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Ardennite, tiragalloite and medaite: structural control of $(As^{5+},V^{5+},Si^{4+})O_4$ tetrahedra in silicates

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ABSTRACT

Several silicate-minerals, such as ardennite – $Mn_4^{2+}MgAl_5[Si_5(As^{5+},V^{5+})O_{22}](OH)_6$, $Z = 2$, tiragalloite – $Mn_4^{2+}[Si_3As^{5+}O_{12}(OH)]$, $Z = 4$ and medaite – $Mn_6^{2+}[Si_5(V^{5+},As^{5+})O_{18}(OH)]$, $Z = 4$ possess $(V^{5+},As^{5+},P^{5+})O_4$ tetrahedra. Using electron-microprobe analysis (EMPA) and single-crystal X-ray diffraction methods, the crystal chemistry of ardennite from Salam-Château, Belgium and the Vernetto mine, Italy, tiragalloite from the Gambatesa mine, Italy, and medaite from the Molinello mine, Italy and the Fianel mine, Switzerland, were studied. Structure refinements converged to R_1 values of 2.10–5.67%. According to chemical analysis, the Σ(As+V+P) content increases with decreasing Si content. Thus, Si replaces pentavalent cations in tetrahedral coordination. The $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedra are categorized by their connections to SiO_4 tetrahedra. The $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedron of ardennite is isolated, and those of tiragalloite and medaite terminate a tetrahedral chain. The $<T–O>$ of the isolated $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedron shows a positive correlation with the mean ionic radius. For $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedra with one $T–O–T$ link, $<T–O>$ and mean ionic radius are also correlated. In addition, the longest bridging T–O bond occurs between $(As,V,P,Si)O_4$ and the adjacent SiO_4 tetrahedron. The bridging O atom is over-bonded to satisfy the charge requirement of Σ(As+V+Si).

KEYWORDS: ardennite, tiragalloite, medaite, crystal structure, As, V, pentavalent cations, tetrahedral site.

Introduction

ARDENNITE – $Mn_4^{2+}MgAl_5[Si_5(As^{5+},V^{5+})O_{22}](OH)_6$, $Z = 2$, tiragalloite – $Mn_4^{2+}[Si_3As^{5+}O_{12}(OH)]$, $Z = 4$ and medaite – $Mn_6^{2+}[Si_5(V^{5+},As^{5+})O_{18}(OH)]$, $Z = 4$ are Mn-rich silicate minerals, which possess $(V^{5+},As^{5+},P^{5+})O_4$ tetrahedra. Due to their scarce occurrence, compositional heterogeneity and small crystal size, the crystal structure of these minerals has not been adequately studied. Ardennite has been described as a rock-forming mineral from a variety of As- and/or V-enriched Fe^{2+}-Mn sediments, metamorphosed under a wide range of $P–T$ conditions (Pasero *et al.*, 1994). In contrast, tiragalloite and mediate are known only from a few localities. The type locality of tiragalloite and medaite is Val Graveglia (including the Gambatesa, Molinello and Cassagna mines), Genova, Liguria, Italy (Gramaccioli *et al.*, 1979*a*,*b*, 1980*a*,*b*, 1981, 1982). As tiragalloite and medaite are found together in apparent textural equilibrium, and considering their close structural and chemical relations, it is reasonable to assume that they crystallized concurrently (Gramaccioli *et al.*, 1982). Gramaccioli *et al.* (1980*b*) suggested that they formed at low temperature and relatively low water fugacity. Further investigation of their stability fields and phase relations is desirable.

The crystal structure of ardennite, space group *Pnmm* (orthorhombic) (Donnay and Allmann,

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1968), consists of chains of edge-sharing [MO_6] octahedra extending along the *b* axis and linked to [TO_4] and [T_3O_{10}] groups (Fig. 1*a*). There are two larger polyhedra *A*(1) and *A*(2) mainly occupied by Mn^{2+}. The largest octahedron, *M*(3), is occupied by both trivalent and divalent cations, e.g. Al^{3+} and Mg^{2+}, whereas the $M(1)O_6$ and $M(2)O_6$ octahedra are occupied only by trivalent cations. The *T*(1), *T*(2) and *T*(3) sites are occupied exclusively by Si, and *T*(4) is dominated by the pentavalent cations, As^{5+}, V^{5+} and P^{5+}.

The crystal structures of tiragalloite (Fig. 1*b*) and medaite (Fig. 1*c*) were solved by Gramaccioli *et al*. (1979*b*) and Gramaccioli *et al*. (1981), and show strong similarities. The space group of both minerals is $P2_1/n$ (monoclinic). The 6- and 7-coordinated Mn(1)−Mn(4) sites in tiragalloite and Mn(1)−Mn(6) in medaite are occupied primarily by Mn^{2+}. These crystallographically independent 6- and 7-coordinated polyhedra form a wavy ribbon (Fig. 1*b*,*c*), that links to TO_4 tetrahedra including an $(As^{5+},V^{5+})O_4$ tetrahedron.

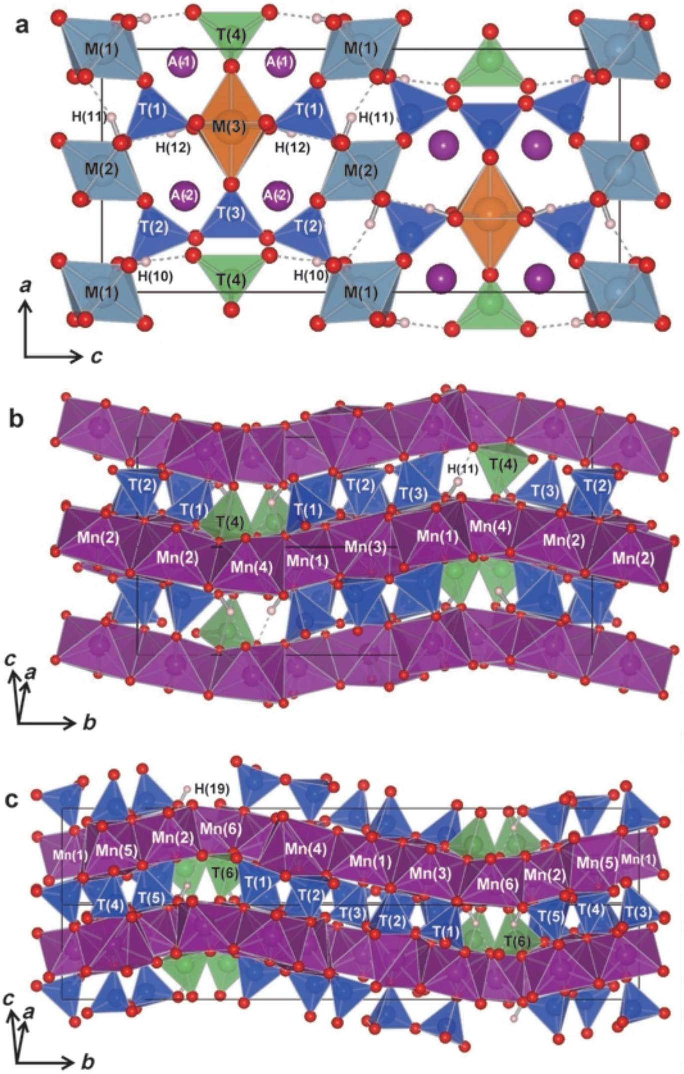

FIG. 1. Crystal structures of ardennite (*a*), tiragalloite (*b*) and medaite (*c*) drawn with the program *VESTA* (Momma and Izumi, 2008).

The crystal structure of tiragalloite has three tetrahedrally-coordinated sites, *T*(1)−*T*(3), that are occupied by Si and one tetrahedrally-coordinated site, *T*(4), primarily occupied by As^{5+} and V^{5+}. Medaite has five *T* sites, *T*(1)−*T*(5), occupied by Si and one *T* site, *T*(6), occupied largely by As^{5+} and V^{5+}. Both minerals have a silanol group, and these groups belong to the category of tetrahedra with one bridging O atom (Nyfeler and Armbruster, 1998).

In this study, we have investigated the crystal chemistry of two ardennite specimens, one tiragalloite, and two medaite specimens in order to clarify their structural and compositional variations.

Experimental methods

Samples

Ardennite: One specimen from each of the following localities was studied: (1) Salam-Château, Ardennes, Belgium (type locality: Donnay and Allmann, 1968), and (2) Vernetto mine, Val Lanzo, Torino, Piedmont, Italy.

Tiragalloite: A specimen from the Gambatesa mine, Val Graveglia, Liguria, Italy (type locality: Gramaccioli *et al*., 1979*a*,*b*, 1980*b*) was studied.

Medaite: (1) A specimen from the Mn mine at Molinello, Val Graveglia, Liguria, Italy (type locality: Gramaccioli *et al*., 1980*a*, 1981, 1982), and (2) from the Mn ore deposit at Fianel, Val Ferrera, Graubünden, Switzerland (Brugger and Berlepsch, 1996; Brugger and Gieré, 2000) were studied. Fianel is the type locality of the Mn-vanadates fianelite, $Mn_2V(V,As)O_7{\cdot}2H_2O$ (Brugger and Berlepsch, 1996) and ansermetite, $MnV_2O_6{\cdot}2H_2O$ (Brugger *et al*., 2003), and of the silicate-vanadate scheuchzerite, $Na(Mn,Mg)_9[VSi_9O_{28}(OH)](OH)_3$ (Brugger *et al*., 2006), which are compositionally and paragenetically related to medaite.

Ardennite from Salam-Château, Belgium forms prismatic crystals up to 1 cm long or cleavable aggregates. In contrast, the crystal size of ardennite from the Vernetto mine, Italy, is small (<0.1 mm in length). Ardennite crystals from both localities are orange-brown. Tiragalloite forms aggregates of bright orange grains up to 0.2−0.3 mm in size. Medaite from the Molinello mine, Italy, forms reddish-brown prismatic crystals up to 2 mm long. In the specimen studied, a medaite-rich veinlet cuts massive braunite. Medaite from Fianel, Switzerland, forms tiny anhedral reddish-brown crystals (<0.05 mm).

Chemical analysis (EMPA)

The chemical compositions of ardennite, tiragalloite, and medaite were analysed using the JEOL JXA-8200 electron probe microanalyser at the University of Bern. Silicon, Ti, Al, Cr, V, Fe, Mn, Mg, Ca, Na, K, Cu, Ni, As and P were measured using an accelerating voltage of 15 kV and a probe current of 20 nA, with a final beam diameter of 1 μm. The following standards were used: wollastonite (Si, Ca), synthetic ilmenite (Ti, Fe), anorthite (Al), synthetic eskolaite (Cr), synthetic shcherbinaite (V), synthetic tephroite (Mn), synthetic spinel (Mg), albite (Na), orthoclase (K), tennantite (Cu), synthetic bunsenite (Ni), arsenopyrite (As) and synthetic $CePO_4$ (P). The $\phi(\rho Z)$ modified ZAF method (Bastin *et al*., 1984, 1986) was used for data correction.

Single-crystal structure refinements

X-ray diffraction data for single crystals of ardennite, tiragalloite and medaite were collected using a Bruker SMART APEX II CCD diffractometer. Crystals were mounted on glass fibres and intensity data were measured at room temperature using graphite-monochromatized Mo-*K*α radiation (λ = 0.71069 Å). Preliminary lattice parameters and an orientation matrix were obtained from three sets of frames and refined during the integration process of the intensity data. Diffraction data were collected with ω scans at different φ settings (φ−ω scan) (Bruker, 1999). Data were processed using the *SAINT* program (Bruker, 1999). An empirical absorption correction using *SADABS* (Sheldrick, 1996) was applied. Structural refinement was done with the *SHELXL-97* program (Sheldrick, 1997) using scattering factors for neutral atoms. All cation sites were initially refined without any restraints. Sites fully occupied within their standard deviation were fixed during final refinement. However, Mg at *M*(3) and Si at *T*(4) of ardennite, V at *T*(4) of tiragalloite and Si at *T*(6) of medaite were fixed based on the average chemical compositions. The *T*(4) site of the ardennite from Vernetto, Italy, may also include a small amount of P (<0.06 a.p.f.u.). Positions of the H atoms of the OH group were derived from difference-Fourier syntheses. Subsequently, H positions were refined with a fixed U_{iso} value of 0.05 $Å^2$ and a bond-distance restraint of O−H = 0.98(1) Å (Franks, 1973). Bond-valence sums were calculated using the equations of Brown and Altermatt (1985) and the bond-valence parameters of Brese and O'Keeffe (1991).

