

Arsenmedaite, $\text{Mn}_6^{2+}\text{As}^{5+}\text{Si}_5\text{O}_{18}(\text{OH})$, the arsenic analogue of medaite, from the Molinello mine, Liguria, Italy: occurrence and crystal structure

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Abstract: The new mineral species arsenmedaite, ideally $\text{Mn}_6^{2+}\text{As}^{5+}\text{Si}_5\text{O}_{18}(\text{OH})$, has been discovered in quartz veinlets in the braunite ore deposit of the Molinello mine, Graveglia Valley, Ne, Genova, Liguria, Italy. It occurs as orange-reddish prismatic crystals, up to 200 μm in length, with a vitreous lustre, associated with braunite, quartz, calcite, As-rich medaite, calcian rhodocrosite, talc, and ganophyllite. Electron microprobe analysis of arsenmedaite gave (in wt%): $\text{V}_2\text{O}_5 = 1.84$, $\text{As}_2\text{O}_5 = 6.81$, $\text{SiO}_2 = 38.75$, $\text{CaO} = 0.70$, $\text{MnO} = 50.28$, $\text{H}_2\text{O}_{\text{calc}} = 1.42$, total 99.80. On the basis of $\Sigma\text{Me} = 12$ atoms per formula unit, the chemical formula of arsenmedaite is $(\text{Mn}_{5.89}\text{Ca}_{0.10})_{\Sigma 5.99}[(\text{As}_{0.49}\text{V}_{0.17})_{\Sigma 0.66}\text{Si}_{5.35}]_{\Sigma 6.01}\text{O}_{17.69}(\text{OH})_{1.31}$. The main diffraction lines are [d in Å (relative intensity) hkl]: 3.266 (100) 081, 3.159 (72) 052, 3.094 (82) -221 , 2.963 (83) 091, 2.935 (79) 211, 2.788 (68) 072, and 2.612 (98) 082. The crystal-structure study gives a monoclinic unit cell, space group $P2_1/n$, with $a = 6.7099(3)$, $b = 29.001(1)$, $c = 7.5668(3)$ Å, $\beta = 95.469(3)^\circ$, $V = 1465.7(1)$ Å³, $Z = 4$. The crystal structure has been solved and refined to $R_1 = 0.062$ on the basis of 3526 reflections with $F_o > 4\sigma(F_o)$ and 287 parameters. Arsenmedaite is isotypic with medaite. In its crystal structure, six- to seven-fold coordinated Mn-centred polyhedra form wavy ribbons linked to TO_4 tetrahedra centred by Si and (As,V). Its formation is likely related to the late-stage circulation of As- and Mn-rich hydrothermal fluids during the final stages of the Alpine tectono-metamorphic evolution of the manganese ore deposits of Eastern Liguria.

Key-words: arsenmedaite; new mineral species; sorosilicates; manganese; arsenic; crystal structure; Molinello mine; Graveglia Valley; Liguria.

1. Introduction

Manganese ores of Graveglia Valley, Monte Alpe, Cerchiara, and Monte Nero mines in Eastern Liguria are well known for the outstanding variety and rarity of hydrothermal minerals (e.g., Cortesogno *et al.*, 1979; Basso *et al.*, 2008; Bindi *et al.*, 2013; Carbone *et al.*, 2013; Kampf *et al.*, 2013, 2017; Kolitsch *et al.*, 2018). Among the twenty-nine mineral species having their type-locality in Liguria, more than half comes from the Mn deposits of Graveglia Valley. Polyphase mineral assemblages in manganese ores occur within metacherts of the Northern Apennine ophiolitic units (“*Diaspri di Monte Alpe*” Formation), which underwent prehnite–pumpellyite facies metamorphism ($P = 0.25 \pm 0.05$ GPa, $T = 275 \pm 25$ °C) followed by hydrothermal mobilisation along fractures under decreasing thermobaric conditions (Cabella *et al.*, 1991, 1998). Circulation of fluids within extensional fractures led to further concentration of dispersed elements such as As, V and Te,

favouring the formation of minerals with peculiar or unique crystal-chemical features, like tiragalloite (Gramaccioli *et al.*, 1980) and medaite (Gramaccioli *et al.*, 1982).

Preliminary energy-dispersive spectrometry (EDS) analyses showed Mn, As, Si, and minor V and Ca as the only elements with $Z > 8$; these elements are characteristic of tiragalloite, ideally $\text{Mn}_4^{2+}\text{As}^{5+}\text{Si}_3\text{O}_{12}(\text{OH})$. However, stoichiometric ratios did not agree with this species, on the contrary being close to the medaite-like stoichiometry, i.e. $\text{Mn}_6^{2+}(\text{As}, \text{V})\text{Si}_5\text{O}_{18}(\text{OH})$. Indeed, the As-dominant nature of these crystals prompted their crystal-chemical investigation. Quantitative chemical data, as well as the crystal-structure refinement, unequivocally showed that the studied sample was actually the arsenic analogue of medaite. Owing to this chemical relationship, the new mineral species was named arsenmedaite. The mineral and its name have been approved by the IMA-CNMNC, under the number 2016-099. Holotype material is deposited in the mineralogical collection of the Museo di Storia Naturale, Università di Pisa,

Via Roma 79, Calci, Pisa (Italy), under catalogue number 19901, and in the mineralogical collection of the Dipartimento di Scienze della Terra, dell'Ambiente e della Vita (DISTAV), Università degli Studi di Genova, Corso Europa 26, Genova, Italy, under catalogue number MO483.

This paper reports the description of arsenmedaite and discusses its relationships with medaite.

2. Occurrence and mineral description

2.1. Occurrence and physical properties

Arsenmedaite was collected in small quartz veinlets, a few mm in thickness, cutting the braunite ore bodies hosted by Jurassic metacherts ("Diaspri di Monte Alpe" Formation), which in turn overlay the mafic-ultramafic ophiolitic sequence of Northern Apennines (Cabella *et al.*, 1998).

Arsenmedaite was identified in few specimens collected in the Molinello mine (latitude 44°20'43"N, longitude 9°27'32"E), Graveglia Valley, Ne, Genova, Liguria, Italy. It occurs as orange-reddish prismatic crystals, up to 200 µm in length, with a vitreous lustre and a white streak. Arsenmedaite is brittle, with a good {1 0 0} cleavage and a parting normal to the elongation; fracture is irregular. Microhardness as well as density were not measured owing to the very small amount of the available material. Calculated density, based on the empirical formula, is 3.772 g cm⁻³. This value can be compared with the density measured by Gramaccioli *et al.* (1982) for medaite, *i.e.* 3.70(5) g cm⁻³.

