Solid solution between piemontite and androsite-(La), a new mineral of the epidote group from Andros Island, Greece

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ABSTRACT

A new member of the epidote group, androsite-(La), was found at Andros Island, Cyclades, Greece, as an accessory constituent of metamorphic Mn-rich rocks. Associated minerals are rhodochrosite, braunite, rhodonite, spessartine, and quartz. The mineral is brown-red in color, transparent with vitreous luster and very strong pleochroism. Lattice parameters are $a = 8.896(1)$, $b = 5.706(1)$, $c = 10.083(1)$ Å, $\beta = 113.88(1)°$, $V = 468.0(1)$ Å^3, $Z = 2$, space group $P2_1/m$. Crystal-structure refinement and chemical analyses yielded the ideal formula $(Mn,Ca)REEAlMn^{3+}Mn^{2+}(SiO_4)(Si_2O_7)O(OH)$. Another Mn-rich sample of the epidote group was found at Varenche Mn-mine, Valle di Saint Barthélemy, Western Alps, Italy; because of its chemical composition and crystallographic features, it can be considered an intermediate member of the piemontite–androsite-(La) series.

INTRODUCTION

Until 1988, the only known REE-bearing mineral of the epidote group was allanite, which can be described by the ideal formula $CaREEAl_2Fe^{2+}(Si_3O_{11})O(OH)$. In recent years other epidote minerals containing lanthanide elements as dominant cations in the A2 site have been described. In the structure of dissakisite-(Ce), $CaREEAl_2Mg(Si_3O_{11})O(OH)$ (Grew et al. 1991), the excess positive charge due to REE^{3+} replacing Ca is balanced by the substitution of Mg. This mineral is therefore considered to be the Mg analog of allanite. Dollaseite-(Ce), $CaREEAlMg_2(Si_3O_{11})F(OH)$ (Peacor and Dunn 1988), is characterized by a more complex substitution. The presence of two divalent cations in the octahedral sites is coupled with the substitution of F^- for O^{2-} on the O4 site. A new member of the epidote group with the formula $(Ca,REE)REE(Mg,Fe)MnAl(Si_3O_{11})OH(F,O)$ was found by Sokolova et al. (1991) at Inyl'chek Massif, Kirgiziya (former USSR). In this mineral, subsequently named khristovite-(Ce) by Pautov et al. (1993), two octahedral sites are mostly occupied by divalent cations (Mg in M1 and Mn in M3). Electrostatic balance is achieved by REE^{3+} substituting for Ca and by the substitution of F for O at the O4 site.

The present paper reports the results of a crystal-chemical study of two REE minerals of the epidote group that have chemical compositions and cation populations not previously recognized in any member of this group. The first one, named androsite-(La) after its original locality (Andros Island, Greece), is a new mineral with the ideal formula $(Mn,Ca)REEMn^{2+}Mn^{3+}Al(Si_3O_{11})O(OH)$ (approved by the International Mineralogical Association Commission on New Minerals and Mineral Names). Type material has been deposited at the Mineralogical Museum of the University of Florence (sample no. 2074/RI). The second mineral, collected at the Varenche mine (Valle di Saint Barthélemy, Western Alps, Italy) is piemontite with REE content greater than that found in any REE-bearing piemontite previously described (Williams 1893; Kramm 1979; Schreyer et al. 1986; Bonazzi et al. 1992; Bermanec et al. 1994). This mineral also has the $Mn^{2+} \rightleftharpoons Ca$ substitution but to a lesser extent than androsite-(La). The chemical composition of these piemontite samples suggests the existence of a continuous solid solution between piemontite and androsite-(La).

OCCURRENCE, PARAGENESIS, AND PHYSICAL PROPERTIES

The sample (79/517) containing androsite-(La) was collected on the heap of a former test pit for Mn ores, situated at an altitude of 950 m on the peak plateau of Petalon Mountain, Andros Island, Cyclades, Greece. The Mn-rich metamorphic rocks at this site are made up of highly oxidized quartzitic schists, quartzites, and Mn-rich pyroxenoid and carbonate rocks (Reinecke 1983; Reinecke and Hatzipanagiotou 1987), among which the more Ca-poor assemblages (e.g., spessartine quartzite, rhodonite + rhodochrosite + braunite felse) occasionally have androsite-(La) as a minor or accessory constituent. The ferromanganoan metasediments in central Andros form part of a volcano-sedimentary sequence that experienced low-grade, high-pressure metamorphism ($P > 11$ kbar, $T = 360–420 °C$; Reinecke, unpublished data) followed along the uplift path by a greenschist facies overprint.

