

Alpeite, $\text{Ca}_4\text{Mn}^{3+}_2\text{Al}_2(\text{Mn}^{3+}\text{Mg})(\text{SiO}_4)_2(\text{Si}_3\text{O}_{10})(\text{V}^{5+}\text{O}_4)(\text{OH})_6$, a new ardennite-group mineral from Italy

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Abstract: Alpeite (IMA2016-072), $\text{Ca}_4\text{Mn}^{3+}_2\text{Al}_2(\text{Mn}^{3+}\text{Mg})(\text{SiO}_4)_2(\text{Si}_3\text{O}_{10})(\text{V}^{5+}\text{O}_4)(\text{OH})_6$, is a new member of the ardennite group from the Monte Alpe mine, Liguria, Italy. It crystallized from V- and Mn-rich hydrothermal fluids in an oxidizing environment. Alpeite occurs as intergrowths of plates, flattened on {1 0 0} and exhibiting the forms {1 0 0}, {0 0 1}, {0 1 2} and {1 0 2}. The mineral is brownish red and transparent with a vitreous to silky lustre and beige streak. Crystals are brittle with a curved and stepped fracture, and a perfect cleavage on {1 0 0} and good cleavages on {0 1 0} and {0 0 1}. The Mohs' hardness is 5½ to 6. The calculated density is 3.374 g cm^{-3} . The mineral is inert in concentrated HCl at room temperature. Optically, alpeite crystals are biaxial (–), with $\alpha = 1.747(3)$, $\beta = 1.785(3)$ and $\gamma = 1.808(3)$ (white light); $2V = 73(2)$; dispersion $r > v$, strong; the optical orientation $X = \mathbf{a}$, $Y = \mathbf{b}$, $Z = \mathbf{c}$. Pleochroism is $Y > Z > X$ in shades of reddish brown. Electron microprobe analyses gave the empirical formula $(\text{Ca}_{3.84}\text{Mn}^{2+}_{0.16})_{\Sigma 4.00}(\text{Mn}^{3+}_{1.33}\text{Al}_{0.67})_{\Sigma 2.00}(\text{Al}_{1.29}\text{Mn}^{3+}_{0.60}\text{V}^{5+}_{0.10})_{\Sigma 1.99}(\text{Mn}^{3+}_{0.70}\text{Mg}_{0.65}\text{Al}_{0.42}\text{Co}^{2+}_{0.20})_{\Sigma 1.97}(\text{SiO}_4)_2(\text{Si}_3\text{O}_{10})[(\text{V}^{5+}_{0.75}\text{Si}_{0.25})\text{O}_4](\text{OH})_6$, based on 280 atoms per formula unit. Alpeite is orthorhombic, $Pnmm$, with the unit-cell parameters: $a = 8.9421(11)$, $b = 6.0534(6)$, $c = 18.9781(18) \text{ Å}$, $V = 1027.29(19) \text{ Å}^3$ and $Z = 2$. The four strongest lines in the X-ray powder diffraction pattern are [$d_{\text{obs}}/\text{Å} (hkl)$]: 3.022 (93) (1 1 5), 2.673 (100) (1 1 6), 2.572 (69) (2 0 6) and 1.5112 (83) (0 4 0, 4 2 7). The crystal structure was refined to $R_1 = 0.044$ for 834 observed reflections [$F_o > 4\sigma F$]. The structure is the same as that of other members of the ardennite group. It contains chains of edge-sharing Mn^{3+} and Al octahedra extending along the b axis, which are linked into a framework by sharing corners with SiO_4 tetrahedra and with Si_3O_{10} tetrahedral groups. Within the cavities in this framework are 7-coordinated Ca sites. In the structure of alpeite, Mn^{3+} is the dominant cation in the $M1$ site and is the dominant trivalent cation in the $M3$ site, while in all other members of the ardennite group [ardennite-(As), ardennite-(V) and kannanite], Al is the dominant cation in the $M1$ site and is the dominant trivalent cation in the $M3$ site.

Key-words: alpeite; new mineral; ardennite group; crystal structure; Monte Alpe mine; Italy.

1. Introduction

The manganese mines in the eastern part of Liguria (northern Apennines, Italy) have in recent decades yielded many interesting, rare and new minerals. The Mn ores of the Graveglia Valley (Gambatesa, Cassagna and Molinello mines) and the nearby La Spezia province (Cerchiara and Monte Nero mines) underwent complex, multi-stage hydrothermal circulation of fluids along extensional fractures, which resulted in the concentration of dispersed elements such as As, V, Ba, Sr and Te in secondary veins (Gramaccioli *et al.*, 1980; Cabella *et al.*,

1993; Basso *et al.*, 2008; Kampf *et al.*, 2013; Carbone *et al.*, 2013; Bindi *et al.*, 2011, 2013; Kampf *et al.*, 2016) and produced polyphase mineral assemblages of outstanding variety and rarity (Cortesogno *et al.*, 1979; Cabella *et al.*, 1991).