Optical properties of arsenmedaite were not measured, owing to the very small amount of available material and its chemical heterogeneity, arsenmedaite being associated with As-rich medaite. The mean refractive index, obtained from the Gladstone-Dale relationship (Mandarino, 1979, 1981), using the empirical formula and calculated density, is 1.766. Likely, optical properties of arsenmedaite could be very similar to those of medaite (Gramaccioli *et al.*, 1982).

Arsenmedaite is a late-stage mineral, crystallizing from As- and Mn-rich hydrothermal fluids that circulated through a network of fractures during the final stages of the tectono-metamorphic Apenninic events, under relatively low-*T* and low-*f*(H₂O) conditions (*e.g.*, Cortesogno *et al.*, 1979; Gramaccioli *et al.*, 1982). In the studied specimen (Fig. 1), arsenmedaite is associated with braunite, quartz, calcite, As-rich medaite, calcian rhodochrosite, talc, and ganophyllite. The absence of ardenite-group minerals with trisilicate groups (Si₃O₁₀)⁸⁻ and isolated (SiO₄)⁴⁻, (VO₄)³⁻, or (AsO₄)³⁻ tetrahedra in the crystal structure suggests the formation of arsenmedaite in those veins may occur under peculiar stabilizing conditions, which locally prevent hydrolysis and favour polymerization of (AsO₄)³⁻ and (SiO₄)⁴⁻ tetrahedra to form chain fragments and complex polyanions.

2.2. Chemical data

Electron microprobe analyses of two samples of arsenmedaite and As-rich medaite were obtained through wavelength-dispersive spectrometry (WDS) mode using a

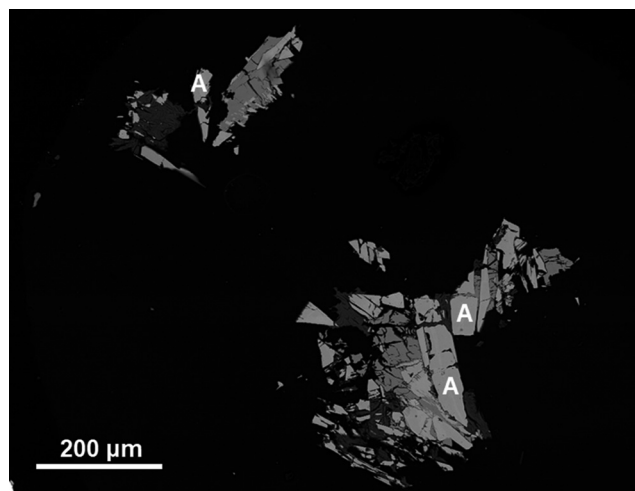


Fig. 1. Backscattered electron image of arsenmedaite (indicated by the label A) in prismatic crystals (light grey), associated with calcian rhodochrosite (grey) and talc (dark grey).

Superprobe JEOL JXA 8200 instrument at the "Eugen F. Stumpfl" laboratory, Leoben University, Austria. The operating conditions were: accelerating voltage 15 kV, beam current 10 nA, nominal beam size 1 µm. Standards (element, emission line) were: rhodonite (Mn-*Kα*, Si-*Kα*), GaAs (As-*Lα*), vanadium (V-*Kα*), and diopside (Ca-*Kα*). Counting times of 20 s on the peak and 10 s on the backgrounds were applied for all the elements. The occurrence of H₂O as (OH)⁻ groups is suggested by the crystal-structure refinement; however, owing to the scarcity of available material, a direct H₂O determination was not performed.

Electron microprobe data for arsenmedaite are given in Table 1, whereas Table 2 reports chemical data for As-rich medaite and literature data given by Gramaccioli *et al.* (1982) and Nagashima & Armbruster (2010). The chemical formulae were recalculated on the basis of 12 cations (except H⁺) per formula unit, in agreement with Nagashima & Armbruster (2010). In this way, the amount of (OH)-groups was determined by the requirement of electroneutrality. The chemical formulae of arsenmedaite and As-rich medaite can be written as (Mn_{5.89}Ca_{0.10})Σ_{5.99}[(As_{0.49}V_{0.17})Σ_{0.66}Si_{5.35}]Σ_{6.01}O_{17.69}(OH)_{1.31} and (Mn_{5.84}Ca_{0.12})Σ_{5.96}[(V_{0.42}As_{0.38})Σ_{0.80}Si_{5.24}]Σ_{6.04}O_{17.88}(OH)_{1.12}, respectively.

The ideal formula of arsenmedaite is Mn²⁺₆As⁵⁺₆Si₅O₁₈(OH), corresponding to (in wt%) As₂O₅ 13.52, SiO₂ 35.34, MnO 50.08, H₂O 1.06, sum 100.00.

2.3. Micro-Raman spectroscopy

Unpolarized micro-Raman spectra were obtained on a polished sample of arsenmedaite in nearly-backscattered geometry with a Jobin-Yvon Horiba XploRA Plus apparatus, equipped with a motorized *x-y* stage and an Olympus BX41 microscope with a 100× objective. The 532 nm line of a solid-state laser was used, attenuated to 50%. The minimum lateral and depth resolution was set to a few µm. The system was calibrated using the 520.6 cm⁻¹ Raman band of

Table 1. Chemical data of arsenmedaite.

	1	2	3	4	5	6	7	8	9	10	Average	e.s.d.
Oxide (wt%)												
V ₂ O ₅	1.55	1.45	1.26	1.62	1.79	1.89	2.02	2.26	2.18	2.40	1.84	0.38
As ₂ O ₅	9.54	8.46	8.28	7.15	6.06	6.05	6.02	5.69	5.53	5.30	6.81	1.47
SiO ₂	37.73	38.51	38.13	38.60	38.85	39.41	38.71	39.36	39.13	39.04	38.75	0.53
CaO	0.71	0.70	0.76	0.69	0.62	0.66	0.67	0.73	0.67	0.76	0.70	0.04
MnO	50.04	50.19	50.14	50.11	50.26	50.36	50.38	50.45	50.63	50.26	50.28	0.18
H ₂ O _{calc}	1.18	1.26	1.39	1.41	1.50	1.45	1.52	1.47	1.55	1.51	1.42	0.12
Total	100.75	100.57	99.96	99.58	99.08	99.82	99.32	99.96	99.69	99.27	99.80	0.54
Element (apfu)												
T sites												
V ⁵⁺	0.14	0.13	0.12	0.15	0.16	0.17	0.18	0.21	0.20	0.22	0.17	0.03
As ⁵⁺	0.69	0.61	0.60	0.52	0.44	0.44	0.44	0.41	0.40	0.38	0.49	0.11
Si ⁴⁺	5.21	5.30	5.28	5.35	5.40	5.42	5.37	5.41	5.39	5.40	5.35	0.17
ΣT atoms	6.04	6.04	6.00	6.02	6.00	6.03	5.99	6.03	5.99	6.00	6.01	0.02
(As+V)	0.83	0.74	0.72	0.67	0.60	0.61	0.62	0.60	0.60	0.60	0.66	0.08
Si _{exc} *	0.21	0.30	0.28	0.35	0.40	0.42	0.37	0.41	0.39	0.40	0.35	0.07
Mn sites												
Ca ²⁺	0.11	0.10	0.11	0.10	0.09	0.10	0.10	0.10	0.10	0.11	0.10	0.01
Mn ²⁺	5.85	5.86	5.89	5.88	5.91	5.87	5.91	5.87	5.91	5.89	5.89	0.02
ΣMn atoms	5.96	5.96	6.00	5.98	6.00	5.97	6.01	5.97	6.01	6.00	5.99	0.02
OH	1.09	1.16	1.29	1.30	1.39	1.33	1.41	1.35	1.42	1.39	1.31	0.11

Note: *Si_{exc} (apfu) = Si (apfu) – 5.