In Mn-rich silicate-carbonate rock 79/517, minute grains of androsite-(La) (commonly with a maximum diameter of 20–60 μm, rarely up to 200 μm) are randomly interspersed in a fine- to medium-grained matrix of rho-

TABLE 1. Calculated and observed powder diffraction data for androsite

hkl	d_{calc}*	I_{calc}**	d_{obs}	I/I_o
$\bar{1}01$	7.886	26	7.89	20
101	5.152	16	5.16	10
$\bar{1}02$	4.964	14	4.98	25
110	4.671	16	4.68	20
002	4.610	11	4.62	10
012	3.586	7	3.594	20
$\bar{2}11$	3.506	41	3.504	40
210	3.312	11	3.318	10
201	3.265	8	3.270	10
$\bar{3}02$	2.908	24	} 2.897	100
$\bar{1}13$	2.895	100		
020	2.853	35	2.857	45
300	2.712	15	}	
013	2.706	31	2.707	60
120	2.692	37	}	
$\bar{3}11$	2.616	53	2.615	60
202	2.576	29	2.576	35
$\bar{1}22$	2.474	8	—	—
022	2.426	8	2.429	15
$\bar{3}13$	2.387	14	2.389	20
$\bar{2}22$	2.311	14	2.312	15
$\bar{4}01$	2.180	23	2.178	60
221	2.148	20	2.145	60
$\bar{2}23$	2.111	16	2.112	20
023	2.091	16	2.086	25
222	1.912	13	1.913	20
$\bar{2}24$	1.873	11	1.876	20
$\bar{1}33$	1.655	$\bar{1}3$	1.655	35
$3\bar{2}2$	1.642	11	1.639	20
$\bar{4}24$	1.622	23	1.623	40

* The d values calculated on the basis of $a = 8.896(1)$, $b = 5.706(1)$, $c = 10.083(1)$ Å, $\beta = 113.88(1)°$.
** Intensities calculated using XPOW software, version 2.0 (Downs et al. 1993). Only reflections with $I/I_o > 8$ are listed.

TABLE 2. Crystal data and experimental details

	VA-1a	AND-517
Space group	$P2_1/m$	$P2_1/m$
Cell parameters:		
a (Å)	8.890(2)	8.896(1)
b (Å)	5.690(1)	5.706(1)
c (Å)	10.135(2)	10.083(1)
β (°)	114.44(2)	113.88(1)
V (Å³)	466.7(2)	468.0(1)
Z	2	2
Crystal size (μm)	48 × 64 × 256	32 × 60 × 65
Theta range (°)	2–32	2–32
Scan mode, scan width	ω, 2.8°	ω, 2.8°
Scan speed (°/min)	1.0–3.3	0.9–2.7
Refl. used for ψ scan: hkl	153	124
Relative χ angle (°)	86.9	87.4
Min. transmission (%)	84.3	92.4
Independent refl.	1693	1455
Observed refl.	1219	1130
$F_o > n\sigma_{F_o}$	$n = 8$	$n = 6$
R_{merge} (%)	2.02	2.30
R (%)	2.40	2.63
R_w (%)	2.01	2.03

Note: AND-517 = androsite; VA-1a = manganoan REE-rich piemontite from Varenche.

dochrosite, patchy rhodonite, fine-grained subhedral braunite, and rare fishnet-type garnet (85 mol% spessartine, 9 mol% grossular, 6 mol% andradite). Androsite-(La) crystals are subhedral to euhedral, untwinned, brown-red in color, transparent, with vitreous luster. Pleochroism in plane-polarized light is very strong: X = pale orange-brown and Z = deep brown-red (Y not determined). The mean refractive index, calculated from the Gladstone-Dale relationship using the constants given by Mandarino (1976), is 1.877. The observed density is >4.03 g/cm³ (it sinks in Clerici solution); the calculated value is 4.21 g/cm³.

The second mineral was found in a fine-grained, reddish-brown gneiss (VA90/1) sampled on the dump of the abandoned Mn mine at Varenche, Valle di Saint Barthélemy, a few kilometers northeast of Nus, Valle d'Aosta, Italy. The metasedimentary rocks at Varenche probably form part of the Tsaté nappe (= Combin Unit s.s., Dal Piaz 1988; Marthaler and Stampfli 1989), a composite nappe made up of calcschists, MORB-type metabasalts and metagabbros, serpentinites, and pelagic (partly manganiferous) metasediments, which were metamorphosed at greenschist-facies conditions. They locally retain relics of a low-grade, high-pressure metamorphism (Sperlich 1988; Reinecke, unpublished data). The highly oxidized, Mn-rich rocks consist mainly of varicolored spessartine-

