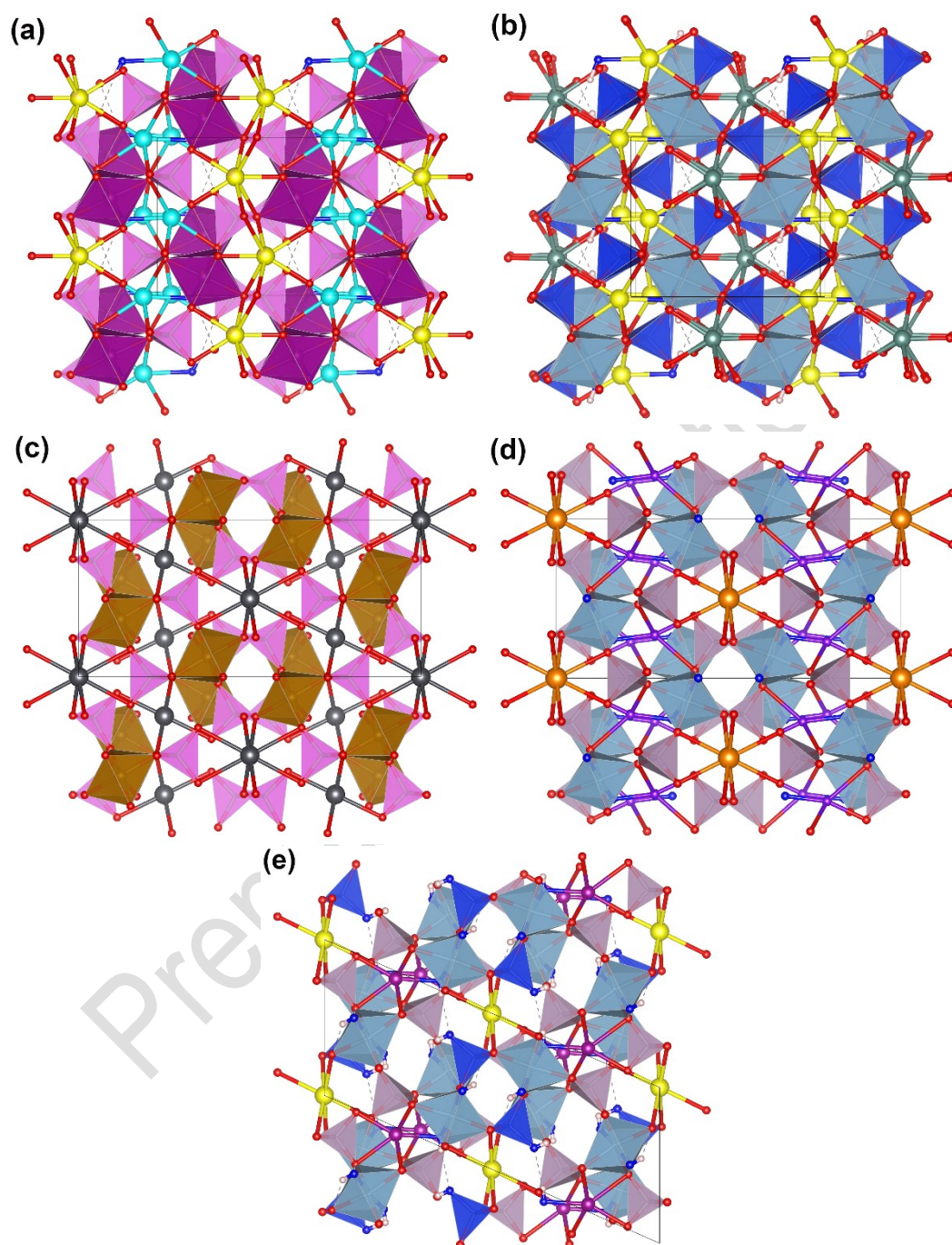


**Figure 5.** Mn *K*-edge EXAFS (a) and Fourier transform, uncorrected for phase-shift (b) of piccoliite from Valletta mine.