Herein, we report the first new mineral species from the Monte Alpe mine (also known as Monte Alpe di Maissana). This mineral, named alpeite for the locality, is a new member of the ardennite group, the other members of which are ardennite-(As), ardennite-(V) and kannanite. Alpeite is the only member of the group containing essential Mn^{3+} .

The mineral and name were approved by the IMA Commission on New Minerals, Nomenclature and Classification prior to publication (IMA2016-072). The description is based upon one holotype specimen deposited in the collections of the Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, CA 90007, USA and catalogue number 66288.

2. Occurrence

The new mineral was discovered in October 2015 by one of the authors (FC) at the Monte Alpe mine, western and eastern slopes of Monte Alpe (44°18'24"N, 9°32'00"E), Tre Monti mining concession, Castiglione Chiavarese (Genova Prov.) and Maissana (La Spezia Province), Liguria, Italy. This now-abandoned mine exploited W-E trending manganiferous veins. The geology is similar to that of the more famous Val Graveglia manganese district to the east (Cortesogno *et al.*, 1979; Marchesini & Pagano, 2001). Stratiform manganese ores are located near the base of a chert sequence in the 'Diaspri di Monte Alpe' formation, which overlays Jurassic ophiolites of the northern Apennines (Cabella *et al.*, 1998). Alpeite is a secondary mineral that crystallized from V- and Mn-rich hydrothermal fluids, which circulated through a system of fractures during the final tectono-metamorphic stage of the deposit. Other minerals found with alpeite include braunite, dolomite, quartz, todorokite and ganophyllite. More information on the deposit and its minerals can be found in Castellaro & Passarino (2011) and references therein.

Although the manganese mineralization at the Monte Alpe mine shares a common petrogenetic environment with the deposits of the Graveglia Valley, the abundance of minerals such as aegirine, hematite and piemontite in the paragenesis suggests that the hydrothermal fluids were strongly oxidizing, resulting in the mobilization and subsequent recrystallization of the Mn ore. Such strongly oxidizing conditions in the secondary veins were necessary for the formation of alpeite.

Medaite was also found in alpeite-free veins crosscutting the Mn ore at Monte Alpe (Castellaro & Passarino, 2011). The absence of alpeite in those veins seems to suggest that the formation of a vanadium-bearing ardennite phase with trisilicate groups $(\text{Si}_3\text{O}_{10})^{8-}$ and isolated $(\text{VO}_4)^{3-}$ and $(\text{SiO}_4)^{4-}$ tetrahedra in the crystal structure might occur under particular stabilizing conditions, which locally favour hydrolysis and disfavour polymerization of $(\text{VO}_4)^{3-}$ and $(\text{SiO}_4)^{4-}$ tetrahedra to form chain fragments, as in the medaite structure (Gramaccioli *et al.*, 1982).

3. Physical and optical properties

Alpeite occurs as intergrowths of plates up to about 0.3 mm in diameter (Fig. 1). Plates are flattened on {100} and exhibit the forms {100}, {001}, {012} and {102} (Fig. 2). No twinning was observed. Crystals

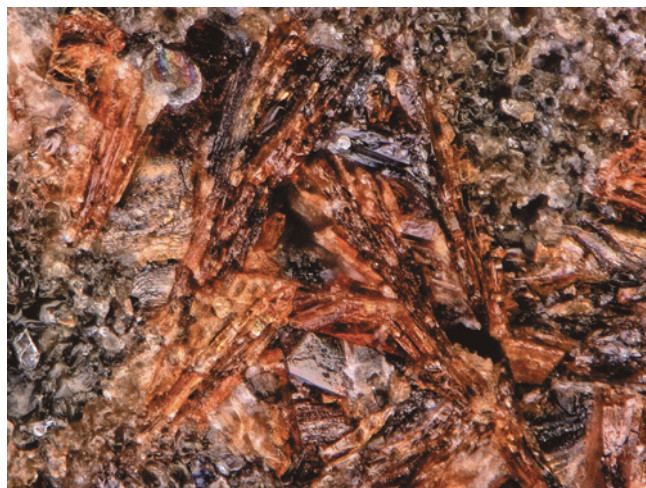


Fig. 1. Alpeite crystals, field of view 0.5 mm across.