Table 2. Chemical data of As-rich medaite compared with data available in literature.

Oxide	As-rich medaite (n = 10)			Medaite [1]	Medaite [2]	Medaite [3]
	wt%	Range	e.s.d.	wt%		
V ₂ O ₅	4.58	4.33–4.77	0.13	7.44	8.13	7.94
As ₂ O ₅	5.32	5.06–5.68	0.22	2.11	1.53	5.23
SiO ₂	38.14	37.62–38.56	0.31	38.09	37.95	35.53
Al ₂ O ₃	–	–	–	–	0.01	0.01
MgO	–	–	–	–	–	0.05
CaO	0.82	0.68–0.88	0.06	1.30	1.42	0.60
MnO	50.16	49.94–50.48	0.19	49.94	48.83	46.95
FeO	–	–	–	0.31	–	–
NiO	–	–	–	–	0.01	0.02
CuO	–	–	–	–	0.10	0.07
Na ₂ O	–	–	–	–	0.00	0.02
H ₂ O _{calc}	1.22	–	–	–	1.25	0.90
Total	100.24	–	–	99.19	99.23	97.32

Note: [1] Molinello mine, Gramaccioli *et al.* (1982); [2] Molinello mine, Nagashima & Armbruster (2010); [3] Fianel, Nagashima & Armbruster (2010).

Si before each experimental session. Spectra were collected through multiple acquisitions with single counting times of 60 s.

The Raman bands observed in the spectral region between 200 and 1200 cm⁻¹ are shown in Fig. 2. For the sake of comparison, the Raman spectrum of medaite, taken from the RRUFF project website (Lafuente *et al.*, 2015), is shown. Within experimental uncertainties, the two spectra are very similar. In the range 300–700 cm⁻¹, the two main features are represented by bands at 355 and 650 cm⁻¹. The latter could be attributed to the bending modes of Q² Si-centred tetrahedra, whereas the former could be due to the overlapping of the symmetrical bending of AsO₄ groups and the Mn–O stretching and bending vibrations,

in agreement with Frost *et al.* (2014). The spectral range between 700 and 1200 cm⁻¹ is characterized by strong bands at 853 and 875 cm⁻¹, likely related to the symmetrical stretching of AsO₄ groups and the symmetrical stretching of Q¹Si-centred tetrahedra. Moreover, in accord with Frost *et al.* (2014), the band at 771 cm⁻¹ could be interpreted as the antisymmetrical stretching of the AsO₄ groups. Finally, weak bands ranging between 922 and 995 cm⁻¹ could be related to the symmetrical stretching of Q² Si-centred tetrahedra.

2.4. Crystallography

Owing to the small amount and small size of the available material (a fraction of the crystal used for the single-crystal

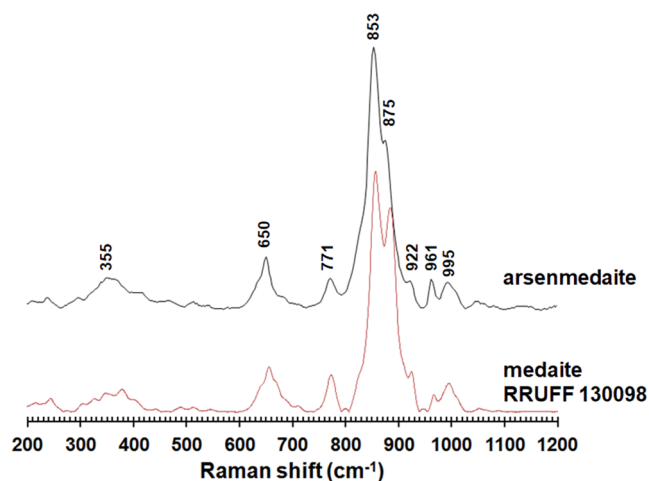


Fig. 2. Micro-Raman spectrum of arsenmedaite, compared with the spectrum of medaite (RRUFF Project #130098; Lafuente *et al.*, 2015) in the spectral region between 200 and 1200 cm^{-1} (online version in colour).

study), X-ray powder diffraction data were collected with a 114.6 mm Gandolfi camera and Ni-filtered $\text{Cu-K}\alpha$ radiation. Unfortunately, notwithstanding an exposure of one week, only few very weak reflections were observed. Consequently, only the calculated X-ray powder diffraction pattern is given in Table 3.

X-ray intensity data collections on both arsenmedaite and As-rich medaite were performed using a Bruker Smart Breeze diffractometer equipped with an air-cooled CCD detector and graphite-monochromatized $\text{Mo-K}\alpha$ radiation. The detector-to-crystal working distance was 50 mm. Data were collected using ω and ϕ scan modes, in 0.5° slices, with an exposure time of 25 s per frame, and they were corrected for Lorentz-polarization factor, absorption, and background effects using the software package Apex2 (Bruker AXS Inc, 2004). In the following, only the procedure related to the refinement of the crystal structure of arsenmedaite is reported.

The statistical tests on the distribution of $|E|$ values ($|E^2 - 1| = 0.916$) and the systematic absences agree with the space-group symmetry of medaite, $P2_1/n$ (Gramaccioli *et al.*, 1981; Nagashima & Armbruster, 2010). The refined unit-cell parameters are $a = 6.7099(3)$, $b = 29.001(1)$, $c = 7.5668(3)$ Å, $\beta = 95.469(3)^\circ$, $V = 1465.7(1)$ Å³, $Z = 4$. The $a:b:c$ ratio is 0.2314:1:0.2609. The crystal structure was refined using Shelxl-2014 (Sheldrick, 2015) starting from the atomic coordinates of medaite (Gramaccioli *et al.*, 1981). Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). In the first steps of the refinement, the following scattering curves were used: Mn vs. \square at the $Mn(1)$ – $Mn(6)$ sites; Si vs. \square at the $T(1)$ – $T(5)$ sites; As vs. \square at the $T(6)$ site; and O vs. \square at the $O(1)$ – $O(19)$ positions. All these sites were found fully occupied, and their site occupation factor (s.o.f.) was fixed to 1, the only exception being the $Mn(5)$ – $Mn(6)$, and $T(6)$ sites. Indeed, the s.o.f. at the $T(6)$ site was refined using the scattering curves of As

Table 3. Calculated X-ray powder diffraction data for arsenmedaite. Intensities and d_{hkl} were calculated using the software *PowderCell* 2.3 (Kraus & Nolze, 1996) on the basis of the structural model given in Table 5. The seven strongest reflections are given in bold.