**Figure 6.** Crystal structure of piccolite, as seen down **c** (a). In (b) and (c), the chains of octahedra, decorated on both sides by  $(AsO_4)$  tetrahedra and running along **c**, are shown along **b** and **a**, respectively. Symbols: light pink polyhedra = As-centred tetrahedra; purple polyhedra = Mn-centred polyhedra; light blue ellipsoids = A1 site; yellow ellipsoids = A2 site; red ellipsoids = O1-O6 sites; blue ellipsoid: O7 site; white sphere: H7 site; dashed lines represent hydrogen bonds. Figure obtained with Vesta 3 (Momma and Izumi, 2011).



**Figure 7.** The framework of octahedra and tetrahedra in piccolite (a), pilawite-(Y) (b), carminite (c), palermoite (d) and attakolite (e), as seen along the chain direction. Seven-fold to eight-fold coordinated cations and their bonds are shown as ball-and-stick. Symbols: light pink polyhedra = As-centred tetrahedra; violet polyhedra = P-centred tetrahedra; blue polyhedra = Si-centred tetrahedra; purple polyhedra = Mn-centred polyhedra; cyan polyhedra = Al-centred octahedra; spheres: light blue = Na; yellow = Ca; red = O; purple = Mn;

greyish blue = Y; dark grey = Pb; orange = Sr; violet = Li; blue anion site hosting (OH) groups; white = H; dashed lines represent hydrogen bonds. Figure obtained with Vesta 3 (Momma and Izumi, 2011).

**Table 1.** Italian type minerals containing essential Mn<sup>3+</sup>.

Mineral species	Formula	Ref.
Alpeite *	Ca <sub>4</sub> Mn <sup>3+</sup> <sub>2</sub> Al <sub>2</sub> (Mn <sup>3+</sup> Mg)(SiO <sub>4</sub> ) <sub>2</sub> (Si <sub>3</sub> O <sub>10</sub> )(V <sup>5+</sup> O <sub>4</sub> )(OH) <sub>6</sub>	1
Aldomarinioite #	Sr <sub>2</sub> Mn <sup>3+</sup> (AsO <sub>4</sub> ) <sub>2</sub> (OH)	2
Braunite #	Mn <sup>2+</sup> Mn <sup>3+</sup> <sub>6</sub> (SiO <sub>4</sub> )O <sub>8</sub>	3
Cerchiarait-(Mn) *	Ba <sub>4</sub> Mn <sup>3+</sup> <sub>4</sub> O <sub>3</sub> (OH) <sub>3</sub> (Si <sub>4</sub> O <sub>12</sub> )[Si <sub>2</sub> O <sub>3</sub> (OH) <sub>4</sub> ]Cl	4
Coralloite *	Mn <sup>2+</sup> (H <sub>2</sub> O) <sub>4</sub> [Mn <sup>3+</sup> <sub>2</sub> (OH) <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub> ]	5
Demagistrisite *	(BaCa <sub>2</sub> )Mn <sup>3+</sup> <sub>4</sub> [Si <sub>3</sub> O <sub>10</sub> ][Si <sub>2</sub> O <sub>7</sub> ](OH) <sub>4</sub> ·3H <sub>2</sub> O	6
Lavoisierite #	Mn <sup>2+</sup> <sub>8</sub> [Al <sub>10</sub> (Mn <sup>3+</sup> Mg)](PO <sub>4</sub> )(SiO <sub>4</sub> ) <sub>4</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> (Si <sub>3</sub> O <sub>10</sub> )(OH)	7
Lombardoite #	Ba <sub>2</sub> Mn <sup>3+</sup> (AsO <sub>4</sub> ) <sub>2</sub> (OH)	2
Manganiakasakaite-(La) #	(CaLa)(Mn <sup>3+</sup> AlMn <sup>2+</sup> )(Si <sub>2</sub> O <sub>7</sub> )(SiO <sub>4</sub> )O(OH)	8
Manganiandrosite-(Ce) #	(Mn <sup>2+</sup> Ce)(Mn <sup>3+</sup> AlMn <sup>2+</sup> )(Si <sub>2</sub> O <sub>7</sub> )(SiO <sub>4</sub> )O(OH)	9
Manganiceladonite *	K(MgMn <sup>3+</sup> □)Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	10
Mozartite *	CaMn <sup>3+</sup> (SiO <sub>4</sub> )(OH)	11
Piccoliite #	CaNaMn <sup>3+</sup> <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub> O(OH)	12
Piemontite #	(CaCa)(AlAlMn <sup>3+</sup> )(Si <sub>2</sub> O <sub>7</sub> )(SiO <sub>4</sub> )O(OH)	13
Piemontite-(Sr) *	(CaSr)(AlAlMn <sup>3+</sup> )(Si <sub>2</sub> O <sub>7</sub> )(SiO <sub>4</sub> )O(OH)	14
Strontiomelane #	Sr[Mn <sup>4+</sup> <sub>6</sub> Mn <sup>3+</sup> <sub>2</sub> ]O <sub>16</sub>	15