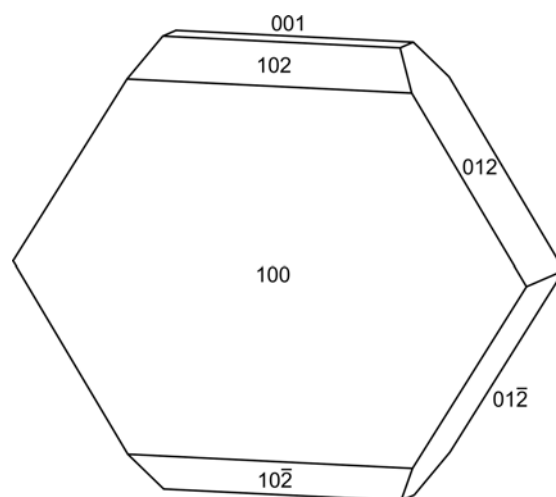


Fig. 2. Crystal drawing of alpeite, clinographic projection.

are brownish-red and transparent with a vitreous lustre and beige streak. The mineral is non-fluorescent. Crystals are brittle with a curved and stepped fracture. Three cleavages were observed, one perfect on {100} and two good on {010} and {001}. The Mohs' hardness is 5½ to 6 based upon scratch tests. The density could not be measured because fragments are nearly invisible in Clerici solution. The calculated density is 3.374 g cm^{-3} , based on the empirical formula. The mineral is inert in concentrated HCl at room temperature. Optically, alpeite crystals are biaxial (–), with $\alpha = 1.747(3)$, $\beta = 1.785(3)$, $\gamma = 1.808(3)$ (measured in white light). The $2V$ measured directly on a spindle stage is $73(2)$; the calculated $2V$ is 74.3 . Dispersion is $r > v$, strong and the optical orientation is $X = \mathbf{a}$, $Y = \mathbf{b}$, $Z = \mathbf{c}$. The pleochroism in shades of reddish brown is $Y > Z > X$. The Gladstone–Dale compatibility, $1 - (K_P/K_C)$, is 0.018 based upon the empirical formula, in the range of superior compatibility (Mandarino, 2007).

Table 1. Analytical data (in wt%) for alpeite.

Constituent	Mean	Range	SD	Standard
CaO	20.45	19.99–20.67	0.20	Diopside
MgO	2.49	2.41–2.82	0.10	Diopside
CoO	1.43	0.91–1.98	0.25	Co metal
Mn ₂ O ₃	[20.90]	20.17–21.84	0.49	Rhodonite
MnO*	1.08			
Mn ₂ O ₃ *	19.70			
Al ₂ O ₃	11.52	10.56–12.02	0.36	Sanidine
SiO ₂	29.92	28.63–30.74	0.62	Diopside
V ₂ O ₅	7.36	6.50–8.51	0.58	V metal
H ₂ O**	5.13			
Total	99.08			

* Mn²⁺ and Mn³⁺ allocated according to assigned site occupancies.

** Calculated on the basis of charge balance and O = 28 *apfu*.

4. Chemical composition

Quantitative analyses (14 points on 8 crystals) were performed at the University of Utah on a Cameca SX-50 electron microprobe with four wavelength-dispersive spectrometers (WDS). Analytical conditions were: 15 kV accelerating voltage, 30 nA beam current and a beam diameter of 10 µm. Alpeite exhibited no obvious damage under the electron beam. Counting times were 20 s on peak and 10 s on + and – background. No other elements were detected by energy-dispersive spectrometry. Other likely elements were sought by WDS, but none were above the detection limits; most notably, no Fe was observed. Raw X-ray intensities were corrected for matrix effects with a $\varphi(\rho z)$ algorithm (Pouchou & Pichoir, 1991). Because insufficient material was available for a direct determination of H₂O, the amount of water was calculated on the basis of O = 28 and H = 6 atoms per formula unit (*apfu*), as determined by the crystal-structure analysis (see below). Analytical data are given in Table 1.

The empirical formula, assuming all Mn to be trivalent and all V to be pentavalent, is Ca_{3.84}Mn³⁺_{2.79}Al_{2.38}Mg_{0.65}Co_{0.20}Si_{5.25}V⁵⁺_{0.85}O₂₈H₆, which has a net excess charge of +0.14. Allocating cations according to the structural evidence (see below) and assigning 0.16 Mn as divalent (consistent with its placement in the Ca site) results in (Ca_{3.84}Mn²⁺_{0.16}) Σ 4.00(Mn³⁺_{1.33}Al_{0.67}) Σ 2.00(Al_{1.29}Mn³⁺_{0.60}V⁵⁺_{0.10}) Σ 1.99(Mn³⁺_{0.70}Mg_{0.65}Al_{0.42}Co²⁺_{0.20}) Σ 1.97(SiO₄)₂(Si₃O₁₀)[(V³⁺_{0.75}Si_{0.25})O₄](OH)₆, which has a small charge deficiency of –0.02.

The end-member formula is Ca₄Mn³⁺₂Al₂(Mn³⁺Mg)(SiO₄)₂(Si₃O₁₀)(V⁵⁺O₄)(OH)₆, which requires CaO 21.39, MgO 3.84, Mn₂O₃ 22.58, Al₂O₃ 9.72, SiO₂ 28.64, V₂O₅ 8.67, H₂O 5.15, total 100 wt%.