Results

Chemical compositions

The average chemical compositions of the samples studied are given in Table 1, where total Mn, V and As are reported as MnO, V_2O_5 and As_2O_5 respectively. The total (Si+As+V+P) content based on average chemical compositions is 6.05–6.08 a.p.f.u. in ardennite, 4.04 a.p.f.u. in tiragalloite, and 6.08–6.21 a.p.f.u. in medaite. On the basis of this structure, there are a maximum of six OH groups in ardennite, and a maximum of one OH group in tiragalloite and medaite. However, the estimated OH content is often greater than the expected value. This implies some Mn could be trivalent in ardennite, and some V could be trivalent in both tiragalloite and medaite. The procedure used to construct the chemical formula is as follows:

(1) the total number of cations (except H^+) is normalized to 16 (ardennite), 8 (tiragalloite), and 12 (medaite);

(2) all Si, As and P are assigned to the *T* sites;

(3) the *T*-site V^{5+} is calculated as [6−(Si+As+P)] (ardennite), [4−(Si+As)] (tiragalloite), and [6−(Si+As)] (medaite), and excess V is assigned to the octahedrally coordinated sites as V^{3+};

(4) the amount of OH is determined by the requirement of electroneutrality.

In the ardennite from Vernetto, Italy, the (Ca+Mn) content is >4, and excess Mn was assigned to the octahedrally coordinated sites as Mn^{3+}.

Crystal structure refinements

Crystallographic data and refinement parameters are summarized in Table 2. The refined atom positions and anisotropic mean-square displacement parameters of ardennite, tiragalloite and medaite samples are listed in Supplementary Tables S1, S2, S3, S4 and S5. Supplementary data have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat_mm.html. The site occupancies of cation sites are summarized in Table 3. Interatomic distances are given in Tables 4, 5 and 6, and selected angles are shown in Supplementary Tables S6, S7 and S8. The crystal structures of ardennite, tiragalloite and

TABLE 1. Chemical compositions (wt.%) and formulae (a.p.f.u.) of ardennite, tiragalloite and medaite samples. (*n*: number of analytical points).

Sample	Ardennite				Tiragalloite		Medaite			
Locality	Salm-Château, Belgium 1		Vernetto, Italy 2		Gambatesa, Italy 3		Molinello, Italy 4		Fianel, Switzerland 5	
	Aver.	Range (*n* = 15)	Aver.	Range (*n* = 25)	Aver.	Range (*n* = 25)	Aver.	Range (*n* = 29)	Aver.	Range (*n* =35)
P_2O_5	–	–	0.23	0.02–0.41	–		–		–	
V_2O_5*	0.51	0.00–0.90	0.33	0.04–1.03	1.35	0.80–1.78	8.13	6.04–8.90	7.94	5.07–10.05
As_2O_5	10.27	8.69–11.47	7.46	5.75–9.53	12.85	9.28–16.86	1.53	0.00–4.09	5.23	1.69–8.34
SiO_2	28.39	27.98–29.36	30.51	28.91–31.26	35.04	32.03–37.92	37.95	35.73–39.08	35.53	32.84–39.41
TiO_2	0.00	0.00–0.01	0.09	0.02–0.14	0.02	0.00–0.11	–		–	
Al_2O_3	24.45	24.04–25.90	21.78	18.53–22.90	0.01	0.00–0.03	0.01	0.00–0.03	0.01	0.00–0.03
Cr_2O_3	0.05	0.02–0.09	0.04	0.00–0.36	–		–		–	
Fe_2O_3	–		0.90	0.49–2.09	–		–		–	
MnO*	23.88	22.61–24.75	23.27	22.18–24.88	47.78	46.59–48.69	48.83	47.99–49.42	46.95	43.37–48.19

MgO	3.44	3.10–3.58	4.20	3.32–4.55	–		–		0.05	0.00–0.20
CaO	1.39	1.18–1.50	4.03	3.31–5.25	1.12	0.93–1.47	1.42	0.94–1.56	0.60	0.50–0.76
NiO	0.00	0.00–0.01	0.04	0.00–0.11	0.01	0.00–0.04	0.01	0.00–0.04	0.02	0.00–0.06
CuO	0.54	0.37–0.99	0.14	0.00–0.30	0.03	0.00–0.16	0.10	0.00–0.18	0.07	0.00–0.25
Na_2O	0.01	0.00–0.03	0.01	0.00–0.05	0.01	0.00–0.05	0.00	0.00–0.02	0.02	0.00–0.20
K_2O	0.01	0.00–0.02	0.01	0.00–0.05	–		–		–	
H_2O (calc.)	4.96		5.80		2.02		1.25		0.90	
Total	97.90		98.84		100.24		99.23		97.32	
Formulae based on:	16 cations				8 cations		12 cations			
P^{5+}	–	–	0.03	0.00–0.06	–		–		–	
As^{5+}	0.95	0.80–1.06	0.68	0.53–0.89	0.64	0.45–0.85	0.11	0.00–0.30	0.39	0.13–0.62
V^{5+}	0.06	0.00–0.11	0.04	0.00–0.12	0.08	0.05–0.11	0.74	0.56–0.81	0.75	0.48–0.95
Si	5.04	4.91–5.16	5.32	5.19–5.47	3.32	3.09–3.52	5.23	5.00–5.33	5.07	4.72–5.53
Ti	0.00	0.00	0.01	0.00–0.02	0.00	0.00–0.01	–		–	
Al	5.11	4.99–5.36	4.48	3.92–4.62	0.00		0.00		0.00	0.00–0.01
						0.00		0.00		
Cr^{3+}	0.01	0.00–0.01	0.01	0.00–0.05	–		–		–	
Fe^{3+}	–		0.12	0.06–0.28	–		–		–	
Mn^{2+}	3.59	3.42–3.66	3.44	3.29–3.78	3.85	3.79–3.91	5.70	5.65–5.75	5.68	5.47–5.85
Mg	0.91	0.81–0.95	1.09	0.89–1.16	–		–		0.01	0.00–0.04
Ca	0.26	0.22–0.29	0.75	0.61–1.01	0.11	0.09–0.15	0.21	0.14–0.23	0.09	0.08–0.11
Ni	0.00	0.00	0.01	0.00–0.02	0.00	0.00	0.00	0.00	0.00	0.00–0.01
Cu	0.07	0.05–0.13	0.02	0.00–0.04	0.00	0.00–0.01	0.01	0.00–0.02	0.01	0.00–0.03
Na	0.00	0.00–0.01	0.00	0.00–0.02	0.00	0.00–0.01	0.00	0.00–0.01	0.00	0.00–0.06
K	0.00	0.00	0.00	0.00–0.01	–		–		–	
Cation sum	16.00		16.01		8.00		12.00		12.00	

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* Total V as V_2O_5, Cr as Cr_2O_3, Fe as Fe_2O_3, Mn as MnO and As as As_2O_5.

1: $(Ca_{0.26}Mn^{2+}_{3.59}Cu_{0.07}Mg_{0.08})_{\Sigma 4.00}(Mg_{0.83}Al_{5.11}Cr^{3+}_{0.01}V^{3+}_{0.05})_{\Sigma 6.00}[Si_{5.00}(Si_{0.04}As^{5+}_{0.95}V^{5+}_{0.01})]O_{22.13}(OH)_{5.87}$

2: $(Ca_{0.75}Mn^{2+}_{3.25})_{\Sigma 4.00}(Mn^{3+}_{0.19}Mg_{1.09}Al_{4.48}Fe^{3+}_{0.12}Cr^{3+}_{0.01}Cu_{0.02}Ni_{0.01}Ti_{0.01}V^{3+}_{0.04})_{\Sigma 5.97}[Si_{5.00}(Si_{0.32}As^{5+}_{0.68}P^{5+}_{0.03})_{\Sigma 1.03}]O_{21.25}(OH)_{6.75}$

3: $(Mn^{2+}_{3.85}Ca_{0.11}V^{3+}_{0.04})_{\Sigma 4.00}[Si_{3.00}(As^{5+}_{0.64}Si_{0.32}V^{5+}_{0.04})]O_{11.72}(OH)_{1.28}$

4: $(Mn^{2+}_{5.70}Ca_{0.21}Cu_{0.01}V^{3+}_{0.08})_{\Sigma 6.00}[Si_{5.00}(V^{5+}_{0.64}Si_{0.23}As^{5+}_{0.13})]O_{17.85}(OH)_{1.15}$

5: $(Mn^{2+}_{5.68}Ca_{0.09}Mg_{0.01}Cu_{0.01}V^{3+}_{0.21})_{\Sigma 6.00}[Si_{5.00}(V^{5+}_{0.54}As^{5+}_{0.39}Si_{0.07})]O_{18.14}(OH)_{0.86}$

TABLE 2. Experimental details of the single-crystal X-ray diffraction analysis of ardennite, tiragalloite, and medaite samples*.

Sample	Ardennite		Tiragalloite	Medaite	
Locality	Salm-Château, Belgium	Vernetto, Italy	Gambatesa, Italy	Molinello, Italy	Fianel, Switzerland
Crystal size (mm)	0.100 × 0.080 × 0.025	0.080 × 0.065 × 0.020	0.045 × 0.04 × 0.03	0.13 × 0.11 × 0.015	0.025 × 0.025 × 0.025
Space group	*Pnmm* (Orthorhobmic) $Z = 2$	*Pnmm* (Orthorhobmic) $Z = 2$	$P2_1/n$ (Monoclinic) $Z = 4$	$P2_1/n$ (Monoclinic) $Z = 4$	$P2_1/n$ (Monoclinic) $Z = 4$
Cell parameters					
a (Å)	8.7163(2)	8.7452(6)	6.6783(1)	6.7079(7)	6.6748(1)
b (Å)	5.8131(1)	5.8314(4)	19.9075(3)	28.8700(35)	28.8203(5)
c (Å)	18.5199(3)	18.5891(12)	7.5750(1)	7.5754(9)	7.5444(2)
β (°)	90	90	95.475(1)	95.309(5)	95.363(1)
V (Å^3)	938.38(3)	947.98(11)	1002.49(3)	1460.7(3)	1444.96(5)
$D_{calc.}$ (g cm^{-3})	3.692	3.662	3.780	3.732	3.823
$\theta_{min.}$(°)	2.2	2.2	2.0	1.4	2.8
$\theta_{max.}$(°)	30.0	30.0	30.5	29.7	30.0
μ (mm^{-1})	5.786	5.822	9.207	7.451	7.532
Collected reflections	6366	11641	21034	11489	31050
Unique reflctions	1518	1547	3067	4048	4087
R_{int} (%)	2.10	4.07	5.67	4.70	8.20
R_s (%)	1.89	2.32	4.14	6.61	10.8
Miller index limits	$-11 \leqslant h \leqslant 12$, $-8 \leqslant k \leqslant 8$, $-25 \leqslant l \leqslant 24$	$-12 \leqslant h \leqslant 12$, $-8 \leqslant k \leqslant 8$, $-26 \leqslant l \leqslant 26$	$-9 \leqslant h \leqslant 9$, $-28 \leqslant k \leqslant 28$, $-10 \leqslant l \leqslant 10$	$-6 \leqslant h \leqslant 9$, $-29 \leqslant k \leqslant 40$, $-10 \leqslant l \leqslant 9$	$-9 \leqslant h \leqslant 7$, $-40 \leqslant k \leqslant 34$, $-10 \leqslant l \leqslant 10$
R_1 (%)	1.80	2.43	2.83	5.67	4.88
wR_2 (%)	4.64	6.09	5.71	14.69	10.60
No. of parameters	139	140	195	285	284
Weighting scheme**	$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2 + 0.79P]$	$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2 + 0.79P]$	$w = 1/[\sigma^2(F_o^2) + (0.0093P)^2 + 1.50P]$	$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 11.52P]$	$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 5.94P]$
$\Delta\rho_{max.}$ (e Å^{-3})	0.474 at 0.76 Å from O(2)	0.581 at 0.68 Å from *A*(1)	0.718 at 0.76 Å from O(9)	1.620 at 0.87 Å from Mn(3)	1.126 at 1.31 Å from O(13)
$\Delta\rho_{min.}$ (e Å^{-3})	−0.609 at 0.32 Å from *T*(3)	−0.577 at 0.32 Å from *T*(4)	−0.700 at 0.58 Å from Mn(4)	−1.406 at 0.65 Å from Mn(6)	−1.767 at 0.58 Å from Mn(1)

* Average chemical formulae are represented in Table 1.