\* Liguria type localities; # Piedmont (and Aosta Valley) type localities.

Refs.: 1 Kampf *et al.* (2017); 2 Cámara *et al.* (2022); 3 Haidinger (1828); 4 Basso *et al.* (2000); 5 Callegari *et al.* (2012); 6 Cámara *et al.* (2021b); 7 Orlandi *et al.* (2013); 8 Biagioni (2019); 9 Cenko-Tok *et al.* (2006); 10 Lepore *et al.* (2017); 11 Basso *et al.* (1993); 12 This work; 13 Kenngott (1853); 14 Bonazzi *et al.* (1993); 15 Meisser *et al.* (1999).

**Table 2.** Chemical data (in wt%) for piccolite

Oxide	<i>Montaldo di Mondovì</i> (n = 10)			<i>Valletta</i> (n = 13)			Probe standard
	mean	range	s.u.	mean	range	s.u.	
P <sub>2</sub> O <sub>5</sub>	0.06	0.00 – 0.14	0.04	0.08	0.03 – 0.14	0.04	apatite
V <sub>2</sub> O <sub>5</sub>	0.47	0.45 – 0.50	0.02	0.08	0.05 – 0.11	0.02	V <sub>2</sub> O <sub>3</sub> (synth.)
As <sub>2</sub> O <sub>5</sub>	48.06	47.21 – 48.90	0.53	47.90	46.91 – 48.72	0.51	GaAs (synth.)
SiO <sub>2</sub>	0.10	0.06 – 0.12	0.02	0.15	0.10 – 0.51	0.11	wollastonite
Mn <sub>2</sub> O <sub>3</sub>	17.48	17.07 – 18.00	0.30	16.20	15.35 – 16.80	0.43	rhodonite
MnO <sub>2</sub> *				6.28			
Mn <sub>2</sub> O <sub>3</sub> *				10.50			
Fe <sub>2</sub> O <sub>3</sub>	9.74	9.11 – 10.24	0.34	8.32	7.17 – 9.33	0.90	magnetite
MgO	1.67	1.58 – 1.84	0.09	4.12	3.72 – 4.87	0.46	periclase
CaO	13.84	13.65 – 14.04	0.11	15.44	14.62 – 16.34	0.55	wollastonite
ZnO	-	-	-	0.07	0.00 – 0.15	0.05	Zn (synth.)
SrO	-	-	-	0.13	0.06 – 0.28	0.06	celestine
Na <sub>2</sub> O	5.54	5.21 – 5.75	0.16	5.01	4.65 – 5.32	0.21	jadeite
H <sub>2</sub> O <sub>calc</sub> **	1.86			1.90			
Total	98.82			99.98			

Note: s.u. = standard uncertainty

\*The Mn<sup>4+</sup>/Mn<sup>3+</sup> ratio was calculated on the basis of 6 cations and 10 anions pfu; \*\*H<sub>2</sub>O was calculated on the basis of one OH group pfu.

