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Abstract

An unusual REE- and Pb-rich epidote group mineral (up to 10 wt% PbO) related to piemontite was found at Nezilovo, Macedonia, at the upper part of Babuna river, about 40 km SW Skopje, where a mica schist with red mica, quartz, ardennite, gahnite, franklinite(?) and piemontite occurs within a metamorphic complex (so-called "mixed series").

X-ray single-crystal structure refinement ($\underline{a} = 8.880(1)$ Å, $\underline{b} = 5.681(1)$ Å, $\underline{c} = 10.166(3)$ Å and $\beta = 114.66(2)°$, space group P 2_1/m, Z = 2, R = 3.35 and $R_w = 3.26\%$) and electron microprobe analyses indicate a chemical formula varying between: $Ca_{1.31}REE_{0.27}Pb_{0.14}Mn_{1.00}Fe_{0.51}Al_{1.66}Mg_{0.08}Zn_{0.05}(Si_2O_7)(SiO_4)O(OH,F)$ and $Ca_{1.17}REE_{0.26}Pb_{0.28}Mn_{0.97}Fe_{0.56}Al_{1.55}Mg_{0.08}Zn_{0.05}(Si_2O_7)(SiO_4)O(OH,F)$. This mineral is an intermediate member between piemontite, hypothetical $CaPbAl_2Mn(Si_2O_7)(SiO_4)O(OH,F)$ – related to hancockite and allanite. Charge balance for the trivalent REE at the ten-coordinated A2 site is obtained by two-valent elements on octahedral M1 and M3 sites. Two-valent cations on M3 increase the M3-O distance which leads to a stronger kinking of the Si1-O9-Si2 angle which ranges from 138° for REE-rich piemontite to 164° for clinozoisite. For Nezilovo piemontite an intermediate Si1-O9-Si2 value of 149° was obtained.

Piemontite from Nezilovo is deep red, nearly black, with adamantine luster and greyish-pink streak. The unusual mineral is brittle, with uneven fracture and without observed cleavage. Following forms were measured: {001}, {100}, {301}, {101}, {105}, {–102}, {–101}, {–201}, {–301} and {011}. The crystals are often twinned parallel to {100} and then have sections of isometric shape. Monocrystals are flattened on {001} and elongated parallel to $\underline{b}$. This piemontite is optically negative with $60° < 2V_x < 65°$. Refractive indices are very high (n > 1.80). The optical orientation is similar to allanite, Y = $\underline{b}$, X : c = 23° in acute angle β. The mineral is pleochroic: X = yellow-brown, Y = brown-red, and Z = purple-brown.

Keywords: piemontite, Pb, REE, electron microprobe analysis, crystal chemistry, structure refinement, X-ray single crystal data, Nezilovo, Macedonia.

Introduction

Epidote group minerals have the general formula $A_2M_3Si_3O_{12}OH$, where M sites are octahedrally coordinated, the A1 site is 9- or even 10-coordinated and the A2 site is 10-coordinated. A-O distances for A1 and A2 vary in a wide range between 2.3 Å and 3.2 Å. A1 is generally occupied by Ca^{2+} with minor substitutions of Mn^{2+} and/or Fe^{2+}. A2 may be occupied by Ca^{2+} but Sr^{2+}, Pb^{2+}, REE^{3+} and minor Mn^{2+}, Fe^{2+} or Ba^{2+} could substitute for it (DEER et al., 1986). If trivalent cations enter A2, charge balance could be obtained either by two-valent cations on M sites or by vacancies. M2 is dominated by Al, while M1 and M3 are suitable for a variety of cations such as Fe^{3+},

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Fe^{2+}, Mn^{3+}, Mn^{2+}, Al^{3+}, Mg^{2+}, U^{4+}, Th^{4+} or V^{3+}. In addition, it is known that these minerals may bear some fluorine substituting the OH-group or O (PEACOR and DUNN, 1988).