** The function of the weighting scheme is $w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$, where $P = (\mathrm{Max}(F_o^2) + 2F_c^2)/3$, and the parameters *a* and *b* are chosen to minimize the differences in the variances for reflections in different ranges of intensity and diffraction angle.

TABLE 3. Site occupancies of ardennite (a), tiragalloite (b) and medaite (c) samples*.

(a) **Ardennite**	Salm-Château, Belgium	Vernetto, Italy
A(1)	Mn 0.790(8), Ca 0.210(8)	Mn 0.57(1), Ca 0.43(1)
A(2)	Mn 0.865(8), Ca 0.135(8)	Mn 0.80(1), Ca 0.20(1)
M(1)	Al 1.0	Al 0.878(4), *Me* 0.122(4)**
M(2)	Al 1.0	Al 1.0
M(3)	Mg 0.42, Al 0.511(4), *Me* 0.069(4)**	Mg 0.54, Al 0.279(5), *Me* 0.181(5)**
T(1)	Si 1.0	Si 1.0
T(2)	Si 1.0	Si 1.0
T(3)	Si 1.0	Si 1.0
T(4)	Si 0.04, As 0.833(6), V 0.127(6)	As 0.730(4), Si 0.270(4)

(b) **Tiragalloite**	Gambatesa, Italy
Mn(1)	Mn 1.0
Mn(2)	Mn 1.0
Mn(3)	Mn 0.938(9), Ca 0.062(9)
Mn(4)	Mn 1.0
T(1)	Si 1.0
T(2)	Si 1.0
T(3)	Si 1.0
T(4)	As 0.700(3), Si 0.220(3), V 0.08

(c) **Medaite**	Molinello, Italy	Fianel, Switzerland
Mn(1)	Mn 1.0	Mn 1.0
Mn(2)	Mn 1.0	Mn 1.0
Mn(3)	Mn 1.0	Mn 1.0
Mn(4)	Mn 1.0	Mn 1.0
Mn(5)	Mn 0.85(2, Ca 0.15(2)	Mn 1.0
Mn(6)	Mn 1.0	Mn 1.0
T(1)	Si 1.0	Si 1.0
T(2)	Si 1.0	Si 1.0
T(3)	Si 1.0	Si 1.0
T(4)	Si 1.0	Si 1.0
T(5)	Si 1.0	Si 1.0
T(6)	V 0.595(9), As 0.175(9), Si 0.23	V 0.837(8), As 0.093(8), Si 0.07

* Mg at *M*(3) of ardennite and Si at *T*(4) of ardennite from Belgium, V at *T*(4) of tiragalloite, and Si at *T*(6) of medaite were fixed using the average chemical compositions. The *T*(4) site of the ardennite from Vernetto is considered to include also a small amount of P.

** According to the chemical analyses, *Me* in ardennite samples can be Cu + V (Salm-Château, Belgium) and Mn + Fe (Vernetto, Italy) respectively. *Me* was refined using the scattering curve of Mn.

medaite samples are shown in Fig. 1. Structure refinements in this study converged to R_1 values of 2.10−5.67 %.

The site occupancies of the *M* sites in ardennite are $(Al_{1.0})^{M(1)}(Al_{1.0})^{M(2)}[Mg_{0.42}Al_{0.511(4)}(Cu+V)_{0.069(4)}]^{M(3)}$ for the Salm-Château sample, and $[Al_{0.878(4)}(Mn+Fe)_{0.122(4)}]^{M(1)}(Al_{1.0})^{M(2)}[Mg_{0.54}Al_{0.279(5)}(Mn+Fe)_{0.181(5)}]^{M(3)}$ for the Vernetto sample. The *T*(1)−*T*(3) sites are fully occupied by Si. The occupancy of *T*(4) = $[0.833(6)As^{5+}+0.127(6)V^{5+}+0.04Si^{4+}]$ at Salm-Château and = $[0.730(4)As^{5+}+0.270(4)Si^{4+}]$ atVernetto (Table 3). Thus, as the dominant cation at *T*(4) in both samples is As^{5+}, both specimens in this study can be described as ardennite-(As). In addition to Ca, the *A*(1) and *A*(2) sites of the Salm-Château sample are assumed to contain 0.08 Mg a.p.f.u.

According to the result of structural refinement of tiragalloite, the Mn(1), Mn(2) and Mn(4) sites are fully occupied by Mn whereas Ca occupies the 7-coordinated Mn(3) site. The site occupancy of Mn(3) = [0.938(9)Mn+0.062(9)Ca]. The *T*(1)−*T*(3) sites are fully occupied by Si. The

TABLE 4. Selected bond distances (Å) in ardennite samples.

	Salm-Château, Belgium	Vernetto, Italy		Salm-Château, Belgium	Vernetto, Italy
A(1)–O(1) ×2	2.186(1)	2.218(2)	*A*(2)–O(2) ×2	2.124(1)	2.134(2)
O(5) ×2	2.313(1)	2.333(1)	O(6) ×2	2.295(1)	2.304(1)
O(12)	2.211(2)	2.227(2)	O(9)	2.147(2)	2.179(2)
Mean (V)	2.242	2.266	Mean (V)	2.197	2.211
O(3)	2.390(2)	2.376(2)	O(7)	2.509(2)	2.493(2)
O(8)	2.472(2)	2.490(2)	O(4)	2.918(2)	2.923(2)
Mean (VII)	2.296	2.314	Mean (VII)	2.345	2.353
M(1)–O(1) ×2	1.907(1)	1.906(1)	*M*(2)–O(2) ×2	1.882(1)	1.886(1)
O(3) ×2	1.999(1)	2.020(1)	O(4) ×2	1.938(1)	1.937(1)
O(10) ×2	1.8529(9)	1.862(1)	O(11) ×2	1.8804(9)	1.886(1)
Mean	1.920	1.929	Mean	1.900	1.903
M(3)–O(5)	2.166(2)	2.170(2)	*T*(1)–O(1) ×2	1.623(1)	1.625(1)
O(6)	2.043(2)	2.076(2)	O(4)	1.642(2)	1.640(2)
O(7) ×2	1.971(1)	1.992(2)	O(7)	1.662(2)	1.662(2)
O(12) ×2	1.930(1)	1.940(2)	Mean	1.638	1.638
Mean	2.002	2.018			
T(2)–O(2) ×2	1.612(1)	1.611(1)	*T*(3)–O(6) ×2	1.649(2)	1.638(2)
O(3)	1.649(2)	1.648(2)	O(8) ×2	1.652(2)	1.649(2)
O(8)	1.654(2)	1.658(2)	Mean	1.651	1.644
Mean	1.632	1.632			
T(4)–O(5) ×2	1.726(2)	1.710(2)	O(10)···O(9)	2.690(2)	2.699(3)
O(9) ×2	1.664(2)	1.645(2)	O(11)···O(10)	2.703(2)	2.721(3)
Mean	1.695	1.678	O(12)···O(11)	2.810(2)	2.820(3)

T(4) site is occupied by As, Si and V with As as the dominant cation. The average occupancy of this site = [0.700(3)As+0.220(3)Si+0.08V].

For medaite, the Mn(1), Mn(2), Mn(3) and Mn(6) sites and the 7-coordinated Mn(4) site are fully occupied by Mn. The large 7-coordinated Mn(5) site in medaite from Molinello is occupied by [0.85(2)Mn+0.15(2)Ca], whereas in medaite from Fianel the Mn(5) site is fully occupied by Mn. Sites *T*(1)–*T*(5) are fully occupied by Si. The site occupancy of *T*(4) = [0.595(9)V+0.175(9)As+0.23Si] at Molinello and = [0.827(8)V+0.093(8)As+0.07Si] at Fianel (Table 3). The Si contents are fixed, based on the average chemical compositions. The locations for V and As are varied during refinements. The dominant cation in both samples at *T*(6) is V.

The results of bond-valence calculations for the three minerals are given in Table 7. The calculated bond-valence sums and refined H positions indicate that OH groups are at O(10), O(11) and O(12) in ardennite, O(11) in tiragalloite, and O(19) in mediate. The assignment of hydroxyl groups agree with previous studies (Donnay and Allmann, 1968; Gramaccioli *et al*., 1979*b*, 1981).

Discussion

Chemical composition and Si distribution at the T sites

Structural formulae of ardennite, tiragalloite and medaite clearly indicate that in each mineral one of the *T* sites is occupied mainly by pentavalent cations, i.e. As, V and/or P. The pentavalent cations in these minerals often do not reach 1 a.p.f.u. (Fig. 2), implying that non-pentavalent cations such as Si^{4+} and Al^{3+} also contribute to the $(As,V,P)O_5$ tetrahedron in order to fill the site. However, the studies of tiragalloite and medaite by Gramaccioli *et al*. (1980*b*, 1982) concluded that replacement of As and/or V by Si is unlikely. Three reasons were put forward:

TABLE 5. Selected bond distances (Å) in tiragalloite sample.

Mn(1)−O(1)	2.199(2)	Mn(2)−O(2)	2.138(2)
O(3)	2.236(2)	O(6)	2.286(2)
O(5)	2.137(2)	O(9)	2.286(2)
O(6)	2.309(2)	O(9)′	2.272(2)
O(8)	2.102(2)	O(12)	2.219(2)
O(12)	2.264(2)	O(13)	2.079(2)
Mean	2.208	Mean	2.213
Mn(3)−O(4)	2.615(2)	Mn(4)−O(1)	2.226(2)
O(7)	2.921(2)	O(2)	2.212(2)
O(8)	2.095(2)	O(3)	2.195(2)
O(9)	2.133(2)	O(5)	2.154(2)
O(10)	2.373(2)	O(6)	2.212(2)
O(12)	2.228(2)	O(11)	2.311(2)
O(13)	2.148(2)	Mean	2.218
Mean	2.359		
T(1)−O(4)	1.680(2)	*T*(2)−O(7)	1.632(2)
O(5)	1.593(2)	O(8)	1.596(2)
O(6)	1.620(2)	O(9)	1.612(2)
O(7)	1.620(2)	O(10)	1.641(2)
Mean	1.628	Mean	1.620
T(3)−O(10)	1.650(2)	*T*(4)−O(1)	1.682(2)
O(11)	1.658(2)	O(2)	1.642(2)
O(12)	1.619(2)	O(3)	1.665(2)
O(13)	1.595(2)	O(4)	1.725(2)
Mean	1.631	Mean	1.679
O(11)···O(1)	2.725(3)		

(1) the final difference-Fourier did not show any evidence of substitution of As atoms by much lighter atoms;

(2) As−O and Si−O bond lengths are so similar that they cannot be distinguished;

(3) there is a problem of charge balance.

They also pointed out that in their chemical analyses, Si was possibly overestimated, and V and As were underestimated.