**Table 3.** Measured and calculated X-ray powder diffraction data for piccolite from Montaldo di Mondovì. Intensity and  $d_{hkl}$  (in Å) were calculated using the software PowderCell 2.3 (Kraus and Nolze, 1996) based on the structural model given in Table 5. The seven strongest reflections are given in bold. Intensities were visually estimated: vs = very strong; ms = medium-strong; m = medium; w = weak; vw = very weak.

$I_{obs}$	$d_{obs}$	$I_{calc}$	$d_{calc}$	$hkl$	$I_{obs}$	$d_{obs}$	$I_{calc}$	$d_{calc}$	$hkl$
w	5.73	11	5.74	1 1 0			19	2.325	3 2 0
<b>m</b>	<b>4.85</b>	57	4.88	1 0 2	<b>m</b>	<b>2.325</b>	9	2.321	2 1 4
w	4.05	14	4.09	1 1 2			9	2.310	2 2 3
vw	3.805	6	3.822	2 1 0	w	2.239	5	2.249	3 1 3
		14	3.633	2 1 1	w	2.171	9	2.165	1 1 5
w	3.607	11	3.579	0 2 1	w	2.000	5	1.994	2 1 5
<b>m</b>	<b>3.470</b>	35	3.462	1 2 0	w	1.888	5	1.886	4 2 1
		59	3.223	1 1 3	w	1.888	7	1.880	0 4 0
<b>vs</b>	<b>3.167</b>	7	3.199	2 1 2	vw	1.814	5	1.818	3 3 2
		100	3.162	0 2 2	vw	1.772	5	1.782	3 1 5
w	2.932	20	2.922	0 0 4			12	1.767	4 0 4
w	2.786	16	2.786	2 2 1			24	1.731	2 4 0
		30	2.753	3 1 0	m	1.732	14	1.730	0 2 6
<b>m</b>	<b>2.742</b>	11	2.728	2 1 3			19	1.717	3 3 3
		14	2.705	0 2 3	vw	1.661	4	1.657	5 1 2
<b>ms</b>	<b>2.683</b>	53	2.680	3 1 1	m	1.607	8	1.612	2 2 6
		37	2.604	1 1 4			27	1.600	3 3 4
<b>ms</b>	<b>2.580</b>	50	2.575	2 2 2			18	1.581	0 4 4
m	2.495	32	2.491	3 1 2	m	1.584	11	1.578	5 1 3
vw	2.442	14	2.441	2 0 4					

**Table 4.** Crystal and experimental data for piccolite.

<b>Crystal data</b>	<i>Montaldo di Mondovì</i>	<i>Valletta</i>
Crystal size (mm)	0.080 × 0.040 × 0.035	0.243 × 0.194 × 0.119
Cell setting, space group	Orthorhombic, <i>Pbcm</i>	Orthorhombic, <i>Pbcm</i>
<i>a</i> (Å)	8.8761(9)	8.8889(2)
<i>b</i>	7.5190(8)	7.5269(1)
<i>c</i>	11.6890(12)	11.6795(2)
<i>V</i> (Å <sup>3</sup> )	780.12(12)	781.43(2)
<i>Z</i>	4	4
<b>Data collection and refinement</b>		
Radiation, wavelength (Å)	MoKα, 0.71073	MoKα, 0.71073
Temperature (K)	293	293
2θ <sub>max</sub> (°)	72.10	91.33
Measured reflections	12281	66269
Unique reflections	1885	3442
Reflections with <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> )	1554	3242
<i>R</i> <sub>int</sub>	0.0256	0.0708
<i>R</i> <sub>σ</sub>	0.0193	0.0208
Range of <i>h</i> , <i>k</i> , <i>l</i>	-14 ≤ <i>h</i> ≤ 14, -12 ≤ <i>k</i> ≤ 12, -19 ≤ <i>l</i> ≤ 16	-17 ≤ <i>h</i> ≤ 17, -15 ≤ <i>k</i> ≤ 15, -23 ≤ <i>l</i> ≤ 23
<i>R</i> <sub>1</sub> [ <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> )]	0.0250	0.0260
<i>R</i> <sub>1</sub> (all data)	0.0358	0.0288
<i>wR</i> <sub>2</sub> (on <i>F</i> <sub>o</sub> <sup>2</sup> )	0.0506	0.0576
Goof	1.115	1.289
Refined parameters	88	88
Maximum and minimum residual peak ( <i>e</i> Å <sup>-3</sup> )	0.71 (at 0.54 Å from O1) -1.21 (at 1.29 Å from As1)	0.99 (at 0.57 Å from As1) -1.13 (at 0.21 Å from O1)