5. X-ray crystallography and crystal-structure determination

Powder X-ray diffraction data for alpeite were obtained on a Rigaku R-Axis Rapid II curved-imaging-plate microdiffractometer utilizing monochromatized MoK α

radiation. A Gandolfi-like motion on the φ and ω axes was used to randomize the sample. Observed *d* values and intensities were derived by profile fitting using JADE 2010 software (Materials Data Inc.). Data are given in Table 2. The unit-cell parameters refined from the powder data using JADE 2010 with whole-pattern fitting are, *a* = 8.9394(12), *b* = 6.0488(8), *c* = 18.954(3) Å and *V* = 1024.9(2) Å³.

Single-crystal structure data were obtained on the same instrument noted above. The Rigaku CrystalClear software package was used for processing of structure data, including the application of an empirical multi-scan absorption correction using ABSCOR (Higashi, 2001). Systematic absences were consistent with space group *Pnmm*, as reported for other members of the ardennite group. The structure was solved by direct methods using SIR2011 (Burla *et al.*, 2012) and then atom coordinates were transformed to correspond to those in the structure of ardennite-(As) (Nagashima & Armbruster, 2010). SHELXL-2013 (Sheldrick, 2015) was used for the refinement of the structure. The occupancies of all cation sites were refined (see below) and all H atom sites were located in difference Fourier maps. The H sites were refined with soft restraints of 0.82(3) Å on the O–H distances (the value recommended in the SHELX documentation) and with the *U*_{eq} of each H set to 1.5× that of the corresponding OH site. Data collection and refinement details are given in Table 3, atom coordinates and displacement parameters in Table 4, selected bond distances in Table 5, a scattering factor analysis in Table 6 and a bond valence analysis in Table 7. The Crystallography Information File, including reflection data, is available online as Supplementary Material linked to this article on the GSW website of the journal, <http://eurjmin.geoscience.world.org>.

6. Discussion of the structure

The crystal structure of alpeite (Fig. 3) is the same as that of other members of the ardennite group (Table 8). It contains three different chains of edge-sharing octahedra (*M*1O₆, *M*2O₆ and *M*3O₆) extending along the *b* axis, which are linked into a framework by sharing corners with *T*1O₄ and *T*4O₄ tetrahedra and with *T*2₂*T*3O₁₀ tetrahedral groups. Within the cavities in this framework are two 7-coordinated cation sites, *A*1 and *A*2. As noted by Barresi *et al.* (2007), the general formula for the ardennite group can be written *A*²⁺₄(*M*³⁺₅*M*²⁺)(*T*⁴⁺₅*T*⁵⁺)O₂₂(OH)₆. In terms of individual cation sites, the formula can be written as *A*²⁺₁*A*²⁺₂*M*¹⁺₂*M*²⁺₂(*M*³⁺₃*M*³⁺₂)(*T*¹⁺₄O₄)₂(*T*²⁺₂*T*³⁺₄O₁₀)(*T*⁴⁺₅O₄)O₂₂(OH)₆.

The occupancies (site populations) for the cation sites based upon our refinement of the alpeite structure are shown in column 2 of Table 6. We also used the program OccQP (Wright *et al.*, 2001) to analyse the likely site populations based upon the EPMA composition and the results of the structure refinement. This program uses quadratic equations in a constrained least-squares formulation to optimize

Q2 Table 2. Powder X-ray diffraction data (*d* in Å) for alpeite. Only calculated lines with *I* ≥ 4 are shown.