Chemical compositions evaluated in this study clearly indicate a negative correlation between

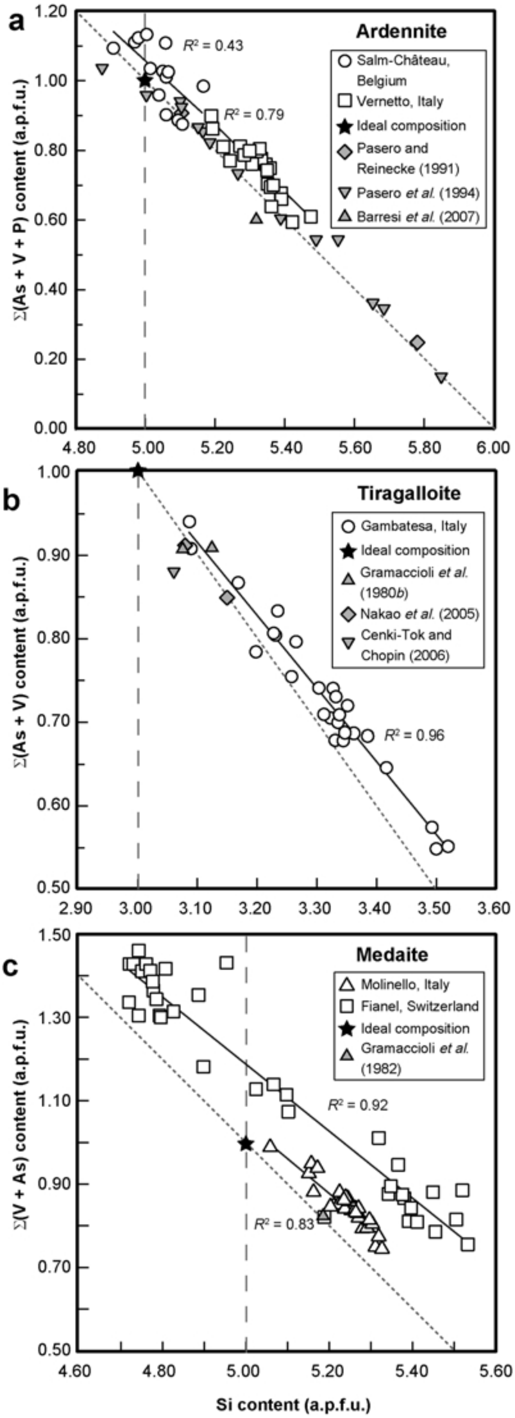

FIG. 2. Variation of Σ(As+V+P) content as a function of Si content in ardennite (*a*), tiragalloite (*b*) and medaite (*c*). The chemical composition of ardennite-(V) reported by Barresi *et al*. (2007) was re-normalized to a cation sum = 16. Associated errors of data points are considerable smaller than the symbols.

TABLE 6. Selected bond distances (Å) in medaite samples.

	Molinello, Italy	Fianel, Switzerland		Molinello, Italy	Fianel, Switzerland
Mn(1)–O(8)	2.184(4)	2.159(4)	Mn(2)–O(1)	2.144(4)	2.125(4)
O(9)	2.141(4)	2.135(4)	O(3)	2.225(5)	2.162(4)
O(11)	2.106(4)	2.099(4)	O(5)	2.343(4)	2.300(4)
O(12)	2.267(4)	2.248(4)	O(6)	2.131(4)	2.107(4)
O(12)′	2.178(4)	2.166(4)	O(15)	2.054(4)	2.041(4)
O(14)	2.330(4)	2.319(4)	O(18)	2.249(4)	2.246(4)
Mean	2.201	2.188	Mean	2.191	2.164
Mn(3)–O(2)	2.169(4)	2.144(4)	Mn(4)–O(4)	2.446(4)	2.463(4)
O(5)	2.231(4)	2.225(4)	O(7)	3.000(4)	2.957(4)
O(8)	2.247(4)	2.256(4)	O(9)	2.088(5)	2.100(4)
O(14)	2.259(4)	2.254(4)	O(12)	2.209(4)	2.195(4)
O(17)	2.082(4)	2.075(4)	O(14)	2.126(4)	2.122(4)
O(18)	2.229(4)	2.211(4)	O(16)	2.361(4)	2.351(4)
Mean	2.203	2.194	O(17)	2.166(5)	2.164(4)
			Mean	2.342	2.336
Mn(5)–O(7)	2.969(4)	2.982(4)	Mn(6)–O(1)	2.208(4)	2.224(4)
O(8)	2.181(4)	2.162(4)	O(2)	2.219(5)	2.200(4)
O(10)	2.633(5)	2.604(4)	O(3)	2.198(5)	2.182(4)
O(11)	2.112(5)	2.105(4)	O(5)	2.249(4)	2.255(4)
O(13)	2.586(5)	2.580(4)	O(6)	2.152(4)	2.167(4)
O(15)	2.107(4)	2.101(4)	O(19)	2.270(5)	2.261(4)
O(18)	2.216(4)	2.190(4)	Mean	2.216	2.215
Mean	2.401	2.389			
T(1)–O(4)	1.662(5)	1.674(4)	*T*(2)–O(7)	1.652(4)	1.650(4)
O(5)	1.622(5)	1.624(4)	O(8)	1.614(4)	1.620(4)
O(6)	1.592(4)	1.590(4)	O(9)	1.601(5)	1.586(4)
O(7)	1.642(5)	1.632(4)	O(10)	1.642(5)	1.638(4)
Mean	1.630	1.630	Mean	1.627	1.624
T(3)–O(10)	1.649(5)	1.657(4)	*T*(4)–O(13)	1.643(5)	1.648(4)
O(11)	1.598(4)	1.584(4)	O(14)	1.615(4)	1.611(4)
O(12)	1.611(5)	1.614(4)	O(15)	1.598(5)	1.603(4)
O(13)	1.628(5)	1.627(4)	O(16)	1.643(5)	1.638(4)
Mean	1.622	1.621	Mean	1.625	1.625
T(5)–O(16)	1.649(5)	1.657(4)	*T*(6)–O(1)	1.698(4)	1.685(4)
O(17)	1.592(4)	1.588(4)	O(2)	1.648(5)	1.649(4)
O(18)	1.617(4)	1.630(4)	O(3)	1.680(5)	1.669(4)
O(19)	1.665(5)	1.654(4)	O(4)	1.785(5)	1.768(4)
Mean	1.631	1.632	Mean	1.703	1.693
O(19)···O(1)	2.790(6)	2.774(5)			

Σ(As+V±P) and Si contents (Fig. 2). In all specimens, the Σ(As+V±P) content increases with decreasing Si content (Fig. 2). The Σ(As+V+P) *vs* Si contents of ardennite (this study) deviate slightly from the ideal line (dashed line in Fig. 2*a*). Moreover, Σ(As+V) and Si of tiragalloite are 0.55–0.94 and 3.09–3.52 a.p.f.u. respectively, and their variations are greater than the error of chemical analysis. The Si content of tiragalloite reported by Nakao *et al*. (2005), and

TABLE 7. Bond valence sum (v.u.) in ardennite, tiragalloite and medaite samples.

	Ardennite*			Tiragalloite		Medaite	
Site	Salm-Chãteau, Belgium	Vernetto, Italy	Site	Gambatesa, Italy	Site	Molinello, Italy	Fianel, Switzerland
A(1)	2.02	2.09	Mn(1)	1.98	Mn(1)	2.02	2.09
A(2)	2.00	1.99	Mn(2)	1.96	Mn(2)	2.09	2.25
M(1)	2.70	2.77	Mn(3)	1.93	Mn(3)	1.99	2.05
M(2)	2.82	2.80	Mn(4)	1.90	Mn(4)	1.96	1.96
M(3)	2.70	2.87	*T*(1)	4.14	Mn(5)	1.88	2.00
T(1)	4.03	4.03	*T*(2)	4.22	Mn(6)	1.91	1.91
T(2)	4.10	4.09	*T*(3)	4.11	*T*(1)	4.13	4.12
T(3)	3.89	3.96	*T*(4)	4.76	*T*(2)	4.15	4.19
T(4)	4.87	4.66	O(1)	1.81	*T*(3)	4.21	4.23
O(1)	1.88	1.90	O(2)	2.02	*T*(4)	4.17	4.17
O(2)	2.00	1.99	O(3)	1.87	*T*(5)	4.11	4.10
O(3)	1.91	1.94	O(4)	2.06	*T*(6)	4.70	4.97
O(4)	1.89	1.90	O(5)	1.90	O(1)	1.89	1.97
O(5)	1.93	1.93	O(6)	1.88	O(2)	2.02	2.10
O(6)	1.91	1.95	O(7)	2.13	O(3)	1.88	2.03
O(7)	2.05	2.11	O(8)	2.01	O(4)	2.04	2.08
O(8)	2.11	2.11	O(9)	2.02	O(5)	1.87	1.89
O(9)	1.72	1.65	O(10)	2.18	O(6)	1.91	1.93
O(10)	1.07	1.09	O(11)	1.20	O(7)	2.05	2.08
O(11)	0.99	0.97	O(12)	1.96	O(8)	2.08	2.07
O(12)	1.42	1.52	O(13)	1.98	O(9)	1.95	1.98
					O(10)	2.08	2.07
					O(11)	1.99	2.02
					O(12)	2.03	2.06
					O(13)	2.15	2.30
					O(14)	1.99	2.01
					O(15)	2.06	2.05
					O(16)	2.18	2.18
					O(17)	1.95	1.98
					O(18)	1.99	1.98
					O(19)	1.21	1.24

* In ardennite, *A*(1) and *A*(2) are calculated as 7-coordinated polyhedra.

Cenki-Tok and Chopin (2006) is also >3 a.p.f.u. (Fig. 2*b*). Furthermore, the Si content in medaite from Molinello is always >5 a.p.f.u., and the Si variation in the Fianel specimen is larger than that of the Molinello specimen (Fig. 2*c*).

The regression line for the Fianel medaite deviates strongly from ideal substitution (dashed line in Fig. 2*c*) due to the large value for Σ(V+As). This indicates that the medaite from Fianel contains a small amount of V^{3+} occupying the octahedrally-coordinated sites. Thus, we conclude that in some samples Si replaces some of the As, V and P, and formula normalization based on the *T* cations should not be used because of the possibility of octahedrally-coordinated V^{3+}. Instead, normalization on total cations (except H) is obviously a more appropriate normalization scheme.

Cation distribution and structural variation of ardennite

The cell parameters of ardennite from Vernetto, Italy, are larger than those of the Salm-Château specimen. This can be explained by the larger Ca content in the Vernetto specimen compared to the Salm-Château specimen. Calcium preferentially occupies the *A*(1) rather than the *A*(2) site (Table 3). Pasero *et al*. (1994) argued that Ca preferentially enters the larger *A*(2) site and Mg the smaller *A*(1) site. However, their reported

TABLE 8. Site occupancies and interatomic distances (Å) of the 0-bridging and 1-bridging (As^{5+},V^{5+},P^{5+},Si^{4+})O_4 tetrahedra.