Note: for the specimen from Montaldo di Mondovì, (Kolitsch, 2008) gives the following unit-cell parameters (space group *Pbcm*) from his preliminary crystal-structure determination [*R*(*F*) = 0.0195]: *a* = 8.885(2), *b* = 7.535(2), *c* = 11.707(2) Å, *V* = 783.8(3) Å<sup>3</sup>. The weighting scheme is defined as follows:  $w = q / [\sigma^2(F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)/\lambda]$  where  $P = [0.33333 * \text{Maximum of } (0 \text{ or } F_o^2) + (1-0.333333) * F_c^2]$ ; used values are *a* = 0.0210 and *b* = 0.5539 for Montaldo di Mondovì sample and *a* = 0.0121 and *b* = 0.6188 for Valletta sample.

**Table 5.** Atomic sites, multiplicity (m) and Wyckoff letter (W), site occupancy (s.o.), atom fractional coordinates, and equivalent isotropic or isotropic (\*) displacement parameters (in Å<sup>2</sup>) for piccolite.

<i>Holotype (Montaldo di Mondovì)</i>						
Site	mW	s.o.	x/a	y/b	z/c	<i>U</i> <sub>eq/iso</sub>
A1	4d	Na <sub>0.62(1)</sub> Ca <sub>0.38(1)</sub>	0.92503(9)	0.99267(11)	<sup>3</sup> / <sub>4</sub>	0.0154(3)
A2	4c	Ca <sub>0.774(9)</sub> Na <sub>0.226(9)</sub>	0.41855(7)	<sup>3</sup> / <sub>4</sub>	<sup>1</sup> / <sub>2</sub>	0.0196(3)
Mn	8e	Mn <sub>0.902(3)</sub> Mg <sub>0.098(3)</sub>	0.25110(3)	0.38099(4)	0.11573(2)	0.00802(9)
As1	4d	As <sub>1.00</sub>	0.42831(3)	0.01033(3)	<sup>1</sup> / <sub>4</sub>	0.00734(6)
As2	4c	As <sub>1.00</sub>	0.93470(3)	<sup>1</sup> / <sub>4</sub>	0	0.00694(6)
O1	4d	O <sub>1.00</sub>	0.3076(3)	0.8418(3)	<sup>1</sup> / <sub>4</sub>	0.0306(6)
O2	8e	O <sub>1.00</sub>	0.5352(2)	0.0020(2)	0.3699(1)	0.0136(3)
O3	4d	O <sub>1.00</sub>	0.3207(2)	0.1989(2)	<sup>1</sup> / <sub>4</sub>	0.0114(3)
O4	8e	O <sub>1.00</sub>	0.8167(2)	0.0759(2)	0.0061(1)	0.0134(2)
O5	8e	O <sub>1.00</sub>	0.0409(2)	0.2674(2)	0.1192(1)	0.0124(2)
O6	4c	O <sub>1.00</sub>	0.3269(2)	<sup>1</sup> / <sub>4</sub>	0	0.0086(3)
O7	4d	O <sub>1.00</sub>	0.1870(2)	0.5178(2)	<sup>1</sup> / <sub>4</sub>	0.0093(3)
H7	4d	H <sub>1.00</sub>	0.228(5)	0.612(7)	<sup>1</sup> / <sub>4</sub>	0.040(14)*
<i>Cotype (Valletta)</i>						
Site	mW	s.o.	x/a	y/b	z/c	<i>U</i> <sub>eq/iso</sub>
A1	4d	Na <sub>0.498(7)</sub> Ca <sub>0.502(7)</sub>	0.92471(6)	0.99221(7)	<sup>3</sup> / <sub>4</sub>	0.0127(2)
A2	4c	Ca <sub>0.777(7)</sub> Na <sub>0.223(7)</sub>	0.41861(5)	<sup>3</sup> / <sub>4</sub>	<sup>1</sup> / <sub>2</sub>	0.0190(2)
Mn	8e	Mn <sub>0.729(3)</sub> Mg <sub>0.271(3)</sub>	0.25125(2)	0.38212(3)	0.11582(2)	0.00792(6)
As1	4d	As <sub>1.00</sub>	0.42830(2)	0.01147(2)	<sup>1</sup> / <sub>4</sub>	0.00703(3)
As2	4c	As <sub>1.00</sub>	0.93401(2)	<sup>1</sup> / <sub>4</sub>	0	0.00672(3)
O1	4d	O <sub>1.00</sub>	0.3076(2)	0.8431(2)	<sup>1</sup> / <sub>4</sub>	0.0296(5)
O2	8e	O <sub>1.00</sub>	0.53472(11)	0.00294(14)	0.37002(8)	0.01284(16)
O3	4d	O <sub>1.00</sub>	0.31970(16)	0.19908(18)	<sup>1</sup> / <sub>4</sub>	0.0107(2)
O4	8e	O <sub>1.00</sub>	0.81624(12)	0.07521(13)	0.00456(9)	0.01368(16)
O5	8e	O <sub>1.00</sub>	0.04027(11)	0.26646(14)	0.11951(8)	0.01251(15)
O6	4c	O <sub>1.00</sub>	0.32822(14)	<sup>1</sup> / <sub>4</sub>	0	0.00862(17)
O7	4d	O <sub>1.00</sub>	0.18558(16)	0.51972(18)	<sup>1</sup> / <sub>4</sub>	0.0110(2)
H7	4d	H <sub>1.00</sub>	0.220(5)	0.609(8)	<sup>1</sup> / <sub>4</sub>	0.052(15)*