I_{calc}	d_{calc}	hkl	I_{calc}	d_{calc}	hkl
26	6.51	1 1 0	35	2.539	$\bar{1}$ 10 1
10	6.07	1 2 0	27	2.518	2 6 1
19	5.22	0 4 1	37	2.501	0 1 3
58	4.777	1 0 1	39	2.448	0 9 2
30	4.713	1 1 1	14	2.419	$\bar{1}$ 1 3
13	4.068	0 6 1	31	2.319	2 9 0
24	3.342	0 4 2	15	2.319	2 3 2
12	3.332	$\bar{1}$ 2 2	29	2.298	0 10 2
15	3.318	2 1 0	56	2.193	$\bar{3}$ 0 1
100	3.266	0 8 1	10	2.170	3 3 0
56	3.254	2 2 0	16	2.160	0 11 2
72	3.159	0 5 2	14	2.135	1 10 2
45	3.157	2 3 0	22	2.069	2 11 0
22	3.148	$\bar{2}$ 1 1	24	2.062	1 6 3
22	3.130	1 7 1	24	1.997	1 7 3
82	3.094	$\bar{2}$ 2 1	23	1.848	0 3 4
14	3.033	2 4 0	12	1.844	2 10 2
57	3.010	$\bar{2}$ 3 1	19	1.762	0 16 1
38	2.999	1 3 2	44	1.704	$\bar{2}$ 10 3
83	2.963	0 9 1	22	1.667	4 1 0
79	2.935	2 1 1	19	1.664	0 17 1
50	2.893	1 4 2	22	1.659	4 2 0
11	2.888	1 8 1	20	1.658	1 12 3
15	2.822	2 3 1	16	1.634	3 11 1
68	2.788	0 7 2	18	1.607	1 17 1
46	2.747	$\bar{1}$ 9 1	12	1.582	$\bar{2}$ 7 4
18	2.706	0 10 1	11	1.571	3 3 3
17	2.630	2 5 1	12	1.538	$\bar{3}$ 9 3
42	2.626	$\bar{2}$ 0 2	13	1.499	$\bar{3}$ 10 3
29	2.615	$\bar{2}$ 1 2	11	1.458	$\bar{3}$ 11 3
98	2.612	0 8 2			

vs. Si, in order to model the mixed site population (As, V, Si). The $Mn(5)$ and $Mn(6)$ sites are those having the relatively higher U displacement parameters among Mn positions. Consequently, initially the s.o.f. at $Mn(5)$ was refined assuming a mixed (Mn,Ca) occupancy, with $Mn(6)$ fixed to a pure Mn occupancy, in agreement with Gramaccioli *et al.* (1981) and Nagashima & Armbruster (2010). However, since the total amount of refined Ca was about half of that measured through electron microprobe analysis, a mixed (Mn,Ca) occupancy was also refined for the octahedrally coordinated $Mn(6)$ position. The H atom, bonded to O(19), was located through difference-Fourier maps; in order to avoid a too short H–O distance, a constraint on this distance was introduced. In the final stages of the refinement, all the atoms, but the H atom, were refined anisotropically. The refinement converged to $R_1 = 0.062$ on the basis of 3526 reflections with $F_o > 4\sigma(F_o)$ and 287 parameters. Table 4 gives details of the selected crystal, data collection, and refinement. Atom coordinates and equivalent isotropic or isotropic displacement parameters are shown in Table 5, whereas selected bond distances are given in Table 6. In the same tables, details related to the refinement and crystal structure of As-rich medaite are also given. Bond-valence balance for arsenmedaite only, calculated

Table 4. Crystal data and summary of parameters describing data collection and crystal-structure refinement for arsenmedaite and As-rich medaite.

	Arsenmedaite	As-rich medaite
<i>Crystal data</i>		
Crystal size (mm ³)	0.09 × 0.09 × 0.04	0.12 × 0.11 × 0.08
Cell setting, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	
<i>a</i> (Å)	6.7099(3)	6.7133(4)
<i>b</i> (Å)	29.0008(13)	28.904(2)
<i>c</i> (Å)	7.5668(3)	7.5630(5)
β (°)	95.469(3)	95.278(4)
<i>V</i> (Å ³)	1465.74(11)	1461.30(17)
<i>Z</i>	4	4
<i>Data collection and refinement</i>		
Radiation, wavelength (Å)	Mo-Kα, 0.71073	Mo-Kα, 0.71073
Temperature (K)	293	293
2θ _{max} (°)	67.14	73.70
Measured reflections	21233	22063
Unique reflections	5579	6751
Reflections with <i>F</i> _o > 4σ(<i>F</i> _o)	3526	5044
<i>R</i> _{int}	0.0821	0.0379
<i>R</i> σ	0.0974	0.0511
Range of <i>h</i> , <i>k</i> , <i>l</i>	−10 ≤ <i>h</i> ≤ 10, −44 ≤ <i>k</i> ≤ 43, −11 ≤ <i>l</i> ≤ 11	−11 ≤ <i>h</i> ≤ 10, −47 ≤ <i>k</i> ≤ 48, −10 ≤ <i>l</i> ≤ 12
<i>R</i> [<i>F</i> _o > 4σ(<i>F</i> _o)]	0.0623	0.0425
<i>R</i> (all data)	0.1190	0.0697
<i>wR</i> (on <i>F</i> _o ²)	0.1097	0.0799
Goof	1.068	1.063
Number of least-squares parameters	287	287
Maximum and minimum residual peak (<i>e</i> Å ^{−3})	1.29 [at 0.88 Å from O(3)] −1.28 [at 1.18 Å from O(17)]	1.17 [at 0.74 Å from T(6)] −0.93 [at 0.49 Å from T(6)]

using the bond parameters of [Brese & O'Keeffe \(1991\)](#), are reported in [Table 7](#).

3. Description of the crystal structure

The crystal structure of arsenmedaite ([Fig. 3](#)) is isotypic with that of medaite ([Gramaccioli *et al.*, 1981](#); [Nagashima & Armbruster, 2010](#)). Six- to seven-fold coordinated Mn-centred polyhedra form wavy ribbons linked to TO₄ tetrahedra centred by Si and (As,V).