Mineral name	Site	Occupancy	Mean ionic radius*	——— No-bridging bonds ———				<*T*–O>	Sample locality or sample name	References etc
0-bridging tetrahedra										
Ardennite	*T*(4)	Si 0.04, As 0.833(6), V 0.127(6)	0.335	1.664(2)	1.664(2)	1.726(2)	1.726(2)	1.695	Salm-Château, Belgium	This study
	T(4)	As 0.730(4), Si 0.270(4)	0.315	1.645(2)	1.645(2)	1.710(2)	1.710(2)	1.678	Vernetto, Italy	This study
	(As,V)	As 0.905, V 0.095	0.337	1.675(9)	1.675(9)	1.721(10)	1.721(10)	1.698	Salm-Château, Belgium	Donnay and Allmann (1968)
Palenzonaite	*Z*	V 0.975(4), As 0.025	0.355	1.723(2)	1.723(2)	1.723(2)	1.723(2)	1.723	Val Graveglia, Italy	Basso (1987): Palenzonite is a vanadate and belongs to the garnet group.
Calderonite	*T*(1)	V 0.977(29)	0.347	1.649(17)	1.707(11)	1.707(11)	1.799(12)	1.716	Santa Marta, Spain	Del Tánago *et al*. (2003): Calderonite is a vanadate mineral comprising a mixture of (V,Si,As,P)O_4.
	T(2)	V 0.859, Si 0.085, As 0.016, P 0.003	0.333	1.675(16)	1.679(15)	1.727(10)	1.727(10)	1.702		
Dixenite	*T*(1)	Si 0.86(1), As 0.14	0.271	1.620(9)	1.641(5)	1.641(5)	1.641(5)	1.636	Långban, Sweden	Araki and Moore (1981)
	T(2)	Si 0.60(1), As 0.40	0.290	1.662(9)	1.669(5)	1.669(5)	1.669(5)	1.667		
	T(3)	Si 0.24(1), As 0.76	0.317	1.675(5)	1.675(5)	1.675(5)	1.681(10)	1.676		
Johninesite		As 1.00	0.335	1.678(10)	1.694(7)	1.729(8)	1.740(6)	1.710	Kombat mine, Namibia	Grice and Dunn (1994)
Mineral name	Site	Occupancy	Mean ionic radius*	— No-bridging bonds —			Bridging bond	<*T*–O>	Sample locality or sample name	References etc
1-bridging tetrahedra										
Tiragalloite	*T*(4)	As 0.700(3), Si 0.220(3), V 0.08	0.320	1.642(2)	1.665(2)	1.682(2)	1.725(2)	1.679	Gambatesa, Italy	This study
	As(1)	As 1.0	0.335	1.654(5)	1.671(5)	1.687(5)	1.740(5)	1.688	Molinello, Italy	Gramaccioli *et al*. (1979*b*)**
Medaite	*T*(6)	V 0.595(9), As 0.175(9), Si 0.23	0.330	1.648(5)	1.680(5)	1.698(4)	1.785(5)	1.703	Molinello, Italy	This study
	T(6)	V 0.837(8), As 0.093(8), Si 0.07	0.343	1.649(4)	1.669(4)	1.685(4)	1.768(4)	1.693	Fianel, Swtizerland	This study

	V	As 0.19, V 0.81	0.351	1.653(4)	1.655(4)	1.698(4)	1.790(4)	1.699	Molinello, Italy	Gramaccioli *et al.* (1981)**
Saneroite	*T*(6)	Si 0.42(2), V 0.49(1), As 0.09	0.313	1.651(1)	1.662(1)	1.682(1)	1.739(1)	1.684	Molinello 1	Nagashima and Armbruster (in press)
	T(6)	Si 0.34(2), V 0.54(1), As 0.14	0.327	1.657(2)	1.675(2)	1.684(2)	1.755(2)	1.693	Molinello 2	
	T(6)	Si 0.40(2), V 0.52(1), As 0.09	0.319	1.655(1)	1.672(1)	1.683(1)	1.750(1)	1.690	Fianel, Swtizerland	
	T(6)	Si 0.50, V 0.50	0.308	1.644(1)	1.656(1)	1.690(1)	1.736(1)	1.682	Val Graveglia, Italy	Basso and Della Giusta (1980)

* Mean ionic radius was calculated using Si^{4+IV} = 0.26, As^{5+IV} = 0.335 , V^{5+IV} = 0.355, and P^{5+IV} = 0.17 Å after Shannon (1976).

** Bond distances were calculated from the atomic positions. Standard deviations were estimated from those of atomic positions.

Note: Scheuchzerite, $Na(Mn,Mg)_9[VSi_9O_{28}(OH)](OH)_3$, and turtmannite, $(Mn,Mg)_{22.5}Mg_{3-3x}[(V,As)O_4]_3[SiO_4]_3[AsO_3]_xO_{5-5x}(OH)_{20+x}$, were ignored because the former had V disorder in the tetrahedral site (Brugger *et al.*, 2006), and the latter showed three different occupational variants (Brugger *et al.*, 2001).

bond lengths do not agree with the assumed coordination and atom labels.

The *M*(3) site is occupied by Mg^{2+} and trivalent cations such as Al^{3+} and Fe^{3+}, whereas the *M*(1) and *M*(2) sites are occupied solely by trivalent cations. Small amounts of Fe^{3+} and Mn^{3+} also occupy *M*(1). The smallest octahedron, *M*(2), is fully occupied by Al. Mean *M*(2)−O distances of ardennite are almost constant, 1.90(1) Å (Donnay and Allmann, 1968; Pasero *et al.*, 1994; this study). The volumes of *M* octahedra decrease as *M*(3) >*M*(1) >*M*(2). Thus, larger trivalent cations, such as Mn^{3+}, Fe^{3+} and V^{3+}, distribute over *M*(1) and *M*(3), and their site preference is *M*(3) >*M*(1).

Allmann and Donnay (1971) discussed the structural similarity between ardennite and pumpellyite. Subordinate divalent cations occupy *M*(3) in ardennite as well as *X* in pumpellyite. Based on their topology, $M(3)O_6$ octahedra of ardennite and XO_6 octahedra of pumpellyite are similar, In addition, $M(1)O_6$ and $M(2)O_6$ octahedra (ardennite) and YO_6 octahedra (pumpellyite) are also similar. Three H positions in ardennite were determined in this study. The relation between donor and acceptor O atoms and their hydrogen bonds in ardennite can be summarized as follows: O(10)−H(10)···O(9), O(11)−H(11)···O(10) and O(12)−H(12)··· O(11). Although H positions have already been reported by Pasero *et al*. (1994), our coordinates (Table S1) do not confirm those given by these authors.

Cation distribution and structural variation in tiragalloite and medaite

Unit-cell parameters of the Fianel medaite are smaller than those of the Molinello specimen, a result of larger Ca content in the Molinello specimen. The structure of medaite has two 7-coordinated polyhedra, Mn(4) and Mn(5). As the $Mn(5)O_7$ polyhedron is larger than $Mn(4)O_7$, Ca preferentially occupies Mn(5).

Tiragalloite and medaite have silanol groups (Si−OH), which are categorized in a set of $T(OH)O_3$ tetrahedra with one bridging O atom (Nyfeler and Armbruster, 1998). As predicted by Nyfeler and Armbruster (1998), the silanol groups O(11) (in tiragalloite) and O(19) (in medaite) represent the longest *T*−O bonds in the corresponding tetrahedra. In tiragalloite, the *T*(3)−O(11) distance is 1.658 Å, and the average of non-hydroxylated bonds in the same tetrahedron is 1.621 Å. In medaite, the *T*(5)–O(19) distance is 1.654–1.665 Å, and the average of the non-hydroxylated bonds is 1.619–1.625 Å.

Structural variation of the $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ *tetrahedral site*

Several silicate minerals have $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedra (Table 8). Such tetrahedral sites can be categorized by the number of bridging apices to other tetrahedral sites. The $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedra of ardennite are isolated (0-bridging) (Fig. 3*a*), and those of tiragalloite and medaite terminate a chain and have therefore one connected apex (1-bridging) (Fig. 3*b*,*c*).

The 0-bridging $(As,V,P,Si)O_4$ tetrahedron shows a positive correlation between <*T*–O> and mean ionic radius (R^2 = 0.94 in Fig. 4*a*), whereas the corresponding relation for 1-bridging tetrahedra is less pronounced (R^2 = 0.47 in Fig. 4*b*). The 1-bridging tetrahedra are characterized by an expanded bridging bond. In the case of tiragalloite, *T*(4)–O(4) (1.725Å) is the longest bond in the $T(4)O_4$ tetrahedron. The O(4) atom is also shared with the $T(1)O_4$ and the $Mn(3)O_7$ polyhedron. The bond *T*(1)–O(4) (1.680 Å) is also the longest within the SiO_4 tetrahedron. According to Pauling's rule, O(4) receives 2.48 valence units (v.u.), as the sum of 4/4 from *T*(1), 4.78/4 from *T*(4) and 2/7 from Mn(3). This value is larger than the expected 2 v.u. of O. Thus, O(4) is 'over-bonded' to satisfy the charge requirement of Σ(As+V+Si). In order to balance the excess bond valence, *T*(1)–O(4) and *T*(4)–O(4) expand. A similar balancing effect is also observed for medaite; *T*(6)–O(4) (1.768–1.785 Å) and *T*(1)–O(4) (1.662–1.674 Å) are the longest bonds in the corresponding tetrahedra.

Other silicate minerals possess 2-, 3- and 4-connected $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedra.

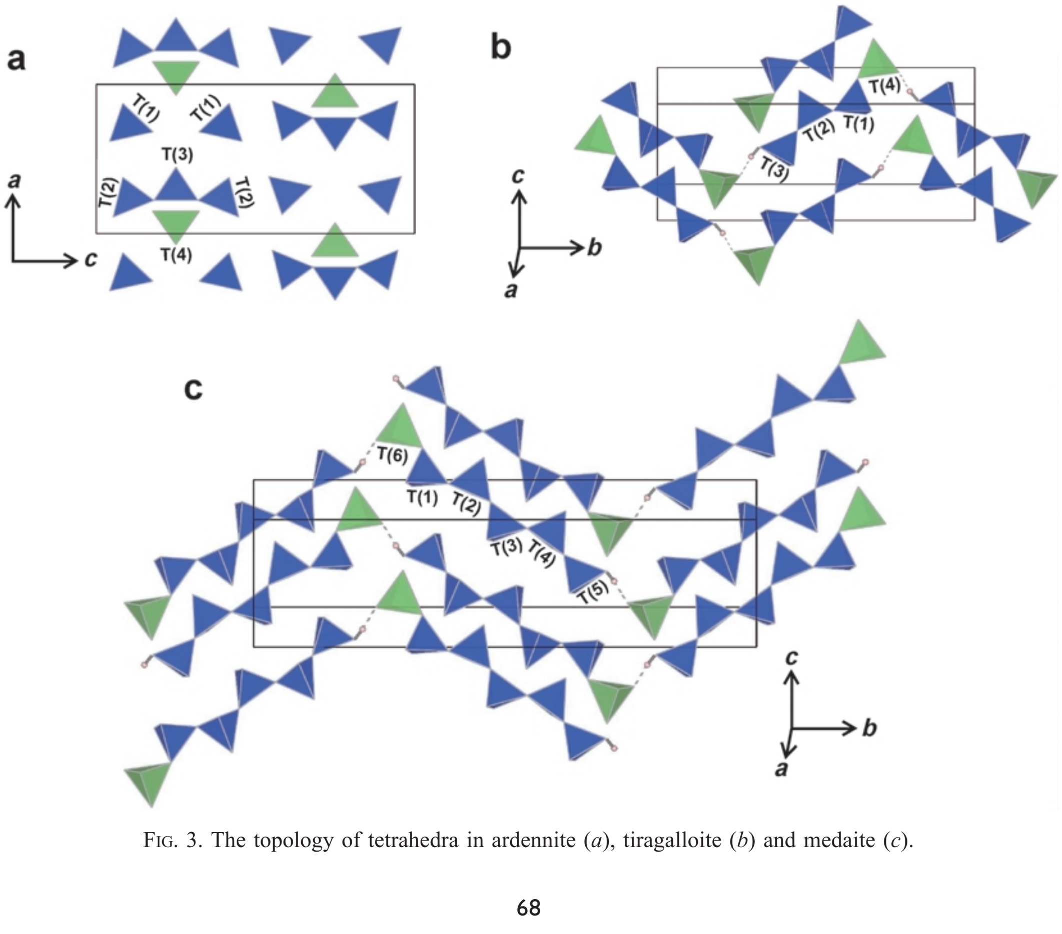

FIG. 3. The topology of tetrahedra in ardennite (*a*), tiragalloite (*b*) and medaite (*c*).