**Table 6.** Selected bond lengths (in Å) for piccolite.

		Montaldo di Mondovi	Valletta
<i>A1</i>	–O7	2.327(2)	2.321(2)
	–O1	2.411(3)	2.409(2)
	–O5 ×2	2.500(2)	2.492(1)
	–O5 ×2	2.579(2)	2.584(1)
	–O3	2.614(2)	2.606(2)
	–O4	3.206(2)	3.187(1)
	average	2.658	2.651
<i>A2</i>	–O6	2.259(2)	2.250(1)
	–O2 ×2	2.441(2)	2.436(1)
	–O4 ×2	2.465(2)	2.468(1)
	–O2 ×2	2.641(2)	2.645(1)
	–O1	3.160(1)	3.161(1)
	Average	2.630	2.630
<i>Mn</i>	–O6	1.804(1)	1.813(1)
	–O7	1.961(1)	1.967(1)
	–O4	2.038(1)	2.040(1)
	–O5	2.052(1)	2.068(1)
	–O2	2.111(1)	2.115(1)
	–O3	2.172(1)	2.174(1)
	Average	2.023	2.029
<i>D.I.*</i>		0.04637	0.04578
<i>As1</i>	–O1	1.660(2)	1.660(2)
	–O2 ×2	1.694(1)	1.692(1)
	–O3	1.710(2)	1.711(1)
	average	1.690	1.690
<i>D.I.*</i>		0.00877	0.00843
<i>As2</i>	–O4 ×2	1.678(1)	1.682(1)
	–O5 ×2	1.688(1)	1.690(1)
	average	1.683	1.690
<i>D.I.*</i>		0.00281	0.00232
<i>O7</i>	H7	0.80(6)	0.74(6)
<i>O1</i>	H7	1.87(6)	1.93(6)
<i>O7</i>	<i>O1</i>	2.661(3)	2.665(3)
<i>O7</i>	–H7– <i>O1</i>	175(5) <sup>o</sup>	179(6) <sup>o</sup>

\* *D.I.* Distortion index of bond lengths (Baur, 1974)



**Table 7.** Refined vs. calculated site-scattering values (electrons per formula unit) and site population for piccolite.