Following monoclinic minerals of the same structure type have been distinguished within the epidote group: clinozoisite, $Ca_2Al_3(Si_2O_7)(SiO_4)$ $(O,OH)_2$ (DOLLASE, 1968); epidote, Ca_2FeAl_2 $(Si_2O_7)(SiO_4)(O,OH)_2$ (DOLLASE, 1971); hancock-ite, $CaPb(Al,Fe)_3(Si_2O_7)(SiO_4)(O,OH)_2$ (DUNN, 1985; HOLTSTAM and LANGHOF, 1994); allanite-(Ce), $Ca(Ce,La)(Al,Fe)_3(SiO_4)_3(OH)$ (PAN and FLEET, 1991); allanite-(La), $(La,Ca)_2(Al,Fe)_3$ $(SiO_4)_3(OH)$ (LEVINSON, 1966); allanite-(Y), $Ca(Y,La,Ce)(Al,Fe)_3(SiO_4)_3(OH)$ (LEVINSON, 1966); dissakisite-(Ce), $Ca(Ce,La)MgAl_2Si_3O_{12}$ (OH) (GREW et al., 1991); dollaseite-(Ce), $CaREE^{3+}Mg_2AlSi_3O_{11}(OH)F$ (PEACOR and DUNN, 1988); mukhinite, $Ca_2Al_2VSi_3O_{12}(OH)$ (SHEPEL and KARPENKO, 1969); piemontite $Ca_2(Mn,Fe)$ $Al_2(Si_2O_7)(SiO_4)(O,OH,F)_2$ (DOLLASE, 1969); strontiopiemontite $(Ca,Mn)(Sr,Ca)(Mn,Al,Fe)$ $Al(Mn,Fe,Al)(Si_2O_7)(SiO_4)(O,OH,F)_2$ (BONAZZI et al., 1990). In addition, BONAZZI and MENCHETTI (1993) reported a new member of the epidote group with the composition $(Mn,Ca)REE$ $AlMn^{3+}Mn^{2+}(Si_3O_{11})O(OH)$ from Andros (Cyclades, Greece) occurring in Mn-rich metasediments.

Occurrence of Pb- and REE-rich piemontite

Nezilovo is known as a locality with an important positive Ba anomaly leading to the formation of barium silicates like cymrite, sanbornite and celsian (BERMANEC, 1992). Already JANČEV (1990) reported that piemontite from Nezilovo has about 3–4 wt% PbO. A slight enrichment of Pb was also found in the whole rock analyses of the mica schists containing the rare mineral ardennite (BERMANEC, 1992). In addition to the Pb- and REE-rich piemontite there are few more Pb-containing minerals found in the Nezilovo area: magnetoplumbite (BERMANEC et al., 1993); hedyphane (JANČEV, 1984; BERMANEC et al., 1993); galenite (BERMANEC, 1992). Probably, the Pb minerals formed before Ba invaded the metamorphic rock.

Pb- and REE-rich piemontite was found as accessory phase in the low grade metamorphic mica schist occurring with quartz, red mica, ardennite, gahnite and another opaque spinel (franklinite?) (BERMANEC, 1992). This rock is part of the so-called "mixed series" at the upper part of Babuna river (JANČEV, 1990; BERMANEC, 1992).

Experimental procedures

Pb- and REE-rich piemontite was analyzed using a Camebax Microbeam electron microprobe (University of Mainz) with an operating voltage of 15 kV and 10 nA current. Results are given in table 1. Wollastonite was used as a standard for Ca and Si, synthetic $MnTiO_3$ for Mn and Ti, albite for Na, orthoclase for K, synthetic Al_2O_3 for Al, synthetic Fe_2O_3 for Fe, vanadinite for Pb, willemite for Zn and synthetic REE glass for La, Ce and Nd. The measuring time was 15 sec for Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and Pb; 30 sec for Zn and 50 sec for Ce, La, Nd, Y, Th, U, Ba and Sr.

The crystal chosen for structural investigation was $0.125 \times 0.125 \times 0.075$ mm in size. X-ray intensity data were collected on a CAD4 single-crystal diffractometer with graphite monochromatized MoKα-radiation up to $\Theta = 25°$ in Ω scan mode. Cell dimensions were refined from reflections with $20° > \Theta > 10°$ in monoclinic symmetry yielding $a = 8.880(1)$ Å, $b = 5.681(1)$ Å, $c = 10.166(3)$Å, $\beta = 114.66(2)°$, $V = 466$ Å^3. Data reduction, including background and Lorentz-polarization corrections, was carried out using the SDP (ENRAF NONIUS, 1983) program library. The data were empirically corrected for absorption using psi-scans. 1556 reflections were collected of which 1334 were unique.