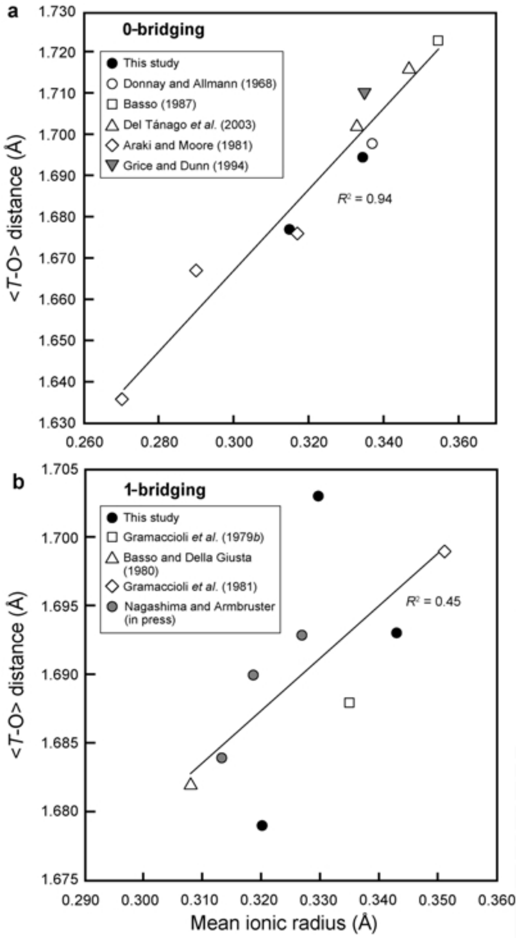

FIG. 4. Variation of <*T*–O> distances for 0-bridging $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedra (Å) (*a*), and 1-bridging $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedra (*b*) as a function of mean ionic radius of $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedron (Å) based on the data shown in Table 8.

The $As^{5+}O_4$ tetrahedron of kolicite $(Mn_7(OH)_4[As_4Zn_4Si_2O_{16}(OH)_4]$, Peacor, 1980) forms the centre of a triplet of tetrahedra and has two adjacent ZnO_4 tetrahedra. The $(As^{5+},Si^{4+})O_4$ tetrahedron of Si-rich bergslagite $[CaBe(As^{5+},Si)O_4(OH)]$ is linked to three BeO_4 tetrahedra (Raade *et al.*, 2006).

The $(As^{5+},Si^{4+})O_4$ tetrahedra in filatovite $(K[(Al,Zn)_2(As^{5+},Si)_2O_8]$, a member of the feldspar group, are incorporated into a tetrahedral framework (Filatov *et al.*, 2004),. There are four crystallographically independent tetrahedra; two are $(As^{5+},Si^{4+})O_4$ and the other two are $(Al,Zn)O_4$ tetrahedra. Each $(As^{5+},Si^{4+})O_4$ tetrahedron is linked to three $(Al,Zn)O_4$ and one $(As^{5+},Si^{4+})O_4$. The 2-, 3- and 4-bridging $As^{5+}O_4$ tetrahedra mentioned above maintain oxygen charge balance by low valence at adjacent *T* sites which are occupied by Zn^{2+}, Be^{2+} and Al^{3+}. Thus, the scheme to obtain charge balance is different from the 0- and 1-bridging tetrahedra, described for ardennite, and tiragalloite/medaite respectively.

Another example of isolated (0-bridging) tetrahedra occupied by tetra- and pentavalent cations is P-rich olivine reported by Tropper *et al.* (2004) and Schneider and Tropper (2009). The mineral contains up to 23 wt.% P_2O_5 (Schneider and Tropper 2009). Tropper *et al.* (2004) suggested the coupled substitution of $2P^{5+} + (\square)M_{(1,2)} = 2Si^{4+} + (Mg, Fe)M_{(1,2)}$ for the olivine structure. The structural analysis of P-rich olivine has not yet been reported. Thus, a further systematic study of minerals with mixed valence $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedra is required in order to understand the mechanism of charge balance and its effect on the crystal structure.

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TABLE S1. Refined atomic positions of ardennite samples.

Site		Salm-Château, Belgium	Vernetto, Italy	Site		Salm-Château, Belgium	Vernetto, Italy	Site		Salm-Château, Belgium	Vernetto, Italy
A1	x	0.94486(4)	0.94617(6)	T4 (As)	x	0.04243(3)	0.04264(5)	O8	x	0.22317(18)	0.2258(2)
	y	1/4	1/4		y	3/4	3/4		y	1/4	1/4
	z	0.155325(18)	0.15546(3)		z	1/4	1/4		z	0.18086(8)	0.18087(11)
	U_{eq}	0.01014(10)	0.01326(15)		U_{eq}	0.00637(10)	0.00988(16)		U_{eq}	0.0101(3)	0.0115(4)
A2	x	0.39566(4)	0.39662(5)	O1	x	0.12881(12)	0.13036(15)	O9	x	0.15183(19)	0.1502(2)
	y	3/4	3/4		y	0.02530(16)	0.0263(2)		y	3/4	3/4
	z	0.159978(17)	0.15995(3)		z	-0.08282(6)	-0.08177(8)		z	0.17639(8)	0.17743(12)
	U_{eq}	0.00949(10)	0.01241(14)		U_{eq}	0.00851(19)	0.0103(3)		U_{eq}	0.0135(3)	0.0162(4)
M1	x	0	0	O2	x	0.62411(12)	0.62384(15)	O10	x	0.11259(17)	0.1118(2)
	y	0	0		y	-0.01905(16)	-0.0193(2)		y	3/4	3/4
	z	0	0		z	-0.08292(6)	-0.08283(8)		z	0.03231(8)	0.03336(11)
	U_{eq}	0.00570(13)	0.0080(2)		U_{eq}	0.00852(19)	0.0102(3)		U_{eq}	0.0079(3)	0.0105(4)
M2	x	1/2	1/2	O3	x	0.11086(17)	0.1113(2)	O11	x	0.61341(17)	0.6139(2)
	y	0	0		y	1/4	1/4		y	1/4	1/4
	z	0	0		z	0.05260(8)	0.05398(11)		z	0.03609(8)	0.03572(11)
	U_{eq}	0.00698(13)	0.00810(18)		U_{eq}	0.0088(3)	0.0124(4)		U_{eq}	0.0080(3)	0.0100(4)
M3	x	0.67916(7)	0.68069(8)	O4	x	0.61717(17)	0.6163(2)	O12	x	0.69784(18)	0.6979(2)
	y	-0.00151(9)	-0.00158(12)		y	3/4	3/4		y	1/4	1/4
	z	1/4	1/4		z	0.04181(8)	0.04145(11)		z	0.18253(8)	0.18221(11)
	U_{eq}	0.00767(19)	0.0086(2)		U_{eq}	0.0084(3)	0.0102(4)		U_{eq}	0.0125(3)	0.0126(4)
T1	x	0.76474(6)	0.76328(8)	O5	x	0.92758(19)	0.9287(2)	H10	x	0.126(5)	0.123(6)
	y	3/4	3/4		y	-0.0081(2)	-0.0117(4)		y	3/4	3/4
	z	0.09695(3)	0.09619(4)		z	1/4	1/4		z	0.0845(6)	0.0857(6)
	U_{eq}	0.00363(11)	0.00791(17)		U_{eq}	0.0123(3)	0.0155(4)		U_{iso}	0.05	0.05
T2	x	0.27693(6)	0.27823(8)	O6	x	0.44487(19)	0.4435(2)	H11	x	0.7188(19)	0.715(2)
	y	1/4	1/4		y	0.0110(3)	0.0122(3)		y	1/4	1/4
	z	0.09523(3)	0.09517(4)		z	1/4	1/4		z	0.018(2)	0.014(2)
	U_{eq}	0.00626(12)	0.00858(17)		U_{eq}	0.0122(3)	0.0128(4)		U_{iso}	0.05	0.05
T3	x	0.34294(9)	0.34387(12)	O7	x	0.68104(18)	0.6795(2)	H12	x	0.657(5)	0.657(5)
	y	1/4	1/4		y	3/4	3/4		y	1/4	1/4
	z	1/4	1/4		z	0.17757(8)	0.17642(11)		z	0.1337(10)	0.1332(11)
	U_{eq}	0.00808(15)	0.0090(2)		U_{eq}	0.0115(3)	0.0130(4)		U_{iso}	0.05	0.05

TABLE S2. Anisotropic mean-square displacement parameters of ardennite samples.

Site		Salm-Château, Belgium	Vernetto, Italy	Site		Salm-Château, Belgium	Vernetto, Italy	Site		Salm-Château, Belgium	Vernetto, Italy
A1	U_{11}	0.01181(17)	0.0167(2)	T3	U_{11}	0.0096(3)	0.0109(5)	O6	U_{11}	0.0150(8)	0.0162(10)
	U_{22}	0.00971(15)	0.0098(3)		U_{22}	0.0078(3)	0.0058(5)		U_{22}	0.0110(6)	0.0068(9)
	U_{33}	0.00890(17)	0.0133(3)		U_{33}	0.0069(3)	0.0102(5)		U_{33}	0.0106(7)	0.0155(10)
	U_{23}	0	0		U_{23}	0	0		U_{23}	0	0
	U_{13}	0.00230(12)	0.00391(19)		U_{13}	0	0		U_{13}	0	0
	U_{12}	0	0		U_{12}	0	0		U_{12}	0.0018(5)	0.0025(8)
A2	U_{11}	0.01232(17)	0.0172(2)	T4(As)	U_{11}	0.00671(16)	0.0115(2)	O7	U_{11}	0.0113(7)	0.0124(9)
	U_{22}	0.00849(15)	0.0079(2)		U_{22}	0.00574(14)	0.0057(2)		U_{22}	0.0155(7)	0.0145(10)
	U_{33}	0.00766(16)	0.0121(3)		U_{33}	0.00666(16)	0.0124(3)		U_{33}	0.0077(7)	0.0120(10)
	U_{23}	0	0		U_{23}	0	0		U_{23}	0	0
	U_{13}	-0.00129(11)	-0.00152(18)		U_{13}	0	0		U_{13}	0.0025(5)	0.0022(8)
	U_{12}	0	0		U_{12}	0	0		U_{12}	0	0
M1	U_{11}	0.0060(3)	0.0084(3)	O1	U_{11}	0.0088(5)	0.0109(6)	O8	U_{11}	0.0115(7)	0.0123(9)
	U_{22}	0.0051(2)	0.0058(4)		U_{22}	0.0085(4)	0.0071(6)		U_{22}	0.0123(6)	0.0122(10)
	U_{33}	0.0060(3)	0.0097(4)		U_{33}	0.0082(5)	0.0129(7)		U_{33}	0.0066(6)	0.0099(9)
	U_{23}	-0.00012(18)	0.0000(3)		U_{23}	-0.0007(3)	-0.0011(5)		U_{23}	0	0
	U_{13}	0.0003(2)	0.0008(3)		U_{13}	0.0010(4)	0.0015(5)		U_{13}	0.0016(5)	0.0007(7)
	U_{12}	0.00041(19)	0.0003(3)		U_{12}	-0.0008(3)	-0.0010(5)		U_{12}	0	0
M2	U_{11}	0.0076(3)	0.0088(4)	O2	U_{11}	0.0100(5)	0.0107(6)	O9	U_{11}	0.0118(7)	0.0169(10)
	U_{22}	0.0065(2)	0.0058(4)		U_{22}	0.0079(4)	0.0073(6)		U_{22}	0.0189(7)	0.0163(11)
	U_{33}	0.0068(3)	0.0097(4)		U_{33}	0.0077(5)	0.0125(7)		U_{33}	0.0098(7)	0.0153(11)
	U_{23}	-0.00012(18)	-0.0004(3)		U_{23}	0.0007(3)	0.0001(5)		U_{23}	0	0
	U_{13}	0.0003(2)	0.0003(3)		U_{13}	0.0017(4)	0.0016(5)		U_{13}	0.0018(6)	0.0004(8)
	U_{12}	0.00010(19)	-0.0003(3)		U_{12}	0.0008(3)	0.0005(5)		U_{12}	0	0
M3	U_{11}	0.0100(3)	0.0109(4)	O3	U_{11}	0.0071(6)	0.0101(9)	O10	U_{11}	0.0077(6)	0.0082(8)
	U_{22}	0.0061(3)	0.0054(4)		U_{22}	0.0100(6)	0.0148(10)		U_{22}	0.0088(6)	0.0106(9)
	U_{33}	0.0069(3)	0.0096(4)		U_{33}	0.0094(7)	0.0125(10)		U_{33}	0.0071(6)	0.0126(10)
	U_{23}	0	0		U_{23}	0	0		U_{23}	0	0
	U_{13}	0	0		U_{13}	-0.0008(5)	-0.0012(8)		U_{13}	-0.0007(5)	-0.0007(8)
	U_{12}	-0.00061(19)	-0.0002(3)		U_{12}	0	0		U_{12}	0	0
T1	U_{11}	0.0032(2)	0.0075(3)	O4	U_{11}	0.0079(6)	0.0099(9)	O11	U_{11}	0.0073(6)	0.0081(8)
	U_{22}	0.0047(2)	0.0070(3)		U_{22}	0.0084(6)	0.0079(9)		U_{22}	0.0094(6)	0.0090(9)
	U_{33}	0.0030(2)	0.0093(4)		U_{33}	0.0091(7)	0.0128(10)		U_{33}	0.0075(6)	0.0128(10)
	U_{23}	0	0		U_{23}	0	0		U_{23}	0	0
	U_{13}	0.00001(17)	0.0000(3)		U_{13}	-0.0014(5)	-0.0017(7)		U_{13}	0.0000(5)	0.0006(7)
	U_{12}	0	0		U_{12}	0	0		U_{12}	0	0
T2	U_{11}	0.0060(2)	0.0085(3)	O5	U_{11}	0.0128(7)	0.0145(9)	O12	U_{11}	0.0109(7)	0.0127(9)
	U_{22}	0.0068(2)	0.0071(3)		U_{22}	0.0098(6)	0.0089(10)		U_{22}	0.0179(7)	0.0138(10)
	U_{33}	0.0059(2)	0.0102(4)		U_{33}	0.0145(7)	0.0231(12)		U_{33}	0.0086(7)	0.0114(10)
	U_{23}	0	0		U_{23}	0	0		U_{23}	0	0
	U_{13}	-0.00004(18)	-0.0002(3)		U_{13}	0	0		U_{13}	0.0005(5)	0.0010(8)
	U_{12}	0	0		U_{12}	0.0021(5)	0.0033(8)		U_{12}	0	0