hematite quartzites and braunite- and spessartine-bearing rocks, with variable proportions of rhodochrosite, crossite-magnesioriebeckite, phlogopite, phengite, clinochlore, talc, Na-bearing pyroxene, rutile and barite, and uncommon minerals such as ardennite, Mn-rich berzeliite, kutnahorite, and tirodite (Baldelli et al. 1983; Reinecke, unpublished data). The VA90/1 gneiss contains the relic high-pressure assemblage aegirine ($Jd_{35-37}Ac_{61}Aug_{2-4}$, partly replaced by very fine-grained intergrowths of albite and hematite), spessartine, hematite, colorless crossite, quartz, phengite, with minor rutile and REE-rich piemontite. Abundant albite poikiloblasts in the matrix, manganoan phlogopite replacing phengite and crossite, and magnesioriebeckite rims around crossite are interpreted as members of a lower pressure assemblage. The REE-rich piemontite described here occurs as a few scattered grains, 20–180 μm in diameter, in the gneiss. It forms euhedral, prismatic crystals, brownish-red in color, commonly twinned after {100}, and displays vivid absorption colors (X = pale orange-brown, Y = orange-brown, and Z = bright orange-red).

EXPERIMENTAL METHODS

An X-ray powder pattern of androsite-(La) (Table 1) was obtained from a few minute grains by means of a Gandolfi camera (diameter = 114.6 mm, Ni-filtered Cu$K\alpha$ radiation). For the crystal-structure study, two optically homogeneous crystals, AND-517 and VA-1a, were selected from rock samples 79/517 (Andros) and VA90-1 (Varenche), respectively. Unit-cell parameters and intensity data were measured on an Enraf Nonius CAD4 diffractometer with graphite-monochromatized Mo$K\alpha$ radiation. Crystal data and experimental details are reported in Table 2. Intensities were corrected for Lorentz and

TABLE 3. Atomic positional and displacement parameters for androsite-(La)

	x/a	y/b	z/c	U_{eq} (Å²)
A1	0.7587(1)	0.7500	0.1525(1)	0.0117(3)
A2	0.5922(1)	0.7500	0.4275(1)	0.0110(1)
Si1	0.3504(2)	0.7500	0.0368(2)	0.0086(4)
Si2	0.6937(2)	0.2500	0.2809(2)	0.0080(5)
Si3	0.1915(2)	0.7500	0.3251(2)	0.0066(5)
M1	0.0000	0.0000	0.0000	0.0070(3)
M2	0.0000	0.0000	0.5000	0.0085(6)
M3	0.3130(1)	0.2500	0.2099(1)	0.0129(3)
O1	0.2470(3)	0.9925(5)	0.0266(3)	0.0143(10)
O2	0.3140(3)	0.9746(5)	0.3601(3)	0.0104(10)
O3	0.8052(3)	0.0133(5)	0.3306(3)	0.0116(9)
O4	0.0576(5)	0.2500	0.1317(4)	0.0082(13)
O5	0.0481(4)	0.7500	0.1584(4)	0.0103(14)
O6	0.0796(5)	0.7500	0.4211(4)	0.0097(13)
O7	0.5189(5)	0.7500	0.1773(5)	0.0139(15)
O8	0.5545(5)	0.2500	0.3430(5)	0.0211(17)
O9	0.6036(5)	0.2500	0.1042(5)	0.0174(16)
O10	0.0913(5)	0.2500	0.4338(5)	0.0079(13)
H	0.100(7)	0.2500	0.350(7)	0.07(1)

TABLE 4. Atomic positional and displacement parameters for the REE-rich piemontite from Varenche

	x/a	y/b	z/c	U_{eq} (Å²)
A1	0.7590(1)	0.7500	0.1523(1)	0.0128(3)
A2	0.5942(1)	0.7500	0.4256(1)	0.0123(1)
Si1	0.3440(1)	0.7500	0.0399(1)	0.0082(4)
Si2	0.6893(1)	0.2500	0.2787(1)	0.0081(4)
Si3	0.1864(1)	0.7500	0.3213(1)	0.0072(4)
M1	0.0000	0.0000	0.0000	0.0086(3)
M2	0.0000	0.0000	0.5000	0.0072(5)
M3	0.3020(1)	0.2500	0.2151(1)	0.0126(3)
O1	0.2401(3)	0.9921(4)	0.0327(3)	0.0154(8)
O2	0.3087(3)	0.9763(4)	0.3578(2)	0.0114(8)
O3	0.7998(3)	0.0135(4)	0.3357(3)	0.0139(7)
O4	0.0558(4)	0.2500	0.1313(3)	0.0095(11)
O5	0.0450(4)	0.7500	0.1524(3)	0.0116(11)
O6	0.0740(4)	0.7500	0.4153(4)	0.0101(11)
O7	0.5154(4)	0.7500	0.1768(4)	0.0162(12)
O8	0.5410(4)	0.2500	0.3286(4)	0.0208(14)
O9	0.6153(4)	0.2500	0.1027(4)	0.0203(14)
O10	0.0865(4)	0.2500	0.4311(4)	0.0093(11)
H	0.062(6)	0.2500	0.341(6)	0.05(1)

polarization effects and for absorption (North et al. 1968). Structure refinements were performed using SHELX (Sheldrick 1976) with a weighting scheme $w = k/\sigma_{Fo}^2$. Final refinement cycles, with anisotropic displacement parameters for all atoms other than H, gave R_w values of 2.03 and 2.01% for AND-517 and VA-1a, respectively. Occupancy was refined for M1, M2, M3, A1, and A2 sites. Scattering factors and correction factors for anomalous dispersion were taken from the *International Tables for X-ray Crystallography,* volume IV (Ibers and Hamilton 1974). The atomic coordinates and isotropic displacements for androsite-(La) and piemontite from Varenche are given in Tables 3 and 4, respectively.