<i>I</i> _{obs}	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{calc}	<i>hkl</i>	<i>I</i> _{obs}	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{calc}	<i>hkl</i>
8	9.51	9.4891	5	002			2.1242	4	126
6	8.17	8.0891	7	101			2.1078	8	403
12	5.203	5.1644	6	103	53	2.095	2.0956	17	208
30	5.008	5.0128	20	110			2.0915	29	225
		4.8466	5	111			2.0421	6	316
50	4.749	4.7445	32	004			1.9698	5	127
49	4.448	{ 4.4711 4.4323	12 11	200 112	7	1.9628	1.9644	4	226
							1.9263	5	405
24	4.278	4.3519	10	201			1.8794	5	133
52	4.049	4.0446	29	202	18	1.8675	1.8671	18	028
28	3.907	3.9288	19	113			1.8404	4	227
29	3.647	3.6512	16	203			1.8356	9	415
		3.5964	5	210	13	1.8310	1.8256	8	406
		3.5335	4	211			1.7749	7	1110
		3.4939	4	105			1.7668	9	422
17	3.451	3.4458	8	114	13	1.7631	1.7473	9	135
		3.3630	6	212			1.7297	4	423
51	3.259	3.2539	47	204			1.6815	34	424
		3.1265	6	213	52	1.6766	1.6709	21	330
93	3.022	3.0260	94	115			1.6588	7	417
		2.9807	19	300			1.6314	4	1111
		2.9446	11	301			1.6269	10	408
		2.8936	9	205	49	1.6231	1.6251	36	425
		2.8836	17	022			1.6136	4	229
41	2.869	2.8661	7	214			1.6079	5	0210
		2.8437	11	302	23	1.5805	1.5815	22	0012
		2.8348	21	121			1.5761	4	334
		2.7444	7	122	10	1.5635	1.5632	18	426
100	2.673	2.6750	100	116			1.5198	4	522
		2.6479	11	311	83	1.5112	1.5134	78	040
		2.6113	17	123			1.4986	22	427
69	2.572	2.5822	36	206			1.4468	7	4010
31	2.535	2.5517	61	024	8	1.4414	1.4330	8	428
		2.5239	4	304			1.4219	5	604
		2.5064	17	220			1.3722	5	244
		2.4631	5	313	5	1.3659	1.3658	6	4011
30	2.424	2.4233	39	222			1.3613	4	3112
10	2.385	2.3847	17	117	7	1.3345	1.3370	7	620
		2.3302	33	223			1.3240	5	622
39	2.326	2.3182	12	207			1.3081	10	623
		2.2877	6	125	18	1.3042	1.3056	11	246
		2.2202	18	401			1.2973	8	2014
23	2.209	2.2162	6	224					
		2.1868	12	026					

occupancy assignments based upon site scattering, chemical composition, charge balance, bond valence and cation–anion bond lengths. The site populations proposed in column 4 of Table 6 show how the results of the EPMA can be allocated using evidence provided by the OccQP analysis. The resulting structurally based empirical formula is $(\text{Ca}_{3.84}\text{Mn}^{2+}_{0.16})_{\Sigma 4.00}(\text{Mn}^{3+}_{1.33}\text{Al}_{0.67})_{\Sigma 2.00}(\text{Al}_{1.29}\text{Mn}^{3+}_{0.60}\text{V}^{5+}_{0.10})_{\Sigma 1.99}(\text{Mn}^{3+}_{0.70}\text{Mg}_{0.65}\text{Al}_{0.42}\text{Co}^{2+}_{0.20})$

$\Sigma 1.97(\text{SiO}_4)_2(\text{Si}_3\text{O}_{10})[(\text{V}^{5+}_{0.75}\text{Si}_{0.25})\text{O}_4](\text{OH})_6$ and the end-member formula is $\text{Ca}_4\text{Mn}^{3+}_2\text{Al}_2(\text{Mn}^{3+}\text{Mg})(\text{SiO}_4)_2(\text{Si}_3\text{O}_{10})(\text{V}^{5+}\text{O}_4)(\text{OH})_6$.

Alpeite is a member of the ardennite group (Table 8). Unlike other members of the group, alpeite contains different dominant cations in its *M1* and *M2* sites, Mn^{3+} and Al, respectively. In the structures of the other members of the group, Al dominates both the *M1* and *M2* sites.

Table 3. Data collection and structure-refinement details for alpeite.

Diffractometer	Rigaku <i>R</i> -Axis Rapid II
X-ray radiation/power	MoK α ($\lambda = 0.71075$ Å)/50 kV, 40 mA
Temperature	293(2) K
Structural formula	Ca ₄ (Mn ³⁺ _{1.27} Al _{0.73})(Al _{1.39} Mn ³⁺ _{0.61})(Mn ³⁺ _{0.86} Mg _{1.14})(SiO ₄) ₂ (Si ₃ O ₁₀)[(V ⁵⁺ _{0.77} Si _{0.23})O ₄](OH) ₆
Space group	<i>Pnmm</i>
Unit-cell dimensions	<i>a</i> = 8.9421(11) Å <i>b</i> = 6.0534(6) Å <i>c</i> = 18.9781(6) Å
<i>V</i>	1027.29(19) Å ³
<i>Z</i>	2
Density (for above formula)	3.391 g cm ⁻³
Absorption coefficient	3.798 mm ⁻¹
<i>F</i> (0 0 0)	1032
Crystal size	70 × 40 × 5 µm
θ range	3.13 to 24.98°
Index ranges	$-10 \leq h \leq 10$, $-6 \leq k \leq 7$, $-19 \leq l \leq 22$
Refls. collected/unique	4664/1022; <i>R</i> _{int} = 0.062
Reflections with <i>F</i> > 4 σ <i>F</i>	834
Completeness to $\theta = 24.98^\circ$	99.6%
Max. and min. transmission	0.981 and 0.777
Refinement method	Full-matrix least-squares on <i>F</i> ²
Parameters/restraints	139/3
GoF	1.045
Final <i>R</i> indices [<i>F</i> _o > 4 σ (<i>F</i>)]	<i>R</i> ₁ = 0.0433, <i>wR</i> ₂ = 0.0906
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0569, <i>wR</i> ₂ = 0.0968
Largest diff. peak/hole	+0.94/−0.54 e/Å ³