Site	Refined site scattering	Proposed site population	Calculated site scattering	Calc.* <M-O>	Obs. <M-O>
<i>Montaldo di Mondovi</i>					
A1	14.42(14)	Na <sub>0.64</sub> Ca <sub>0.35</sub>	14.04		
A2	17.97(16)	Ca <sub>0.75</sub> Na <sub>0.24</sub>	17.64		
Mn	47.45(14)	Mn <sup>3+</sup> <sub>1.08</sub> Fe <sup>3+</sup> <sub>0.59</sub> Mg <sub>0.20</sub> Ca <sub>0.10</sub>	46.74	2.010	2.023
<i>Valletta</i>					
A1	15.52(11)	Na <sub>0.53</sub> Ca <sub>0.47</sub>	15.23		
A2	17.99(13)	Ca <sub>0.76</sub> Na <sub>0.23</sub> Sr <sub>0.01</sub>	18.11		
Mn	42.95(13)	Mn <sup>3+</sup> <sub>0.63</sub> Fe <sup>3+</sup> <sub>0.49</sub> Mg <sub>0.48</sub> Mn <sup>4+</sup> <sub>0.34</sub> Ca <sub>0.06</sub>	43.95	2.024	2.029

\* Calculated using ionic radii from Shannon (1976); radius of O<sup>2-</sup> was taken as 1.37 Å considering average coordination number of bonding oxygen atoms.

**Table 8a.** Weighted bond-valences (v.u.) for piccolite.

Montaldo di Mondovi							
Site	A1	A2	Mn	As1	As2	$\Sigma$ anions	$\Sigma$ anions <sub>corr</sub>
O1	0.22	0.04 <sup>↓×2</sup>		1.35		1.61	1.83
O2		0.25 <sup>↓×2</sup> 0.15 <sup>↓×2</sup>	0.34	1.22 <sup>↓×2</sup>		1.96	
O3	0.14		2 <sup>×</sup> →0.28	1.17		1.87	
O4	0.03 <sup>↓×2</sup>	0.23 <sup>↓×2</sup>	0.44		1.28 <sup>↓×2</sup>	1.98	
O5	0.18 <sup>↓×2</sup> 0.15 <sup>↓×2</sup>		0.42		1.25 <sup>↓×2</sup>	1.99	
O6		0.39	2 <sup>×</sup> →0.98			2.33	
O7	0.27		2 <sup>×</sup> →0.57			1.41	2.19
$\Sigma$ cations	1.33	1.71	3.03	4.96	5.06		
WAV	1.34	1.74	2.82	5.00	5.00		
Valletta							
Site	A1	A2	Mn	As1	As2	$\Sigma$ anions	$\Sigma$ anions <sub>corr</sub>
O1	0.24	0.04 <sup>↓×2</sup>		1.34		1.63	1.84
O2		0.25 <sup>↓×2</sup> 0.15 <sup>↓×2</sup>	0.35	1.23 <sup>↓×2</sup>		1.98	
O3	0.15		2 <sup>×</sup> →0.29	1.17		1.90	
O4	0.04 <sup>↓×2</sup>	0.23 <sup>↓×2</sup>	0.44		1.27 <sup>↓×2</sup>	1.97	
O5	0.20 <sup>↓×2</sup> 0.16 <sup>↓×2</sup>		0.40		1.24 <sup>↓×2</sup>	1.99	
O6		0.39	2 <sup>×</sup> →0.88			2.15	
O7	0.29		2 <sup>×</sup> →0.54			1.38	2.20
$\Sigma$ cations	1.48	1.73	2.90	4.97	5.01		
WAV	1.47	1.77	2.90	5.00	5.00		

Notes: Left and right superscripts indicate the number of equivalent bonds involving anions and cations, respectively. Bond valence at mixed-occupancy sites were weighted and their BVS ( $\Sigma$ cations) compared with the weighted atomic valences (WAV) from the empirical formula. BVS of anions ( $\Sigma$ anions) have been corrected considering hydrogen bonds.