In the crystal structure of arsenmedaite there are six independent Mn positions, six independent tetrahedral sites, nineteen oxygen sites, and one hydrogen position. As reported above, manganese cations are six- and seven-fold coordinated. *Mn*(1), *Mn*(2), *Mn*(3), and *Mn*(6) sites show a slightly distorted octahedral coordination, with average bond distances ranging between 2.196 and 2.218 Å, in agreement with previous studies and an ideal <Mn–O> distance (using the ionic radii of ^{VI}Mn²⁺ and ^{III}O^{2−} reported by [Shannon, 1976](#)) of 2.19 Å. Actually, oxygen atoms are three- and four-fold coordinated, and consequently the ideal calculated average <Mn–O> distance should be slightly larger (~2.20 Å). *Mn*(4) and *Mn*(5) have a more distorted octahedral coordination; the coordination sphere is completed by a seventh additional oxygen atom located at distances of *ca.* 3 Å (2.94 and 3.06 Å for *Mn*(4) and *Mn*(5), respectively). According to [Gramaccioli *et al.* \(1981\)](#) and [Nagashima & Armbruster \(2010\)](#), the *Mn*(5) site could be able to host

minor Ca, owing to its larger size with respect to *Mn*(4). In this study, the site occupancy at the *Mn*(5) was refined to Mn_{0.97(1)}Ca_{0.03(1)}; chemical data suggest a Ca content close to 0.10 atom per formula unit (*apfu*), and consequently this element should be hosted in another *Mn* position. Owing to its *U*_{eq} displacement parameter relatively larger than those of the other *Mn* sites, the *Mn*(6) was hypothesized as a potential host for Ca. The refinement of its s.o.f. yields the site occupancy Mn_{0.92(1)}Ca_{0.08(1)}. Taking into account the *Mn* sites, their site occupancy is (Mn_{5.89}Ca_{0.11}), in good agreement with chemical data. Bond-valence sums (BVS) for the *Mn* sites range between 1.83 [at *Mn*(5)] and 2.06 valence unit (v.u) [at *Mn*(2)]. A similar situation occurs in As-rich medaite, with *Mn*(5) and *Mn*(6), both having the site occupancy Mn_{0.94(1)}Ca_{0.06(1)}.

The most striking structural feature of arsenmedaite is the occurrence of the arsenatopentasilicate group [AsSi₅O₁₈(OH)]^{12−} ([Fig. 4](#)). This group is terminated on one side by the *T*(5) tetrahedron, showing a silanol group SiO₃(OH), and on the other side by the *T*(6) tetrahedron hosting As and minor V and Si. In arsenmedaite, the silanol group belongs to a tetrahedron with one bridging O atom, in agreement with [Nyfeler & Armbruster \(1998\)](#). Average <Si–O> distances vary between 1.622 and 1.634 Å, with Si–O distances ranging between 1.585 [*T*(1)–O(9)] and 1.685 Å [*T*(1)–O(4)]. The *T*(6) site is definitely larger than the *T*(1)–*T*(5) sites, with an average <*T*(6)–O> distance of 1.684 Å. This value has to be compared with the average bond distances

Table 5. Atom fractional coordinates and equivalent isotropic or isotropic (*) displacement parameters (\AA^2) for arsenmedaite and As-rich medaite.

Site	Arsenmedaite				As-rich medaite			
	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq/iso}$	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq/iso}$
Mn(1)	0.37048(13)	0.02252(3)	0.15421(12)	0.0082(2)	0.37049(6)	0.02248(2)	0.15425(6)	0.00848(8)
Mn(2)	0.67914(13)	0.31743(3)	0.02173(12)	0.0089(2)	0.67953(7)	0.31745(2)	0.02184(6)	0.00920(9)
Mn(3)	0.45463(13)	0.13680(3)	0.21817(12)	0.0089(2)	0.45485(6)	0.13674(2)	0.21890(6)	0.00913(9)
Mn(4)	0.66866(13)	0.08622(3)	0.91790(12)	0.0104(2)	0.66862(7)	0.08642(2)	0.91788(6)	0.01026(9)
Mn(5)	0.14193(14)	0.07651(3)	0.43876(12)	0.0118(2)	0.14205(7)	0.07646(2)	0.43937(6)	0.01148(12)
Mn(6)	0.47142(13)	0.25266(3)	0.30593(12)	0.0103(2)	0.47116(7)	0.25268(2)	0.30626(6)	0.01085(12)
T(1)	0.6911(2)	0.16727(5)	0.5886(2)	0.0075(3)	0.69156(12)	0.16723(3)	0.58910(10)	0.00730(14)
T(2)	0.6406(2)	0.06259(5)	0.5158(2)	0.0058(3)	0.64087(11)	0.06252(3)	0.51561(10)	0.00653(13)
T(3)	0.8647(2)	0.01227(5)	0.2293(2)	0.0063(3)	0.86496(11)	0.01223(3)	0.22908(10)	0.00664(13)
T(4)	0.8170(2)	-0.09375(5)	0.1677(2)	0.0064(3)	0.81663(11)	-0.09390(3)	0.16716(10)	0.00640(13)
T(5)	0.0386(2)	-0.14538(5)	-0.1112(2)	0.0070(3)	0.03794(11)	-0.14550(3)	-0.11204(10)	0.00704(14)
T(6)	0.49088(11)	0.21418(2)	0.87870(9)	0.0075(2)	0.49137(6)	0.21410(2)	0.87923(5)	0.00771(11)
O(1)	0.6540(6)	0.25730(14)	0.8520(5)	0.0102(8)	0.6544(3)	0.25725(7)	0.8533(3)	0.0112(4)
O(2)	0.4526(6)	0.20252(13)	0.0861(5)	0.0124(8)	0.4516(3)	0.20258(8)	0.0859(3)	0.0129(4)
O(3)	0.2761(6)	0.22574(15)	0.7568(6)	0.0168(9)	0.2771(3)	0.22581(8)	0.7570(3)	0.0157(4)
O(4)	0.6011(6)	0.16669(14)	0.7890(5)	0.0102(8)	0.6021(3)	0.16662(7)	0.7888(3)	0.0110(4)
O(5)	0.5097(6)	0.18514(13)	0.4486(5)	0.0097(8)	0.5100(3)	0.18516(7)	0.4482(3)	0.0099(4)
O(6)	0.8886(6)	0.19792(13)	0.5991(5)	0.0095(8)	0.8894(3)	0.19783(7)	0.6003(3)	0.0105(4)
O(7)	0.7474(6)	0.11313(13)	0.5558(6)	0.0134(8)	0.7478(3)	0.11328(7)	0.5547(3)	0.0126(4)
O(8)	0.4475(6)	0.06978(13)	0.3737(5)	0.0098(8)	0.4476(3)	0.06976(7)	0.3737(3)	0.0090(4)
O(9)	0.5969(6)	0.04189(14)	0.7021(5)	0.0110(8)	0.5978(3)	0.04165(7)	0.7034(3)	0.0101(4)
O(10)	0.8068(6)	0.03109(14)	0.4254(5)	0.0123(8)	0.8051(3)	0.03069(8)	0.4246(3)	0.0128(4)
O(11)	0.0752(6)	0.03662(14)	0.2096(6)	0.0113(8)	0.0750(3)	0.03664(7)	0.2093(3)	0.0110(4)
O(12)	0.6867(6)	0.02254(13)	0.0748(5)	0.0097(8)	0.6876(3)	0.02268(7)	0.0754(3)	0.0090(4)
O(13)	0.8949(6)	-0.04341(13)	0.2474(6)	0.0118(8)	0.8950(3)	-0.04362(7)	0.2470(3)	0.0118(4)
O(14)	0.6314(6)	-0.09011(13)	0.0160(5)	0.0090(8)	0.6321(3)	-0.09007(7)	0.0150(3)	0.0086(4)
O(15)	0.7786(6)	-0.12052(13)	0.3470(6)	0.0116(8)	0.7779(3)	-0.12055(7)	0.3457(3)	0.0105(4)
O(16)	0.0051(6)	-0.11636(13)	0.0726(5)	0.0101(8)	0.0036(3)	-0.11655(7)	0.0719(3)	0.0104(4)
O(17)	0.2527(6)	-0.12752(14)	-0.1514(5)	0.0113(8)	0.2534(3)	-0.12756(8)	-0.1519(3)	0.0114(4)
O(18)	0.8650(6)	-0.13898(13)	-0.2741(5)	0.0082(7)	0.8647(3)	-0.13893(7)	-0.2744(3)	0.0085(4)
O(19)	0.0285(8)	-0.20036(14)	-0.0503(6)	0.0161(9)	0.0284(4)	-0.20067(8)	-0.0508(3)	0.0158(4)
H(19)	0.949(16)	-0.215(4)	-0.151(11)	0.12(5)*	0.949(7)	-0.2172(19)	-0.142(6)	0.061(18)*