* $R_{\text{int}} = \sum |F_o^2 - F_c^2| / \sum F_o^2$ (mean) / $\sum F_o^2$. GoF = $S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$. $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where *a* is 0.0372, *b* is 5.7204 and *P* is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

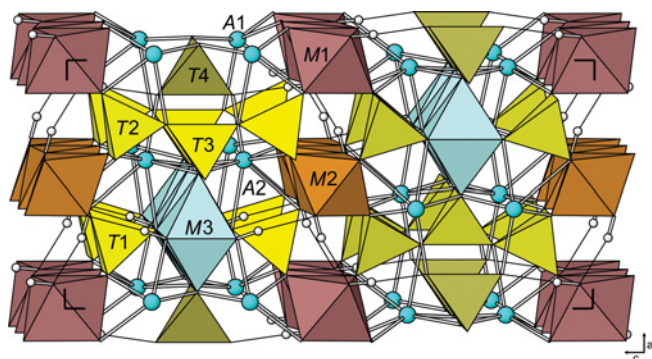


Fig. 3. The crystal structure of alpeite viewed slightly canted down [0 1 0]. *A*–O and O–H bonds shown as sticks; H ··· O hydrogen bonds shown as thin lines.

Alpeite also differs in that Mn³⁺ is the dominant trivalent cation in the *M3* site, while in the other ardennite-group minerals Al is the dominant trivalent cation in this site.

In the closely related structure of cassagnaite, Ca₄Fe³⁺₄V³⁺₂(Si₃O₁₀)(SiO₄)₂O₂(OH)₆, the *M1* site is populated by Mn³⁺, together with Fe³⁺ and Al, whereas the *M2* site is populated by cations such as V³⁺, Mg and Al, ideally trivalent (Basso *et al.*, 2008). Alpeite and cassagnaite show similar crystal chemistry, but differ with respect to the placement of vanadium in their structures; in alpeite it is in a tetrahedral site, whereas in cassagnaite it is in an octahedral site.

Table 4. Atom coordinates and displacement parameters (Å²) for alpeite.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ²³	<i>U</i> ¹³	<i>U</i> ¹²
A1(Ca)	0.95908(17)	0.25	0.15661(8)	0.0157(4)	0.0222(8)	0.0150(9)	0.0098(8)	0	0.0027(6)	0
A2(Ca)	0.41688(17)	0.75	0.15691(8)	0.0149(4)	0.0241(9)	0.0115(9)	0.0091(8)	0	−0.0011(6)	0
M1(Mn,Al)*	0	0	0	0.0109(5)	0.0164(8)	0.0092(8)	0.0070(8)	0.0008(6)	0.0019(5)	0.0016(5)
M2(Al,Mn)*	0.5	0	0	0.0101(6)	0.0160(10)	0.0082(9)	0.0062(9)	0.0009(7)	0.0014(6)	0.0010(7)
M3(Mn,Mg)*	0.69377(18)	−0.0003(3)	0.25	0.0124(6)	0.0198(10)	0.0100(9)	0.0076(9)	0	0	−0.0005(7)
T1(Si)	0.7663(2)	0.75	0.09641(11)	0.0117(5)	0.0172(11)	0.0108(11)	0.0071(10)	0	0.0009(8)	0
T2(Si)	0.2812(2)	0.25	0.09527(11)	0.0125(5)	0.0164(10)	0.0127(11)	0.0083(10)	0	0.0011(8)	0
T3(Si)	0.3585(3)	0.25	0.25	0.0135(7)	0.0218(16)	0.0108(15)	0.0078(15)	0	0	0
T4(V,Si)*	0.0443(2)	0.75	0.25	0.0139(7)	0.0223(12)	0.0098(12)	0.0097(12)	0	0	0
O1	0.1306(4)	0.0332(6)	−0.08063(17)	0.0153(8)	0.0204(19)	0.014(2)	0.0112(18)	−0.0023(17)	0.0003(15)	−0.0009(16)
O2	0.6251(4)	−0.0285(6)	−0.07845(17)	0.0156(8)	0.0204(19)	0.016(2)	0.0102(18)	−0.0004(17)	0.0038(15)	−0.0009(16)
O3	0.1165(6)	0.25	0.0583(3)	0.0193(13)	0.019(3)	0.031(3)	0.008(3)	0	0.002(2)	0
O4	0.6123(6)	0.75	0.0496(3)	0.0193(13)	0.019(3)	0.028(3)	0.011(3)	0	−0.002(2)	0
O5	0.9350(6)	−0.0126(9)	0.25	0.0185(12)	0.028(3)	0.013(3)	0.014(3)	0	0	−0.002(2)
O6	0.4545(5)	0.0198(9)	0.25	0.0169(12)	0.023(3)	0.015(3)	0.013(3)	0	0	−0.004(2)
O7	0.6955(6)	0.75	0.1783(3)	0.0196(13)	0.023(3)	0.026(3)	0.009(3)	0	0.004(2)	0
O8	0.2430(5)	0.25	0.1816(3)	0.0151(12)	0.023(3)	0.017(3)	0.006(3)	0	0.002(2)	0
O9	0.1529(6)	0.75	0.1787(3)	0.0222(13)	0.028(3)	0.024(3)	0.014(3)	0	0.006(2)	0
OH1	0.1126(6)	0.75	0.0312(3)	0.0134(11)	0.018(3)	0.015(3)	0.007(3)	0	−0.004(2)	0
H1	0.120(9)	0.75	0.0736(17)	0.020						
OH2	0.6117(6)	0.25	0.0339(3)	0.0146(11)	0.014(3)	0.016(3)	0.013(3)	0	0.002(2)	0
H2	0.700(4)	0.25	0.023(4)	0.022						
OH3	0.7035(6)	0.25	0.1830(3)	0.0224(13)	0.023(3)	0.031(3)	0.013(3)	0	−0.003(2)	0
H3	0.672(9)	0.25	0.142(2)	0.034						