Preliminary semiquantitative EDS analyses of a few grains of the two minerals indicated their peculiar chemical compositions. For crystals from sample 79-517, normalization to $\Sigma_{cations} = 8.00$ always led to Mn ranging from 2.4 to 2.6 atoms per formula unit (apfu). Quantitative chemical analyses were subsequently obtained using an ARL-SEMQ electron microprobe. The crystals analyzed were those used for the structure refinements. The analyses were performed on $K\alpha$ lines for light elements (F, Mg, Al, Si, Ca, Ti, Mn, Fe, Cu), $L\alpha$ lines for Sr and Y, and $M\alpha$ lines for Th. To avoid intra-REE interferences, La and Ce were determined on $L\alpha$ peaks and Nd, Pr, Sm, and Gd on $L\beta$ peaks. Heavy rare earth elements were not included in the file because they were below the detection limit of the instrument. The REE standards used were those of Drake and Weill (1972). Chemical analyses for crystals AND-517 and VA-1a are given in Table 5.

DISCUSSION

The structure of androsite-(La) is topologically identical to the other monoclinic members of the epidote group. Only minor variations, related to the particular chemical composition, affect the atomic arrangement in androsite-

TABLE 5. Chemical composition (wt%) and atomic proportions of the single crystals studied

	VA-1a	AND-517
CaO	9.403	5.810
SrO	3.490	0.663
La_2O_3	2.950	7.225
Ce_2O_3	6.427	6.673
Pr_2O_3	0.910	1.342
Nd_2O_3	2.840	4.722
Sm_2O_3	0.453	0.313
Gd_2O_3	0.210	0.027
ThO_2	0.937	—
MnO*	11.350	28.288
MgO	1.157	—
CuO	1.813	0.155
Fe_2O_3*	5.516	1.175
Al_2O_3	15.113	8.542
TiO_2	—	0.027
SiO_2	31.330	30.413
F	0.107	0.100
Total	94.006	95.475
−O = F	0.045	0.042
Total	93.961	95.433
Ca	0.964	0.627
Sr	0.194	0.039
La	0.105	0.268
Ce	0.226	0.246
Pr	0.032	0.049
Nd	0.097	0.170
Sm	0.015	0.011
Gd	0.007	0.001
Th	0.020	—
Mn	0.929	2.412
Mg	0.166	—
Cu	0.134	0.012
Fe	0.398	0.089
Al	1.709	1.013
Ti	—	0.002
Si	3.004	3.061
F	0.032	0.032
REE	0.502	0.745

* MnO and Fe_2O_3 as total Mn and Fe, respectively; H_2O not determined. Total cations = 8.0.

TABLE 6. Selected interatomic distances (Å), polyhedral volumes (Å^3), and the numbers of electrons derived from site-occupancy refinements

	VA-1a	AND-517
Si1-O1 × 2	1.643(2)	1.642(3)
Si1-O7	1.580(3)	1.592(4)
Si1-O9	1.629(5)	1.631(6)
Mean	1.624	1.627
V	2.19	2.20
Si2-O3 × 2	1.625(2)	1.630(3)
Si2-O8	1.596(4)	1.598(6)
Si2-O9	1.626(4)	1.631(5)
Mean	1.618	1.622
V	2.17	2.19
Si3-O2 × 2	1.626(2)	1.626(3)
Si3-O5	1.652(3)	1.648(3)
Si3-O6	1.641(5)	1.646(5)
Mean	1.636	1.636
V	2.23	2.23
M1-O1 × 2	2.021(3)	2.104(3)
M1-O4 × 2	1.869(2)	1.873(2)
M1-O5 × 2	2.014(2)	2.053(3)
Mean	1.968	2.010
V	10.10	10.75
e⁻ (M1)	19.1	24.6
M2-O3 × 2	1.869(2)	1.879(2)
M2-O6 × 2	1.913(3)	1.904(3)
M2-O10 × 2	1.883(3)	1.892(4)
Mean	1.889	1.892
V	8.91	8.94
e⁻ (M2)	13.0	13.5
M3-O1 × 2	2.243(3)	2.245(3)
M3-O2 × 2	2.109(2)	2.180(3)
M3-O4	1.993(3)	2.082(4)
M3-O8	1.953(3)	2.020(4)
Mean	2.109	2.159
V	11.93	12.60
e⁻ (M3)	24.0	25.0
A1-O7	2.280(4)	2.246(5)
A1-O3 × 2	2.297(3)	2.248(3)
A1-O1 × 2	2.384(3)	2.313(3)
A1-O5	2.542(4)	2.551(4)
Mean	2.364	2.320
V	15.91	15.44
e⁻ (A1)	21.6	23.0
A2-O7	2.321(4)	2.336(5)
A2-O2 × 2	2.534(2)	2.511(3)
A2-O10	2.599(3)	2.588(4)
A2-O2' × 2	2.670(3)	2.621(3)
A2-O3 × 2	2.792(3)	2.881(3)
A2-O8 × 2	2.983(1)	2.957(1)
Mean	2.688	2.686
V	34.38	34.32
e⁻ (A2)	44.5	48.2
O10-O4	2.936(5)	2.938(7)