given for medaite from the Molinello mine (1.702–1.703 Å – Gramaccioli *et al.*, 1981; Nagashima & Armbruster, 2010) and from Fianel (1.693 Å – Nagashima & Armbruster, 2010). In addition, it can be compared with the average $\langle T(6)\text{--O} \rangle$ distance in As-rich medaite, *i.e.* 1.685 Å. These values are related to the site population of the *T*(6) site. Indeed, the crystal-structure refinements on arsenmedaite and As-rich medaite point to a site scattering of 26.9 and 25.4 electrons per formula unit (*epfu*), respectively. Taking into account the chemical data, the former corresponds to the site population ($\text{As}_{0.49}\text{V}_{0.17}\text{Si}_{0.34}$) (calculated site scattering = 24.8 *epfu*), whereas the latter to ($\text{V}_{0.42}\text{As}_{0.38}\text{Si}_{0.20}$) (calculated site scattering = 25.0 *epfu*). Taking into account the ionic radii proposed by Shannon (1976) for four-fold coordinated As^{5+} , V^{5+} , and Si^{4+} (0.335, 0.355, and 0.26 Å, respectively) and three-fold coordinated O^{2-} (1.36 Å), the average *T*(6)–O distances in arsenmedaite and As-rich medaite should be 1.673 and 1.688 Å, respectively. The BVS at the *T* sites of arsenmedaite range between 3.91 and 4.03 v.u. for the Si-centred tetrahedra and it is of 4.79 v.u. for the As-centred tetrahedra. Assuming the proposed site population, the expected BVS should have been slightly lower, *i.e.*, 4.66 v.u. The greater discrepancy between calculated and observed site scattering values and

average bond distances for arsenmedaite compared to As-rich medaite seems to be related to an overestimation of the Si content at the *T*(6) site, although the lower quality of the crystal-structure refinement of arsenmedaite could be contributing to the discrepancy.

Oxygen atoms are three- to four-fold coordinated. Their BVS range between 1.86 and 2.07 v.u.; only O(19) is significantly underbonded (1.17 v.u.), consistent with its being a hydroxyl group. The hydrogen bond involves the oxygen pair O(19)–O(1), with an O...O distance of 2.772 (6) Å. Using the relationship of Ferraris & Ivaldi (1988), the bond strength of this hydrogen bond is 0.19 v.u.; in this way, the BVS at O(1) and O(19) are 2.09 and 0.98 v.u., respectively.

4. Discussion

Arsenmedaite is the arsenic analogue of medaite; in agreement with Mills *et al.* (2009), these two species form the medaite group. As stressed by Nagashima & Armbruster (2010), pentavalent cations occurring in medaite do not usually reach 1 *apfu*, implying that some non-pentavalent cations have to be hosted at the *T*(6) site. This statement is further confirmed by the crystal-chemical investigation

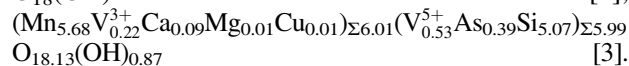
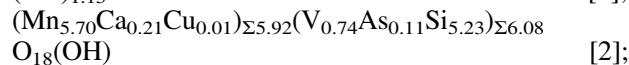
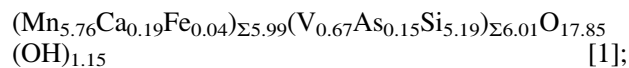
Table 6. Selected bond distances (in Å) in arsenmedaite and As-rich medaite.