**Table 8b.** Weighted bond-valences (v.u.) for pilawite-(Y) (data from Pieczka *et al.* 2015).

Site	Y1	Ca2	Al1	Al2	Si1	Si2	$\Sigma$ anions	$\Sigma$ anions <sub>corr</sub>
O1		0.28 0.24		0.48	0.98		1.98	
O2		0.27 0.23	0.50		0.99		1.99	
O3	0.35		0.55		0.99		1.89	
O4	0.41			0.53	0.97		1.91	
O5		0.24	0.35	0.31		0.91	1.81	
O6	0.27	0.27				1.00	1.54	1.91
O7	0.42 0.29		0.39			0.95	2.05	
O8	0.34 0.19			0.37		0.97	1.87	
O9	0.62		0.74	0.77			2.13	
O10		0.37	0.57	0.58			1.52	2.16
$\Sigma$ cations	2.89	1.90	3.10	3.04	3.93	3.83		
WAV	3.00	1.99	3.00	3.00	4.00	4.00		

**Table 9.** Structural parameters from the Mn *K*-edge EXAFS analysis of piccolliite from Valletta mine

Shell	$S_0^2$	R(Å)	$\sigma^2(\text{Å}^2)$
Mn-O		1.81(1)	0.006(2)
//		1.97(1)	//
//		2.04(1)	//
//		2.07(1)	//
//	0.7 (1)	2.13(1)	//
//		2.18(1)	//
Mn-As		3.27(1)	0.001(1)
//		3.38(1)	//
//		3.54(4)	0.012(5)
//		3.62(4)	//

Notes:  $S_0^2$ = Many-body amplitude reduction factor, R= interatomic distance,  $\sigma^2$ = Debye-Waller factor. Errors as reported in ARTEMIS.

**Table 10.** Mineral species related to piccolliite.

Species	Chemical formula	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	s.g.*	Ref.
Piccolliite	NaCaMn <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub> O(OH)	8.88	7.52	11.69		<i>Pbcm</i>	[1]
Pilawite-(Y)	CaYAl <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub> O(OH)	8.56	7.26	11.18	90.6	<i>P2<sub>1</sub>/c</i>	[2]
Carminite	PbFe <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub>	16.59	7.58	12.28		<i>Cccm</i>	[3]
Crimsonite	PbFe <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub>	16.25	7.47	12.15		<i>Cccm</i>	[4]
Sewardite	CaFe <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub>	16.46	7.43	12.13		<i>Cccm</i>	[5]
Attakolite	CaMnAl <sub>4</sub> [HSiO <sub>4</sub> ][PO <sub>4</sub> ] <sub>3</sub> (OH) <sub>4</sub>	17.21	11.51	7.31	113.83	<i>C2/m</i>	[6] <sup>#</sup>
Bertossaite	Ca <sub>0.5</sub> LiAl <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub>	11.48	15.73	7.23		<i>Imcb</i>	[7]
Palermoite	Sr <sub>0.5</sub> LiAl <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub>	11.55	15.84	7.31		<i>Imcb</i>	[8]
Natropalermoite	Sr <sub>0.5</sub> NaAl <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub>	11.48	16.25	7.29		<i>Imcb</i>	[9]

[1] this work; [2] Pieczka *et al.* (2015); [3] Kharisun *et al.* (1996); [4] Kampf *et al.* (2016); [5] Roberts *et al.* (2002); [6] Blomstrand (1868), redefined by Grice and Dunn (1992); [7] Hatert *et al.* (2011); [8] Moore and Araki (1975); [9] Schumer *et al.* (2017).

\* s.g. = space-group type; # Mead and Mrose (1968) described a monoclinic cell  $a = 11.45$ ,  $b = 15.69$ ,  $c = 7.30$  Å,  $\beta = 91.5^\circ$  which resembles a relaxed cell of palermoite that would correspond to a *I2/m* s.g.