The refinement (weighted $1/\sigma^2$) was done with the program SHELX76 (SHELDRICK, 1976) on the basis of 949 reflections with $I > 3 \sigma(I)$ using neutral atom scattering factors. 82 parameters were refined including coordinates and anisotropic displacement parameters for metal sites. Oxygen positions were refined with isotropic displacement parameters. Test refinements with unconstrained populations indicated that A1 is a Ca site and heavy elements are concentrated on the A2 site. In addition, M2 hosts only Al whereas Mn and Fe are concentrated on M1 and M3. In the final refinement, an average value of 0.25 REE p.f.u. (as determined by electron microprobe analyses) was assigned to A2. The remaining population of A2 was filled with Ca and Pb in an unconstrained ratio, where Ca may also represent minor Mn. The Al/(Mn + Fe) ratio was allowed to vary in M1 and M3. Due to the similarity of Mn and Fe X-ray scattering factors, these elements were not distinguished in the refinement.

The optical orientation was determined using a polarizing microscope equipped with an universal stage. Thin sections were cut parallel to (010) and (001). A mean refractive index was measured by the immersion method using a spindle stage. Crystal forms were measured on a two circle reflecting goniometer.

Tab. 1 Microprobe analyses of Pb- and REE-rich piemontite from Nezilovo, Macedonia.

	11	C 1-2	C1-3	R1-4	R2-5	C3-7	C4-8	C4-9	R1	1	5
SiO_2	31.81	32.06	31.73	32.29	30.95	30.77	31.75	32.52	31.54	31.97	30.52
TiO_2	0.03	0.00	0.06	0.04	0.02	0.04	0.03	0.00	0.05	0.04	0.04
Al_2O_3	14.34	14.63	14.29	14.48	13.21	13.41	14.58	14.78	14.96	14.48	13.70
Fe_2O_3	7.52	7.66	7.55	7.73	7.48	7.62	7.27	7.53	7.14	8.19	7.86
Mn_2O_3	13.93	13.25	13.68	13.91	12.88	13.27	13.87	12.65	13.98	13.95	12.98
La_2O_3	3.88	2.64	3.87	3.61	4.36	4.55	3.26	2.20	2.68	3.62	5.09
Ce_2O_3	3.11	2.63	1.96	1.35	1.59	1.20	2.46	3.06	3.40	1.47	1.82
Nd_2O_3	1.57	1.43	1.26	1.11	1.10	1.07	1.51	1.58	1.77	1.00	0.98
MgO	0.56	0.44	0.52	0.45	0.51	0.54	0.49	0.43	0.56	0.48	0.60
CaO	12.08	12.80	11.88	12.43	10.99	11.16	12.18	12.67	13.02	12.83	11.32
Na_2O	0.19	0.18	0.17	0.13	0.12	0.13	0.24	0.17	0.24	0.18	0.21
K_2O	0.02	0.00	0.02	0.00	0.01	0.00	0.02	0.02	0.00	0.00	0.00
ZnO	0.74	0.65	0.68	0.60	0.65	0.69	0.75	0.70	0.73	0.62	0.68
PbO	6.08	6.27	6.88	6.77	10.35	9.86	5.78	6.37	5.57	6.27	10.28
Total	95.86	94.64	94.55	94.90	94.22	94.31	94.19	94.68	95.64	95.10	96.08
	—	—	—	—	—	—	—	—	—	—	—
#Si^{+4}	3.02	3.04	3.05	3.06	3.08	3.04	3.03	3.08	2.96	3.01	2.98
#Al^{+3}	1.60	1.64	1.62	1.62	1.55	1.56	1.64	1.65	1.66	1.61	1.58
#Fe^{+3}	0.54	0.55	0.55	0.55	0.56	0.57	0.52	0.54	0.51	0.58	0.58
#Mn^{+3}	1.01	0.96	1.00	1.00	0.97	1.00	1.01	0.91	1.00	1.00	0.97
#La^{+3}	0.14	0.09	0.14	0.13	0.16	0.17	0.11	0.08	0.09	0.13	0.18
#Ce^{+3}	0.11	0.09	0.07	0.05	0.06	0.04	0.09	0.11	0.12	0.05	0.07
#Nd^{+3}	0.05	0.05	0.04	0.04	0.04	0.04	0.05	0.05	0.06	0.03	0.03
#Mg^{+2}	0.08	0.06	0.07	0.06	0.08	0.08	0.07	0.06	0.08	0.07	0.09
#Ca^{+2}	1.23	1.30	1.22	1.26	1.17	1.18	1.25	1.29	1.31	1.30	1.19
#Na^{+1}	0.02	0.02	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02
#Zn^{+2}	0.05	0.05	0.05	0.04	0.05	0.05	0.05	0.05	0.05	0.04	0.05
#Pb^{+2}	0.16	0.16	0.18	0.17	0.28	0.26	0.15	0.16	0.14	0.16	0.27
#TOTAL	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00