	Arsenmedaite		As-rich medaite		Arsenmedaite		As-rich medaite	
<i>Mn</i> (1)	–O(11)	2.104(4)	2.104(2)	<i>Mn</i> (2)	–O(15)	2.062(4)	2.063(2)	
	–O(9)	2.162(4)	2.144(2)		–O(6)	2.135(4)	2.134(2)	
	–O(12)	2.175(4)	2.179(2)		–O(1)	2.162(4)	2.154(2)	
	–O(8)	2.177(4)	2.176(2)		–O(3)	2.221(4)	2.223(2)	
	–O(12)	2.260(4)	2.263(2)		–O(18)	2.256(4)	2.254(2)	
	–O(14)	2.345(4)	2.335(2)		–O(5)	2.338(4)	2.338(2)	
	Mean	2.204	2.200		Mean	2.196	2.194	
<i>Mn</i> (3)	–O(17)	2.091(4)	2.085(2)	<i>Mn</i> (4)	–O(9)	2.098(4)	2.095(2)	
	–O(2)	2.151(4)	2.152(2)		–O(14)	2.123(4)	2.129(2)	
	–O(18)	2.226(4)	2.224(2)		–O(17)	2.158(4)	2.156(2)	
	–O(5)	2.241(4)	2.232(2)		–O(12)	2.192(4)	2.192(2)	
	–O(14)	2.261(4)	2.258(2)		–O(16)	2.352(4)	2.361(2)	
	–O(8)	2.275(4)	2.266(2)		–O(4)	2.553(4)	2.527(2)	
	Mean	2.208	2.203		–O(7)	2.945(4)	2.949(2)	
			Mean	2.346	2.344			
<i>Mn</i> (5)	–O(15)	2.092(4)	2.097(2)	<i>Mn</i> (6)	–O(6)	2.155(4)	2.149(2)	
	–O(11)	2.097(4)	2.100(2)		–O(3)	2.203(4)	2.210(2)	
	–O(8)	2.163(4)	2.163(2)		–O(2)	2.204(4)	2.203(2)	
	–O(18)	2.197(4)	2.193(2)		–O(1)	2.210(4)	2.206(2)	
	–O(13)	2.595(4)	2.588(2)		–O(5)	2.239(4)	2.231(2)	
	–O(10)	2.600(4)	2.614(2)		–O(19)	2.297(4)	2.288(2)	
	–O(7)	3.061(4)	3.054(2)		Mean	2.218	2.214	
Mean	2.401	2.401						
<i>T</i> (1)	–O(6)	1.592(4)	1.592(2)	<i>T</i> (2)	–O(9)	1.585(4)	1.594(2)	
	–O(5)	1.621(4)	1.628(2)		–O(8)	1.617(4)	1.619(2)	
	–O(7)	1.639(4)	1.631(2)		–O(10)	1.641(4)	1.636(2)	
	–O(4)	1.685(4)	1.676(2)		–O(7)	1.647(4)	1.648(2)	
	Mean	1.634	1.632		Mean	1.622	1.624	
<i>T</i> (3)	–O(11)	1.599(4)	1.596(2)	<i>T</i> (4)	–O(15)	1.605(4)	1.596(2)	
	–O(12)	1.617(4)	1.614(2)		–O(14)	1.614(4)	1.615(2)	
	–O(13)	1.631(4)	1.631(2)		–O(13)	1.646(4)	1.640(2)	
	–O(10)	1.662(4)	1.656(2)		–O(16)	1.648(4)	1.642(2)	
	Mean	1.628	1.624		Mean	1.628	1.623	
<i>T</i> (5)	–O(17)	1.584(4)	1.591(2)	<i>T</i> (6)	–O(2)	1.649(4)	1.644(2)	
	–O(18)	1.624(4)	1.623(2)		–O(3)	1.669(4)	1.671(2)	
	–O(16)	1.659(4)	1.658(2)		–O(1)	1.686(4)	1.683(2)	
	–O(19)	1.663(4)	1.664(2)		–O(4)	1.732(4)	1.741(2)	
	Mean	1.633	1.634		Mean	1.684	1.685	

of arsenmedaite and As-rich medaite. In addition, Nagashima & Armbruster (2010) proposed an additional chemical variability involving the octahedral positions, with some octahedrally coordinated V^{3+} in medaite from Fianel. The occurrence of V^{3+} in octahedral coordination could be related to the heterovalent substitution $Mn^{2+} + OH^- = V^{3+} + O^{2-}$ and/or $Mn^{2+} + (V,As)^{5+} = V^{3+} + Si^{4+}$.

The chemical analyses available in the literature (Table 2) were recalculated on the basis of 12 cations and 19 anions; in the sample from Fianel, vanadium has been partitioned between V^{3+} and V^{5+} in order to achieve a ratio between octahedral and tetrahedral cations of 1. The OH content was calculated in order to achieve the electrostatic balance.

The following formulae of medaite can be obtained (with rounding errors):



Likely, the deficiency in octahedral cations and the excess of tetrahedral cations in formula [2] could suggest the occurrence of minor V^{3+} also in medaite from the Molinello mine.

Taking into account these formulae, as well as those reported in this work, a Si excess [hereafter $Si_{exc} = Si(apfu) - 5$] is present in all analyses, and the sum $T(As^{5+} + V^{5+})$ varies inversely with $T(Si_{exc})$ in apfu (Fig. 5). The substitution of pentavalent cations by Si has been reported in other minerals, e.g., As^{5+} partially replaced by Si^{4+} in bergslagite,

Table 7. Bond-valence sums (in valence unit, v.u.) for arsenmedaite.

	Mn(1)	Mn(2)	Mn(3)	Mn(4)	Mn(5)	Mn(6)	T(1)	T(2)	T(3)	T(4)	T(5)	T(6)	Σ anions
O(1)		0.37				0.34						1.19	1.90
O(2)			0.38			0.35						1.31	2.04
O(3)		0.31				0.35						1.24	1.90
O(4)				0.13			0.85					1.05	2.03
O(5)		0.23	0.30			0.32	1.01						1.86
O(6)		0.39				0.40	1.09						1.88
O(7)				0.04	0.03		0.96	0.94					1.97
O(8)	0.35		0.27		0.37			1.02					2.01
O(9)	0.37			0.43				1.11					1.91
O(10)					0.11			0.96	0.90				1.97
O(11)	0.43				0.44				1.07				1.94
O(12)	0.35/0.28			0.34					1.02				1.99
O(13)					0.11				0.98	0.94			2.03
O(14)	0.22		0.28	0.41						1.03			1.94
O(15)		0.48			0.44					1.05			1.97
O(16)				0.22						0.94	0.91		2.07
O(17)			0.44	0.37							1.11		1.92
O(18)		0.28	0.31		0.33							1.00	1.92
O(19)						0.27						0.90	1.17
Σ cations	2.00	2.06	1.98	1.94	1.83	2.03	3.91	4.03	3.97	3.96	3.92	4.79	

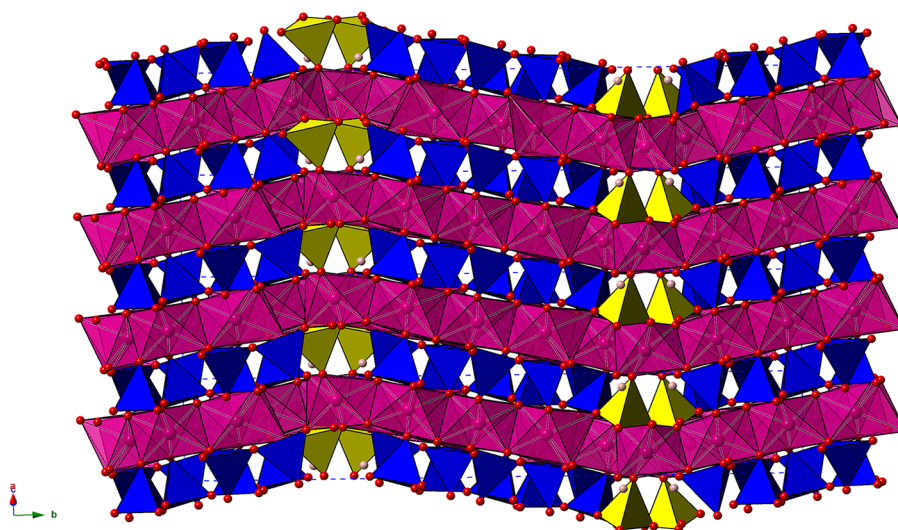


Fig. 3. Crystal structure of arsenmedaite. Polyhedra: violet = Mn sites; blue = T(1)–T(5) sites; yellow = T(6) site. Circles: red = O sites; pink = H site (online version in colour).