FIGURE 1. Parameters of the A1 polyhedron as a function of the Mn^{2+} content of A1. Average of the six smallest A1-O distances is designated $\langle$A1-O$\rangle$; the equation of the regression line is: $y = 2.404 - 0.135x$ ($r = -0.993$). Difference between the seventh (A1-O6) and the sixth largest (A1-O5) distances is designated δ_{7-6}; the equation of the regression line is $y = 0.321 + 0.280x$ ($r = 0.990$). Solid and open squares represent piemontite from Saint Marcel (Dollase 1969) and REE-bearing piemontite crystals, respectively [BR1A, BR2P, BR2H (Bonazzi et al. 1992), BR1P (authors' unpublished data)]; solid circles represents VA1-a and solid triangles AND-517; open circles represent the sample from Nezilovo (Bermanec et al. 1994), for which a content of $Mn^{2+}_{A1} = 0.30$ apfu was assumed (see text).

(La) and to a lesser extent in the REE-rich piemontite from Varenche. The structure consists of two independent edge-sharing octahedral chains, both extending parallel to b: a single chain of M2 octahedra and a composite chain of M1 octahedra with M3 polyhedra attached on alternate sides along its length. The chains are crosslinked by SiO_4 and Si_2O_7 groups, and the remaining cavities are occupied by the A1 and A2 cations. In Table 6 selected interatomic distances and other relevant structural parameters are given.

Site populations

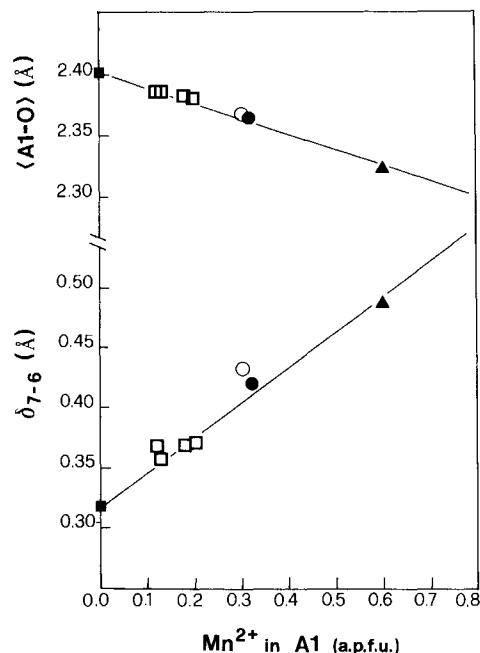**A polyhedra.** On the basis of chemical data and occupancy refinement, we infer that in androsite-(La) the A1

site is occupied by 0.60Mn + 0.40Ca. Such a high content of Mn^{2+} modifies the arrangement of the linked O atoms: The seventh neighbor (O6) is shifted away from A1, so that the latter can be more appropriately described as sixfold-coordinated. This is apparent from the value of the gap between the seventh and the sixth distance (δ_{7-6}), which increases from 0.316 Å in piemontite (Dollase 1969) to 0.490 Å in androsite-(La) (Fig. 1). The high content of Mn^{2+} also affects the mean $^{[6]}\langle$A1-O$\rangle$ distance, which has the very low value of 2.320 Å (Fig. 1).

In the REE-rich piemontite from Varenche, Ca is the prevailing cation in A1. However, the presence of about 0.30 Mn^{2+} (apfu) replacing Ca at this site is consistent with the mean number of electrons determined from the occupancy refinement and accounts for the geometrical features shown by the A1 polyhedron (Fig. 1). In our opinion, a similar site population for A1 should be expected for the Pb- and REE-rich piemontite from Nezilovo (Bermanec et al. 1994). In the 11 analyses published for the latter, the sum Ca + REE + Pb + Na ranges from 1.66 to 1.76 apfu (mean value = 1.70), and the sum Al

+ Fe + Mn + Mg + Zn exceeds 3 apfu, ranging from 3.21 to 3.30 (mean value = 3.27). It is interesting to note that the mean distance $^{[6]}\langle A1\text{-}O\rangle$ and δ_{7-6} (2.367 and 0.431 Å, respectively) closely match the values observed in the crystal VA-1a.