* Refined occupancies: M1(Mn,Al) = 0.635, 0.365(10); M2(Al,Mn) = 0.695, 0.305(10); M3(Mn,Mg) = 0.427, 0.573(10); T4(V,Si) = 0.77, 0.23(2)

Table 5. Selected bond distances (Å) and angles (°) for alpeite.

<i>A1</i> –O3	2.337(5)	<i>M1</i> –OH1(×2)	1.912(3)	Si1–O1(×2)	1.632(4)
<i>A1</i> –OH3	2.340(6)	<i>M1</i> –O1(×2)	1.935(3)	Si1–O4	1.639(5)
<i>A1</i> –O1(×2)	2.379(4)	<i>M1</i> –O3(×2)	2.145(4)	Si1–O7	1.678(5)
<i>A1</i> –O5(×2)	2.391(4)	⟨ <i>M1</i> –O⟩	1.997	⟨Si1–O⟩	1.645
<i>A1</i> –O8	2.583(5)				
⟨ <i>A1</i> –O⟩	2.400	<i>M2</i> –O2(×2)	1.870(3)	Si2–O2(×2)	1.613(4)
		<i>M2</i> –OH2(×2)	1.924(3)	Si2–O3	1.631(6)
<i>A2</i> –O2(×2)	2.280(4)	<i>M2</i> –O4(×2)	2.046(3)	Si2–O8	1.674(5)
<i>A2</i> –O9	2.397(6)	⟨ <i>M2</i> –O⟩	1.947	⟨Si2–O⟩	1.633
<i>A2</i> –O6(×2)	2.429(4)				
<i>A2</i> –O7	2.524(5)	<i>M3</i> –OH3(×2)	1.980(4)	Si3–O6(×2)	1.637(6)
<i>A2</i> –O4	2.683(5)	<i>M3</i> –O7(×2)	2.034(4)	Si3–O8(×2)	1.658(5)
⟨ <i>A2</i> –O⟩	2.432	<i>M3</i> –O6	2.143(5)	⟨Si3–O⟩	1.648
		<i>M3</i> –O5	2.158(6)		
		⟨ <i>M3</i> –O⟩	2.055	V–O9(×2)	1.665(5)
				V–O5(×2)	1.738(6)
				⟨V–O⟩	1.702
Hydrogen bonds					
<i>D</i> –H	<i>d</i> (<i>D</i> –H)	<i>d</i> (H– <i>A</i>)	⟨ <i>DHA</i> ⟩	<i>d</i> (<i>D</i> – <i>A</i>)	<i>A</i>
OH1–H1	0.81	2.02	177	2.823	O9
OH2–H2	0.81	1.97	164	2.757	OH1
OH3–H3	0.82	2.13	175	2.946	OH2

Table 6. Site assignments for alpeite.