TABLE S3. Refined atomic positions and thermal mean-square displacement parameters of tiragalloite sample.

Site	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	0.25888(6)	0.64825(2)	-0.14680(7)	0.00929(11)	0.0104(2)	0.0083(2)	0.0092(3)	0.00069(17)	0.00141(16)	0.00102(16)
Mn2	-0.45780(6)	0.58405(2)	0.54562(7)	0.00894(11)	0.0084(2)	0.0087(2)	0.0099(3)	-0.00033(18)	0.00198(16)	0.00024(16)
Mn3	0.76249(7)	0.50952(2)	0.24390(7)	0.01063(14)	0.0105(2)	0.0115(2)	0.0100(3)	-0.00320(19)	0.00132(17)	-0.00254(17)
Mn4	0.05119(7)	0.74619(2)	0.13817(7)	0.01148(11)	0.0114(2)	0.0100(2)	0.0131(3)	-0.00246(19)	0.00120(17)	-0.00006(16)
T1	0.23096(11)	0.36814(4)	0.08013(11)	0.00682(16)	0.0073(3)	0.0059(4)	0.0072(4)	-0.0002(3)	0.0004(3)	-0.0002(3)
T2	0.26756(11)	0.52089(4)	0.16161(11)	0.00635(16)	0.0071(3)	0.0060(4)	0.0060(4)	-0.0002(3)	0.0004(3)	0.0007(3)
T3	0.04853(11)	0.59791(4)	0.44118(11)	0.00664(16)	0.0064(3)	0.0068(4)	0.0068(4)	-0.0001(3)	0.0003(3)	0.0003(3)
T4(As)	0.42991(5)	0.301643(17)	-0.21229(5)	0.00689(11)	0.00788(16)	0.00689(18)	0.0060(2)	0.00001(14)	0.00103(12)	0.00001(13)
O1	0.2698(3)	0.23819(10)	-0.1842(3)	0.0108(4)	0.0117(10)	0.0081(10)	0.0131(13)	0.0005(8)	0.0037(8)	-0.0024(8)
O2	0.4629(3)	0.31992(10)	-0.4189(3)	0.0127(5)	0.0204(11)	0.0098(10)	0.0084(12)	0.0011(8)	0.0041(8)	0.0017(8)
O3	0.6466(3)	0.28808(12)	-0.0897(3)	0.0160(5)	0.0108(10)	0.0230(13)	0.0137(13)	-0.0022(10)	-0.0014(8)	0.0065(9)
O4	0.3176(3)	0.36971(10)	-0.1209(3)	0.0104(4)	0.0132(10)	0.0112(10)	0.0071(12)	-0.0009(8)	0.0019(8)	-0.0001(8)
O5	0.0307(3)	0.32440(10)	0.0719(3)	0.0107(4)	0.0099(9)	0.0085(10)	0.0139(13)	-0.0013(9)	0.0030(8)	-0.0023(8)
O6	0.4144(3)	0.34328(11)	0.2202(3)	0.0106(4)	0.0113(10)	0.0125(11)	0.0080(12)	0.0005(8)	0.0014(8)	0.0010(8)
O7	0.1774(3)	0.44612(10)	0.1148(3)	0.0116(5)	0.0117(10)	0.0078(10)	0.0147(13)	-0.0041(9)	-0.0019(8)	0.0006(8)
O8	0.3024(3)	0.55379(11)	-0.0251(3)	0.0108(4)	0.0142(10)	0.0105(10)	0.0078(12)	0.0021(8)	0.0011(8)	-0.0010(8)
O9	0.4587(3)	0.51549(10)	0.3078(3)	0.0090(4)	0.0080(9)	0.0108(10)	0.0079(12)	0.0005(8)	-0.0007(7)	0.0007(8)
O10	0.0869(3)	0.55892(11)	0.2551(3)	0.0104(4)	0.0110(9)	0.0125(11)	0.0079(12)	-0.0033(8)	0.0016(8)	0.0033(8)
O11	0.0516(3)	0.67846(10)	0.3860(3)	0.0138(5)	0.0204(11)	0.0068(10)	0.0136(13)	0.0013(9)	-0.0006(9)	-0.0018(8)
O12	0.2224(3)	0.58598(10)	0.6022(3)	0.0090(4)	0.0091(9)	0.0101(10)	0.0075(12)	0.0004(8)	0.0001(7)	0.0006(7)
O13	-0.1667(3)	0.56929(10)	0.4777(3)	0.0099(4)	0.0079(9)	0.0117(10)	0.0104(12)	-0.0017(9)	0.0025(8)	-0.0010(8)
H11	0.110(6)	0.705(2)	0.487(4)	0.05 (U_{iso})						

TABLE S4. Refined atomic positions of medaite samples.

Site		Molinello, Italy	Fianel, Switzerland	Site		Molinello, Italy	Fianel, Switzerland	Site		Molinello, Italy	Fianel, Switzerland
Mn1	x	0.37011(13)	0.37041(15)	T6 (V)	x	0.49437(15)	0.49247(14)	O11	x	1.0746(6)	1.0739(6)
	y	0.02233(3)	0.02258(3)		y	0.21308(3)	0.21348(3)		y	0.03675(14)	0.03680(14)
	z	0.15464(13)	0.15426(13)		z	0.88117(15)	0.88249(13)		z	0.2102(6)	0.2089(6)
	U_{eq}	0.0127(2)	0.0143(2)		U_{eq}	0.0131(4)	0.0057(4)		U_{eq}	0.0156(9)	0.0113(9)
Mn2	x	0.68234(14)	0.68345(14)	O1	x	0.6574(6)	0.6538(6)	O12	x	0.6878(6)	0.6867(6)
	y	0.31735(3)	0.31660(3)		y	0.25717(15)	0.25747(13)		y	0.02268(14)	0.02236(13)
	z	0.02437(14)	0.02673(13)		z	0.8581(6)	0.8580(6)		z	0.0751(6)	0.0750(5)
	U_{eq}	0.0134(2)	0.0094(2)		U_{eq}	0.0158(9)	0.0120(9)		U_{eq}	0.0131(9)	0.0087(9)
Mn3	x	0.45590(13)	0.45452(14)	O2	x	0.4515(7)	0.4512(6)	O13	x	0.8956(6)	0.8977(6)
	y	0.13620(3)	0.13659(3)		y	0.20247(15)	0.20246(13)		y	-0.04391(14)	-0.04412(13)
	z	0.22327(13)	0.22263(12)		z	1.0881(6)	1.0905(5)		z	0.2431(7)	0.2448(6)
	U_{eq}	0.0135(2)	0.0093(2)		U_{eq}	0.0165(9)	0.0106(9)		U_{eq}	0.0184(10)	0.0115(9)
Mn4	x	0.66860(14)	0.67002(13)	O3	x	0.2786(7)	0.2760(6)	O14	x	0.6309(6)	0.6307(6)
	y	0.08722(3)	0.08672(3)		y	0.22578(16)	0.22427(14)		y	-0.09010(14)	-0.09014(13)
	z	0.91799(14)	0.91860(12)		z	0.7603(7)	0.7605(6)		z	0.0123(6)	0.0127(5)
	U_{eq}	0.0143(2)	0.0086(2)		U_{eq}	0.0200(10)	0.0145(10)		U_{eq}	0.0135(9)	0.0086(9)
Mn5	x	0.14129(15)	0.14027(14)	O4	x	0.6085(6)	0.6083(6)	O15	x	0.7774(6)	0.7771(6)
	y	0.07612(3)	0.07644(3)		y	0.16409(15)	0.16481(14)		y	-0.12089(15)	-0.12128(13)
	z	0.44308(15)	0.44126(13)		z	0.7879(6)	0.7926(5)		z	0.3425(6)	0.3447(5)
	U_{eq}	0.0165(3)	0.0115(2)		U_{eq}	0.0144(9)	0.0101(9)		U_{eq}	0.0140(9)	0.0095(9)
Mn6	x	0.47417(14)	0.47452(14)	O5	x	0.5142(6)	0.5103(6)	O16	x	1.0027(6)	1.0025(6)
	y	0.25292(3)	0.25295(3)		y	0.18465(15)	0.18438(13)		y	-0.11709(15)	-0.11735(13)
	z	0.31001(14)	0.31019(12)		z	0.4517(6)	0.4536(5)		z	0.0683(6)	0.0682(5)
	U_{eq}	0.0162(2)	0.0113(2)		U_{eq}	0.0147(9)	0.0093(9)		U_{eq}	0.0158(9)	0.0092(9)
T1	x	0.6963(2)	0.6952(2)	O6	x	0.8925(6)	0.8926(6)	O17	x	1.2531(6)	1.2534(6)
	y	0.16640(6)	0.16629(5)		y	0.19769(15)	0.19739(13)		y	-0.12827(15)	-0.12767(13)
	z	0.5900(2)	0.5915(2)		z	0.6031(6)	0.6002(5)		z	-0.1535(6)	-0.1557(5)
	U_{eq}	0.0121(4)	0.0069(4)		U_{eq}	0.0146(9)	0.0107(9)		U_{eq}	0.0150(9)	0.0090(9)
T2	x	0.6427(2)	0.6413(2)	O7	x	0.7559(6)	0.7525(6)	O18	x	0.8649(6)	0.8640(6)
	y	0.06206(6)	0.06170(5)		y	0.11254(14)	0.11238(13)		y	-0.13940(14)	-0.13968(13)
	z	0.5155(2)	0.5163(2)		z	0.5489(6)	0.5530(5)		z	-0.2771(6)	-0.2799(5)
	U_{eq}	0.0115(3)	0.0057(3)		U_{eq}	0.0168(10)	0.0099(9)		U_{eq}	0.0121(9)	0.0091(9)
T3	x	0.8646(2)	0.8659(2)	O8	x	0.4490(6)	0.4466(6)	O19	x	1.0268(7)	1.0309(6)
	y	0.01194(6)	0.01174(5)		y	0.06951(14)	0.06924(13)		y	-0.20114(15)	-0.20130(14)
	z	0.2283(2)	0.2284(2)		z	0.3755(6)	0.3741(5)		z	-0.0532(6)	-0.0531(5)
	U_{eq}	0.0108(3)	0.0053(3)		U_{eq}	0.0122(9)	0.0086(9)		U_{eq}	0.0187(10)	0.0121(10)
T4	x	0.8158(2)	0.8159(2)	O9	x	0.6000(6)	0.5964(6)	H19	x	0.954(12)	0.972(11)
	y	-0.09424(6)	-0.09457(5)		y	0.04212(15)	0.04149(13)		y	-0.217(3)	-0.217(2)
	z	0.1639(2)	0.1647(2)		z	0.7055(6)	0.7041(5)		z	-0.154(8)	-0.160(6)
	U_{eq}	0.0109(3)	0.0054(3)		U_{eq}	0.0151(9)	0.0097(9)		U_{iso}	0.05	0.05
T5	x	1.0365(2)	1.0384(2)	O10	x	0.8039(6)	0.8061(6)				
	y	-0.14586(6)	-0.14638(5)		y	0.02901(16)	0.02939(14)				
	z	-0.1145(2)	-0.1157(2)		z	0.4241(6)	0.4258(5)				
	U_{eq}	0.0118(4)	0.0054(4)		U_{eq}	0.0178(10)	0.0112(9)				

TABLE S5. Anisotropic mean-square displacement parameters of medaite samples.