CaBe(As⁵⁺,Si)O₄(OH) (Raade *et al.*, 2006), and P⁵⁺ partially substituted by Si⁴⁺ in lavoisierite (Orlandi *et al.*, 2013). In the medaite group, the mechanism of charge balance is not well understood. It could involve the partial oxidation of Mn²⁺ to Mn³⁺ at Mn sites or the protonation of an oxygen atom belonging to the T(6) tetrahedron but the experimental data supporting these hypotheses are still lacking.

Within the medaite group, the classification should be based on the dominant-valency rule (Hatert & Burke, 2008). All available data indicate that the atomic ratio $Si_{exc}/(As + V + Si_{exc})$ is always less than 0.50, thus indicating that the dominant valency is 5+. Among pentavalent

cations, V⁵⁺ and As⁵⁺ are the only ones occurring in detectable amounts in medaite-group samples. Thus, the difference between V- and As-members relies on the As/(As + V) atomic ratio (Fig. 6). However, the finding of Si-dominant medaite cannot be excluded.

Arsenmedaite is a new addition to the series of rare mineral species first described from the Mn ore deposits of Eastern Liguria, and it is the second arsenate-silicate found in the Molinello mine, after the first description of tiragalloite (Gramaccioli *et al.*, 1980). Taking into account the extensive As-to-V substitution, future mineralogical investigations could be able to find the V-analogue of tiragalloite.

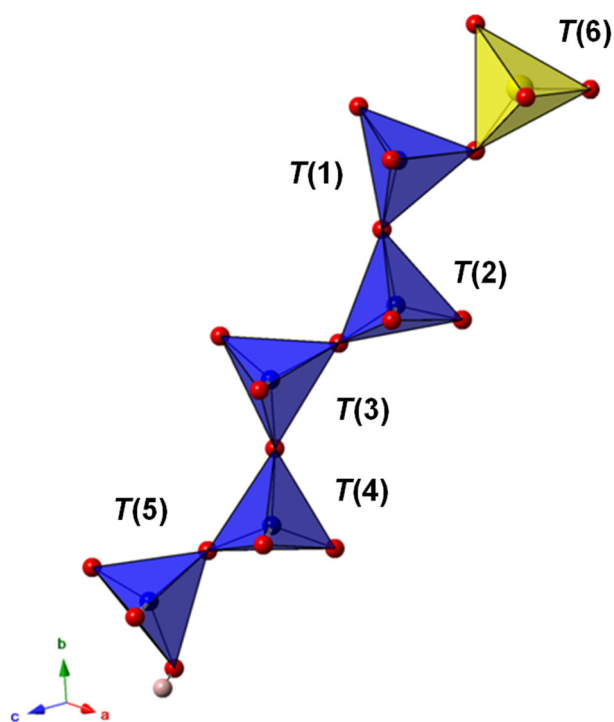


Fig. 4. The arsenatopentasilicate group characterizing the crystal structure of arsenmedaite (online version in colour).

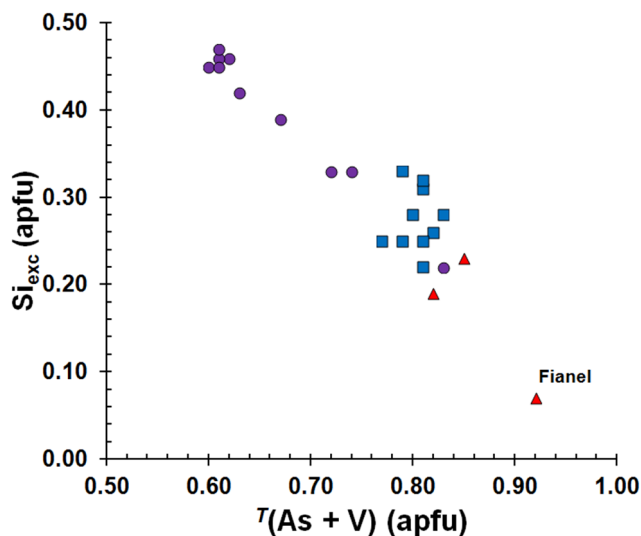


Fig. 5. Correlation between $T(\text{As} + \text{V})$ and Si_{exc} ($= \text{Si} - 5$) in apfu. Symbols: violet circles = arsenmedaite; blue squares = As-rich medaite; red triangles = medaite. All samples from the Molinello mine, with the exception of the sample from Fianel. Data after Gramaccioli *et al.* (1982), Nagashima & Armbruster (2010), and this work (online version in colour).

Acknowledgements: The authors are grateful to the University Centrum for Applied Geoscience (UCAG) for the access to the E.F. Stumpfl electron microprobe laboratory. The studied specimen was kindly provided by the mineral collector Manlio Callandria. The comments of R. James

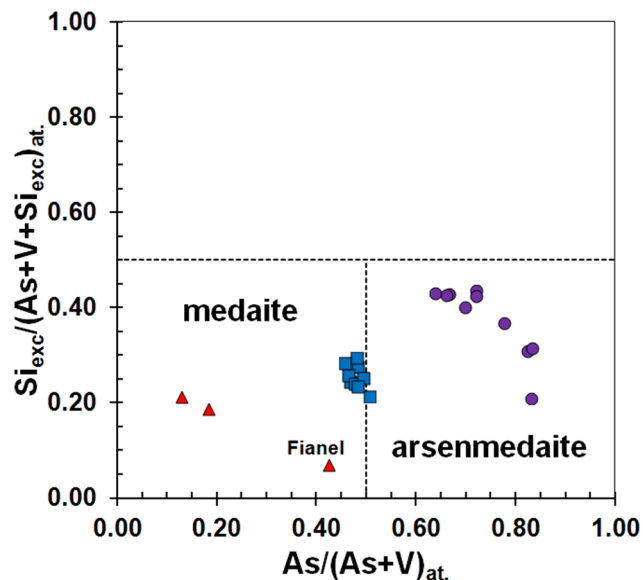


Fig. 6. Chemical variability of members of the medaite group. Same symbols as in Figure 5 (online version in colour).

Evans, an anonymous reviewer, and the Associate Editor Edward Grew helped us improving the paper.

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Received 22 May 2018

Modified version received 9 July 2018

Accepted 9 July 2018