Site	Structure		EPMA*	
	Site population (<i>apfu</i>)	Scattering (<i>epfu</i>)	Site population (<i>apfu</i>)	Scattering (<i>epfu</i>)
<i>A1</i>	2 Ca	40.00	1.92 Ca + 0.08 Mn ²⁺	40.40
<i>A2</i>	2 Ca	40.00	1.92 Ca + 0.08 Mn ²⁺	40.40
<i>M1</i>	1.27 Mn ³⁺ + 0.73 Al	41.26	1.33 Mn ³⁺ + 0.67 Al	41.96
<i>M2</i>	1.39 Al + 0.61 Mn ³⁺	33.37	1.29 Al + 0.60 Mn ³⁺ + 0.10 V ⁵⁺	34.07
<i>M3</i>	0.86 Mn ³⁺ + 1.14 Mg	35.18	0.70 Mn ³⁺ + 0.65 Mg + 0.42 Al + 0.20 Co ²⁺	36.16
<i>T1</i>	2 Si	28.00	2 Si	28.00
<i>T2</i>	2 Si	28.00	2 Si	28.00
<i>T3</i>	1 Si	14.00	1 Si	14.00
<i>T4</i>	0.77 V ⁵⁺ + 0.23 Si	20.93	0.75 V ⁵⁺ + 0.25 Si	20.75

* Occupancies based upon the empirical formula with cation assignments informed by OccQP site optimization.

Table 7. Bond-valence analysis for alpeite. Values are expressed in valence units.

	<i>A1</i>	<i>A2</i>	<i>M1</i>	<i>M2</i>	<i>M3</i>	<i>T1</i>	<i>T2</i>	<i>T3</i>	<i>T4</i>	H1	H2	H3	Sum
O1	0.33		0.55			0.98							1.86
	×2↓		×2↓			×2↓							
O2		0.43		0.58			1.03						2.04
		×2↓		×2↓			×2↓						
O3	0.37		0.31				0.98						1.97
			×2↓→										
O4		0.14		0.36		0.96							1.83
				×2↓→									
O5	0.32				0.31				1.09				2.03
	×2↓→								×2↓				
O6		0.29			0.32			0.97					1.86
		×2↓→						×2↓					
O7		0.22				0.86							1.95

Table 7. (continued).

	A1	A2	M1	M2	M3	T1	T2	T3	T4	H1	H2	H3	Sum
					0.43 ×2↓→								
O8	0.19						0.87	0.91 ×2↓					1.98
O9		0.31							1.32 ×2↓	0.18			1.81
OH1			0.59 ×2↓→							0.82	0.20		2.20
OH2				0.50 ×2↓→							0.80	0.14	1.94
OH3	0.36				0.50 ×2↓→							0.86	2.22
Sum	2.22	2.11	2.90	2.88	2.49	3.78	3.91	3.76	4.82	1.00	1.00	1.00	

The bond strengths are based upon assigned and refined cation occupancies from the structure refinement. Multiplicity is indicated by ×↓→. Si⁴⁺–O bond valence parameters are from [Brown & Altermatt \(1985\)](#). All other bond valence parameters are from [Brese & O’Keeffe \(1991\)](#). Hydrogen-bond strengths, based on O···O bond lengths, are from [Ferraris & Ivaldi \(1988\)](#).

Table 8. Comparison of alpeite with other members of the ardennite group.

	Alpeite	Ardennite-(As)	Ardennite-(V)	Kannanite
Formula (ideal)	Ca ₄ Mn ³⁺ ₂ Al ₂ (Mn ³⁺ Mg) (SiO ₄) ₂ (Si ₃ O ₁₀)(VO ₄)(OH) ₆	Mn ²⁺ ₄ Al ₄ (AlMg) (SiO ₄) ₂ (Si ₃ O ₁₀)(AsO ₄)(OH) ₆	Mn ²⁺ ₄ Al ₄ (AlMg) (SiO ₄) ₂ (Si ₃ O ₁₀)(VO ₄)(OH) ₆	Ca ₄ Al ₄ (AlMg) (SiO ₄) ₂ (Si ₃ O ₁₀)(VO ₄)(OH) ₆
Symmetry	Orthorhombic, <i>Pnmm</i>	Orthorhombic, <i>Pnmm</i>	Orthorhombic, <i>Pnmm</i>	Orthorhombic, <i>Pnmm</i>
Cell parameters	<i>a</i> = 8.9421(11) Å <i>b</i> = 6.0534(6) Å <i>c</i> = 18.9781(18) Å	<i>a</i> = 8.7163(2) Å <i>b</i> = 5.8131(1) Å <i>c</i> = 18.5199(3) Å	<i>a</i> = 8.760(3) Å <i>b</i> = 5.838(2) Å <i>c</i> = 18.56(2) Å	<i>a</i> = 8.881(1) Å <i>b</i> = 5.992(1) Å <i>c</i> = 18.879(2) Å
<i>V</i>	1027.29(19) Å ³	938.38(3) Å ³	949.2(5) Å ³	1004.7(3) Å ³
<i>Z</i>	2	2	2	2
Reference	This study	Nagashima & Armbruster (2010)	Barresi <i>et al.</i> (2007)	Nishio-Hamane & Minakawa (2016)

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