Site		Molinello, Italy	Fianel, Switzerland	Site		Molinello, Italy	Fianel, Switzerland	Site		Molinello, Italy	Fianel, Switzerland	Site		Molinello, Italy	Fianel, Switzerland
Mn1	U_{11}	0.0108(4)	0.0143(6)	T3	U_{11}	0.0078(7)	0.0050(8)	O5	U_{11}	0.015(2)	0.009(2)	O13	U_{11}	0.016(2)	0.010(2)
	U_{22}	0.0125(4)	0.0142(5)		U_{22}	0.0122(7)	0.0064(8)		U_{22}	0.015(2)	0.007(2)		U_{22}	0.009(2)	0.005(2)
	U_{33}	0.0156(5)	0.0144(6)		U_{33}	0.0129(9)	0.0044(8)		U_{33}	0.014(3)	0.011(2)		U_{33}	0.029(3)	0.018(2)
	U_{23}	-0.0013(4)	-0.0014(4)		U_{23}	-0.0001(6)	-0.0006(7)		U_{23}	-0.0007(18)	-0.0030(17)		U_{23}	-0.0045(18)	-0.0040(18)
	U_{13}	0.0054(4)	0.0016(4)		U_{13}	0.0037(6)	-0.0005(6)		U_{13}	0.0024(17)	-0.0033(17)		U_{13}	0.0013(19)	-0.0058(19)
	U_{12}	-0.0003(3)	0.0000(4)		U_{12}	0.0004(6)	0.0009(7)		U_{12}	-0.0001(17)	0.0022(17)		U_{12}	-0.0004(17)	0.0036(17)
Mn2	U_{11}	0.0132(4)	0.0097(5)	T4	U_{11}	0.0089(7)	0.0062(8)	O6	U_{11}	0.013(2)	0.009(2)	O14	U_{11}	0.0111(19)	0.008(2)
	U_{22}	0.0133(4)	0.0085(5)		U_{22}	0.0118(7)	0.0049(8)		U_{22}	0.016(2)	0.011(2)		U_{22}	0.016(2)	0.006(2)
	U_{33}	0.0144(5)	0.0103(5)		U_{33}	0.0125(9)	0.0050(8)		U_{33}	0.016(2)	0.011(2)		U_{33}	0.014(2)	0.011(2)
	U_{23}	-0.0008(4)	-0.0012(4)		U_{23}	0.0004(6)	-0.0002(6)		U_{23}	-0.0024(18)	-0.0005(18)		U_{23}	-0.0013(17)	-0.0026(17)
	U_{13}	0.0053(4)	0.0027(4)		U_{13}	0.0039(6)	0.0003(6)		U_{13}	0.0046(17)	0.0006(18)		U_{13}	0.0042(17)	-0.0011(17)
	U_{12}	-0.0009(3)	-0.0014(4)		U_{12}	0.0004(6)	0.0003(7)		U_{12}	-0.0024(17)	-0.0051(17)		U_{12}	0.0011(16)	0.0005(17)
Mn3	U_{11}	0.0102(4)	0.0083(5)	T5	U_{11}	0.0078(7)	0.0043(9)	O7	U_{11}	0.0116(19)	0.011(2)	O15	U_{11}	0.016(2)	0.010(2)
	U_{22}	0.0138(4)	0.0096(5)		U_{22}	0.0122(7)	0.0070(8)		U_{22}	0.012(2)	0.006(2)		U_{22}	0.017(2)	0.010(2)
	U_{33}	0.0171(6)	0.0103(5)		U_{33}	0.0158(10)	0.0047(8)		U_{33}	0.027(3)	0.012(2)		U_{33}	0.010(2)	0.009(2)
	U_{23}	-0.0007(4)	-0.0005(4)		U_{23}	-0.0005(6)	-0.0003(6)		U_{23}	-0.0003(18)	-0.0036(17)		U_{23}	0.0004(17)	0.0026(17)
	U_{13}	0.0050(4)	0.0018(4)		U_{13}	0.0042(6)	-0.0006(7)		U_{13}	0.0034(18)	-0.0042(18)		U_{13}	0.0071(17)	0.0025(18)
	U_{12}	0.0000(3)	0.0003(4)		U_{12}	-0.0001(6)	0.0008(6)		U_{12}	-0.0032(16)	-0.0017(17)		U_{12}	0.0004(17)	0.0009(17)
Mn4	U_{11}	0.0117(4)	0.0078(5)	T6 (V)	U_{11}	0.0110(5)	0.0059(6)	O8	U_{11}	0.0123(19)	0.007(2)	O16	U_{11}	0.0126(19)	0.011(2)
	U_{22}	0.0152(5)	0.0094(5)		U_{22}	0.0129(5)	0.0067(6)		U_{22}	0.012(2)	0.008(2)		U_{22}	0.017(2)	0.009(2)
	U_{33}	0.0168(6)	0.0086(5)		U_{33}	0.0161(7)	0.0045(6)		U_{33}	0.013(2)	0.011(2)		U_{33}	0.019(3)	0.007(2)
	U_{23}	-0.0023(4)	-0.0018(4)		U_{23}	-0.0004(4)	0.0008(4)		U_{23}	0.0010(17)	-0.0012(17)		U_{23}	-0.0045(18)	-0.0037(17)
	U_{13}	0.0049(4)	0.0010(4)		U_{13}	0.0056(4)	0.0001(4)		U_{13}	0.0053(17)	-0.0006(17)		U_{13}	0.0056(17)	-0.0016(18)
	U_{12}	-0.0016(4)	-0.0018(4)		U_{12}	-0.0005(4)	-0.0002(4)		U_{12}	-0.0005(16)	-0.0007(17)		U_{12}	0.0026(17)	0.0019(17)
Mn5	U_{11}	0.0158(5)	0.0120(5)	O1	U_{11}	0.014(2)	0.011(2)	O9	U_{11}	0.013(2)	0.009(2)	O17	U_{11}	0.0087(18)	0.007(2)
	U_{22}	0.0167(5)	0.0131(5)		U_{22}	0.016(2)	0.005(2)		U_{22}	0.014(2)	0.010(2)		U_{22}	0.023(2)	0.011(2)
	U_{33}	0.0174(6)	0.0092(5)		U_{33}	0.019(3)	0.020(3)		U_{33}	0.019(3)	0.010(2)		U_{33}	0.014(2)	0.009(2)
	U_{23}	-0.0034(4)	-0.0035(4)		U_{23}	-0.0028(18)	0.0020(18)		U_{23}	0.0013(18)	0.0011(18)		U_{23}	-0.0021(18)	-0.0006(17)
	U_{13}	0.0041(4)	0.0005(4)		U_{13}	0.0085(18)	0.0029(19)		U_{13}	0.0047(18)	0.0002(18)		U_{13}	0.0053(16)	0.0008(17)
	U_{12}	-0.0010(4)	-0.0012(4)		U_{12}	-0.0041(17)	-0.0002(17)		U_{12}	0.0015(17)	0.0003(17)		U_{12}	-0.0002(17)	0.0004(17)
Mn6	U_{11}	0.0132(4)	0.0127(5)	O2	U_{11}	0.021(2)	0.018(2)	O10	U_{11}	0.016(2)	0.011(2)	O18	U_{11}	0.0112(19)	0.006(2)
	U_{22}	0.0148(5)	0.0101(5)		U_{22}	0.016(2)	0.008(2)		U_{22}	0.022(2)	0.016(2)		U_{22}	0.014(2)	0.009(2)
	U_{33}	0.0212(6)	0.0116(5)		U_{33}	0.014(2)	0.006(2)		U_{33}	0.015(3)	0.006(2)		U_{33}	0.011(2)	0.012(2)
	U_{23}	0.0026(4)	0.0015(4)		U_{23}	0.0029(17)	0.0011(17)		U_{23}	-0.0002(19)	-0.0014(18)		U_{23}	0.0002(17)	0.0003(18)
	U_{13}	0.0061(4)	0.0026(4)		U_{13}	0.0058(18)	0.0010(18)		U_{13}	0.0028(18)	-0.0026(18)		U_{13}	0.0013(16)	-0.0028(17)
	U_{12}	0.0000(4)	-0.0008(4)		U_{12}	0.0002(18)	0.0014(18)		U_{12}	0.0048(18)	0.0075(18)		U_{12}	0.0014(16)	-0.0005(17)
T1	U_{11}	0.0089(7)	0.0065(9)	O3	U_{11}	0.017(2)	0.012(2)	O11	U_{11}	0.0083(18)	0.008(2)	O19	U_{11}	0.026(2)	0.020(3)
	U_{22}	0.0123(7)	0.0077(8)		U_{22}	0.022(2)	0.017(2)		U_{22}	0.014(2)	0.013(2)		U_{22}	0.016(2)	0.010(2)
	U_{33}	0.0157(10)	0.0063(9)		U_{33}	0.022(3)	0.013(2)		U_{33}	0.025(3)	0.012(2)		U_{33}	0.014(3)	0.006(2)
	U_{23}	0.0006(6)	0.0000(7)		U_{23}	-0.002(2)	0.0005(19)		U_{23}	0.0023(18)	0.0003(18)		U_{23}	-0.0024(18)	0.0004(18)
	U_{13}	0.0044(6)	-0.0008(7)		U_{13}	0.0031(19)	-0.0037(19)		U_{13}	0.0062(18)	-0.0016(18)		U_{13}	0.0017(19)	-0.0045(19)
	U_{12}	-0.0008(6)	-0.0015(7)		U_{12}	0.0043(19)	0.0046(19)		U_{12}	-0.0022(16)	-0.0029(18)		U_{12}	-0.0032(19)	-0.0043(19)
T2	U_{11}	0.0091(7)	0.0056(9)	O4	U_{11}	0.014(2)	0.010(2)	O12	U_{11}	0.0117(19)	0.010(2)				
	U_{22}	0.0118(7)	0.0055(8)		U_{22}	0.015(2)	0.015(2)		U_{22}	0.0112(19)	0.011(2)				
	U_{33}	0.0141(9)	0.0057(9)		U_{33}	0.015(3)	0.006(2)		U_{33}	0.017(2)	0.005(2)				
	U_{23}	0.0003(6)	-0.0002(7)		U_{23}	-0.0002(18)	0.0048(18)		U_{23}	-0.0014(17)	0.0005(17)				
	U_{13}	0.0040(6)	-0.0001(7)		U_{13}	0.0041(17)	0.0024(18)		U_{13}	0.0036(17)	0.0000(18)				
	U_{12}	0.0005(6)	0.0000(7)		U_{12}	-0.0032(17)	-0.0012(18)		U_{12}	0.0001(16)	0.0010(17)				