As in the structure of the other REE-bearing epidote group minerals, lanthanide elements are ordered in A2, mainly to compensate for the charge imbalance occurring on O2 when divalent cations prevail in M3. In androsite-(La) and, to a lesser extent, in the piemontite from Varenche, REEs are the dominant cations in A2. Sr and Th, in the amount determined with the microprobe, were assumed to enter the A2 site, Sr because of its known preference for this site (Dollase 1969; Catti et al. 1989; Bonazzi et al. 1990) and Th because it normally substitutes for lanthanides.

M octahedra. After the site assignment in the A polyhedra, a very high content of Mn (≈ 1.8 apfu) remained to be distributed between the octahedral sites in androsite-(La). Taking into account the analytical data and the exceptionally high number of electrons (24.6) detected for M1, it was assumed that this site is almost completely filled by Mn. The observed mean distance $\langle M1\text{-}O\rangle$ of 2.010 Å indicates that it is Mn^{3+}. The value of the $\langle M3\text{-}O\rangle$ distance (2.159 Å) requires that almost all of the octahedrally coordinated divalent cations necessary for charge balance in the full formula unit enter the largest site, M3. In fact, considering the mean bond distance as a weighted mean of $\langle Mn^{2+}\text{-}O\rangle$ and $\langle Mn^{3+}\text{-}O\rangle$, a site population for M3 of $0.73Mn^{2+} + 0.27Mn^{3+}$ is estimated. [The following values were used: $\langle Mn^{3+}\text{-}O\rangle = 2.058$ Å, from a very Mn-rich piemontite from Saint Marcel, Italy, having a mean number of electrons in M3 = 24.8 and Mn/(Mn + Fe) = 0.96 (Bonazzi 1990); $\langle Mn^{2+}\text{-}O\rangle = 2.197$ Å, from the mineral described by Sokolova et al. (1991).] For the M2 site, usually fully occupied by Al, the occupancy refinement yielded 13.5 electrons, corresponding to about 4% of Fe^{3+} substituting for Al. Similarly, Tillmanns et al. (1984) found small amounts of Fe (or Mn) replacing Al in the M2 site of a piemontite from Lom (Norway). The value of 1.907 Å found by Sokolova et al. (1991) for the $\langle M2\text{-}O\rangle$ mean distance could suggest that, to a small extent, the $Fe^{3+} \rightleftharpoons Al$ substitution also occurs in khristovite-(Ce). In conclusion, in androsite-(La) two of the three octahedral sites are occupied by Mn with Mn^{2+} in M3 and Mn^{3+} in M1. Full occupancy of M1 by Mn^{3+} was obtained in synthetic piemontite crystals by Anastasiou and Langer (1977), but this has never been reported in natural crystals.

For the REE-rich piemontite from Varenche, the simultaneous presence of Mn, Fe, Mg, Al, and Cu in the octahedral sites does not permit an unambiguous determination of the cation distribution among the M sites. Nevertheless, an analysis of the bond distances and of the mean number of electrons (Table 6) provides some constraints. The mean M2-O distance of 1.889 Å agrees well with the presence of only Al in the smallest octahedron of the structure. The mean $\langle M3\text{-}O\rangle$ and $\langle M1\text{-}O\rangle$ distances (2.109 and 1.968 Å, respectively) are greater than the
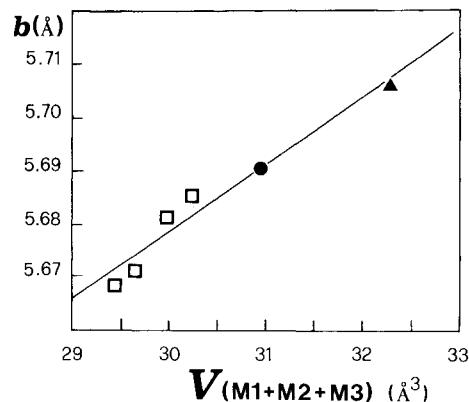

FIGURE 2. The b lattice parameter vs. the sum of the octahedral volumes; the equation of the regression line is $y = 5.294 + 0.0128x$ ($r = 0.979$). Symbols as in Figure 1.

corresponding values calculated (Bonazzi 1990) on the basis of the number of electrons and assuming a site population of only trivalent (Al, Mn^{3+}, Fe^{3+}) cations ($\langle M3\text{-}O\rangle_{calc} = 2.045$ Å and $\langle M1\text{-}O\rangle_{calc} = 1.954$ Å). For the M3 octahedron, the large difference from the calculated value is undoubtedly due to the presence of Mn^{2+}, whereas the small but significantly larger value determined for $\langle M1\text{-}O\rangle$ could be explained with the presence of Mg or Cu^{2+}. These cations have very similar ionic radii and therefore would affect the interatomic distance in the same way. On the other hand, the small observed discrepancy does not justify assigning to M1 all the Mg and Cu derived from the chemical analysis. Furthermore, Cu^{2+}, like Mn^{3+}, is a cation susceptible to Jahn-Teller distortion in sixfold-coordinated sites and therefore should be preferentially located in the more tetragonally distorted M3 octahedron. For this reason it was assumed that Mg substitutes in M1 and Cu in M3.

On the basis of the chemical data and keeping in mind the crystal-chemical relations, the following formulas were obtained: androsite-(La): $(Mn^{2+}_{0.60}Ca_{0.40})(REE^{3+}_{0.72}Ca_{0.24}$-$Sr_{0.04})(M^{3+}_{0.96}Al_{0.04})(Al_{0.96}M^{3+}_{0.04})(M^{2+}_{0.71}M^{3+}_{0.28}Cu_{0.01})Si_3O_{11}$-$(O_{0.97}F_{0.03})(OH)$, with M = 95% Mn + 5% Fe; piemontite from Varenche: $(Ca_{0.67}Mn^{2+}_{0.33})(REE^{3+}_{0.50}Th^{4+}_{0.02}Ca_{0.29}Sr_{0.19})$ $(M^{3+}_{0.50}Al_{0.34}Mg_{0.16})(Al_{1.00})(M^{2+}_{0.28}Cu^{2+}_{0.13}Al_{0.37}M^{3+}_{0.22})(Si_3O_{11})$ $(O_{0.97}F_{0.03})(OH)$, with M = 60% Mn + 40% Fe.

Unit-cell parameters

The greater Mn^{2+}, Mn^{3+}, and Fe^{3+} contents of M sites in androsite-(La) relative to piemontite produce an expansion of the octahedra, which, in turn, results in a lengthening of the b axis. In Figure 2 the linear relation between the b parameter and the sum of the volumes of the three octahedral polyhedra ($V_{M1+M2+M3}$) is shown. The value of the unit-cell volume exhibits a nonlinear increase when plotted against $V_{M1+M2+M3}$ (Fig. 3). This is because the linkage between octahedral chains and tetrahedra becomes closer when greater amounts of Mn^{2+} and REE^{3+} substitute for Ca^{2+}. Consequently, there are rotations of
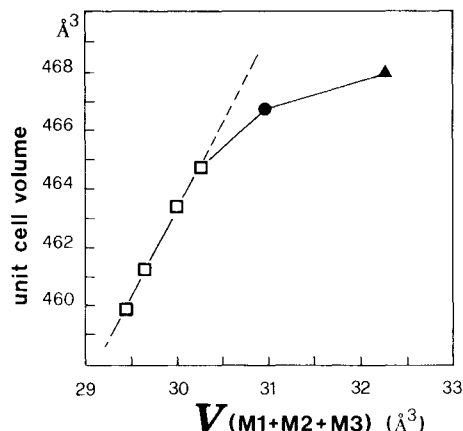
FIGURE 3. The unit-cell volume plotted against the sum of the octahedral volumes. Symbols as in Figure 1.

the polyhedra, as can be seen from the trend of Si1-O9-Si2 and Si2-O8-M3 angles for the REE-bearing piemontite crystals BR2H (148.4°; 138.9°), VA-1a (146.7°; 130.8°), and androsite-(La) (140.0°; 121.6°). These angles also vary significantly with increasing Fe content in members of the clinozoisite-epidote series (Carbonin and Molin 1980). The c parameter shows a more complex behavior. The entry of Mn^{2+}, Mn^{3+}, and Fe^{3+} into the octahedra, as well as the entry of Sr into A2, causes a slight increase in c; REEs produce the opposite effect. Therefore, the ratio of

FIGURE 4. The ratio of c to the unit-cell volume (c/V) (upper line), and the angle β (lower line) vs. the REE content. The equations of the regression lines are $y = 220.77 \times 10^{-4} - 7.30 \times 10^{-4}x$ ($r = -0.996$) and $y = 115.49 - 2.09x$ ($r = -0.979$), respectively. Symbols as in Figure 1.
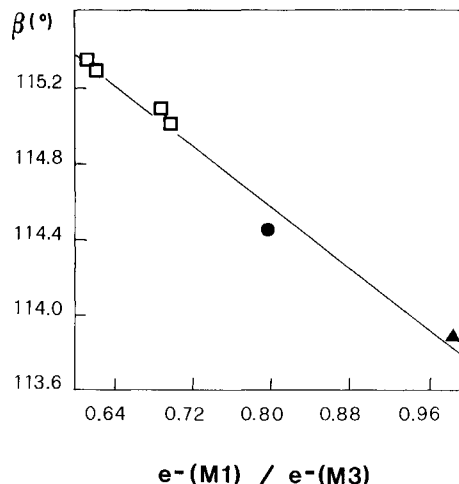

FIGURE 5. Value of angle β plotted against $e^-(M1)/e^-(M3)$ (the ratio of electrons in M1 and M3). The equation of the regression line is $y = 117.82 - 4.06x$ ($r = -0.991$).

c to the unit-cell volume appears to be an accurate measure of the REE content in minerals of the piemontite-androsite series (Fig. 4). A linear correlation between the REE content and β, which in androsite-(La) is 113.88°, is also observed (Fig. 4). The value of β is linearly related to the ratio of the mean number of electrons in M1 to those in M3 (Fig. 5). In fact, the cation ordering between the M1 and M3 sites appears to be related to the REE content. The reason for this is that, in the structure of the epidote group minerals, the substitution of Fe and Mn for Al in M1 is regulated by the volume of the M3 octahedron, which shares the edge O1-O4 with the M1 octahedron (Bonazzi and Menchetti 1995). In epidote-group members containing REE, the volume of M3 is greater because of the presence of divalent cations, and, therefore, the ratio of the mean number of electrons in M1 with respect to those in M3 [$e^-(M1)/e^-(M3)$] increases with REE content.

REE distribution

As already emphasized by Deer et al. (1986), Ce in allanite is always present in greater amounts than lanthanum (Ce/La ratio generally ranges from 2:1 to 3:1) and often constitutes more than one-half of the total REEs. Dollaseite-(Ce) and dissakisite-(Ce) present an analogous trend. Conversely, androsite shows a different distribution of REEs in that La prevails slightly. The chondrite-normalized REE pattern reveals a negative Ce anomaly and on the whole is very similar to that of the REE-bearing piemontite from Mount Brugiana (Bonazzi et al. 1992). Furthermore, in the Pb- and REE-bearing piemontite from Nezilovo (Bermanec et al. 1994), the La content equals or exceeds that of Ce. By way of contrast in piemontite from Varenche Ce prevails, and its normalized pattern displays a flatter slope, suggesting a smaller value of HREE.

CONCLUSIONS

The REE-rich piemontite from Varenche is intermediate in composition and structural parameters between piemontite and androsite-(La). The contents of the A1, A2, and M1 sites are consistent with the hypothesis of a complete series. Solid solution extends to strontiopiemontite, as deduced from the high Sr content (0.19 apfu), and toward the epidote-dissakisite join (Fe^{3+} and Mg of 0.40 and 0.16 apfu, respectively).

In light of these findings, the previously described REE-bearing piemontite samples from Mount Brugiana (Bonazzi et al. 1992) have variable amounts of the androsite-(La) component in solid solution.

The extremely Mn^{2+}- and Mn^{3+}-rich, Fe^{3+}-poor composition of androsite may be caused by an Al- and Fe^{3+}-poor bulk-rock composition and by the coexistence of androsite with braunite, $Mn^{2+}Mn_6^{3+}SiO_{12}$, rhodonite, and quartz. A chemical study of piemontite-bearing manganiferous metapelites and quartzites spatially associated with the Mn-rich silicate-carbonate felses in central Andros (Reinecke 1986) has shown that piemontite with maximum Mn^{3+} contents was present only in Fe^{3+}-poor, Mn^{3+}-saturated (i.e., braunite-bearing) assemblages. Higher bulk-rock Fe^{3+} contents cause decreasing Mn^{3+} and increasing Fe^{3+} in both piemontite (as perhaps also in androsite) and braunite and finally lead to the appearance of hematite in Fe^{3+}-saturated assemblages. Chemical analyses of two Mn-rich silicate-carbonate felses from the type locality, which lack androsite-(La) but are otherwise similar to sample 79/517 (this study), indicate that these rocks have very low Al and Fe contents and high Mn contents (Reinecke et al. 1985, Table 8: 80/40 and 80/114).

An f_{O_2} value close to that of the $CuO + Cu_2O$ buffer is implied by the assemblage braunite + quartz + rhodonite in the pure Mn-Si-O system (Abs-Wurmbach et al. 1983; Figs. 4, 5a, and 5b). This estimate is larger in the natural assemblage because of major solid-solution effects of rhodonite on the braunite + quartz + rhodonite equilibrium. Following Keskinen and Liou (1979), f_{O_2} values of this magnitude stabilize piemontite, $Ca_2Mn\ Al_2Si_3O_{11}O(OH)$, and should also favor the incorporation of considerable Mn^{3+} in androsite-(La).

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