Physical and optical properties of Pb- and REE-rich piemontite

Deep-red to deep-brown, nearly black grains of Pb- and REE-rich piemontite are up to 0.5 mm in size. The unusual piemontite is developed in idiomorphic grains, elongated parallel to the *b* axis and more or less platy on {001}. Following forms were observed {001}, {100}, {301}, {101}, {105}, {–102}, {–101}, {–201}, {–301} and {011}. Sometimes piemontite occurs as solid inclusions in mica. Piemontite has grayish pink streak and it is very brittle.

The refractive indices are > 1.80 and $2V_x$ varies from 60° to 65°; Y = b and X : c = 23 ° in acute angle β. The pleochroism is striking X: yellow-brown, Y: brown-red and Z: purple-brown. The dispersion is strong with r > v.

Chemical composition

The electron microprobe analyses of several grains are given in table 1. The mineral was also checked for the presence of F and its concentration was found to be between 0.20 and 0.45% (corresponding to ca. 0.1 a.p.f.u.), varying from the core to the rims. Fluorine was analyzed on the same microprobe but in separate runs, so the results are not included in table 1. Ba, Sr, Y, U and Th were also checked in microprobe runs but they were found to be not significant in this mineral. These analyses show that this piemontite is zoned mainly with respect to Pb and Ca. Total REE analyses vary between 6.09 wt% and 8.56 wt% whereas the Pb content ranges between 5.57 and 10.35 wt%. The formula was calculated on the basis of 8 cations. This standardization is confirmed by the resulting 3 Si p.f.u. Pb varies between 0.15 to 0.28 a.p.f.u. La from 0.08 to 0.18, Ce from 0.04 to 0.12 and Nd from 0.03 to 0.06 a.p.f.u. The total of the REE's is 0.21–0.30 yielding an average value of 0.25 a.p.f.u. There is a strong positive correlation between Pb and La. A negative correlation between Ca on one hand and Pb + REE on the other clearly indicates their respective substitution. The Mn/Fe molar ratio varies in a rather narrow range between 1.67–1.96

Tab. 2 Fractional coordinates and isotropic displacement parameters for Pb- and REE-rich piemontite from Nezilovo.

atom	x/a	y/b	z/c	Ueq	populations
A1	0.7587(2)	3/4	0.1522(1)	0.0104(5)	1 Ca
A2	0.59166(8)	3/4	0.41960(8)	0.0163(2)	0.25Ce + 0.56(1)Ca + 0.19(1)Pb
M1	0	0	0	0.0076(5)	0.36(1)Mn + 0.64(1)Al
M2	0	0	1/2	0.0079(6)	1 Al
M3	0.2990(1)	1/4	0.2189(1)	0.0096(4)	0.88(1)Mn + 0.12(1)Al
Si1	0.3429(2)	3/4	0.0423(2)	0.0092(6)	
Si2	0.6892(2)	1/4	0.2763(2)	0.0089(6)	
Si3	0.1846(2)	3/4	0.3196(2)	0.0086(6)	
O1	0.2385(5)	0.9919(8)	0.0352(4)	0.0172(8)	
O2	0.3054(4)	0.9783(8)	0.3544(4)	0.0144(7)	
O3	0.7996(5)	0.0148(8)	0.3349(4)	0.0151(7)	
O4	0.0552(7)	1/4	0.1301(6)	0.012(1)	
O5	0.0410(6)	3/4	0.1504(6)	0.013(1)	
O6	0.0732(6)	3/4	0.4136(6)	0.012(1)	
O7	0.5162(7)	3/4	0.1767(6)	0.017(1)	
O8	0.5340(8)	1/4	0.3200(7)	0.023(1)	
O9	0.6193(7)	1/4	0.1017(7)	0.021(1)	
O10	0.0868(6)	1/4	0.4324(5)	0.0088(9)	

Tab. 2a Anisotropic displacement parameters for cation sites × 1000.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
A1	17.3(7)	7.0(7)	10.3(6)	0.0	9.2(5)	0.0
A2	14.5(3)	18.8(4)	16.0(3)	0.0	6.8(2)	0.0
M1	7.8(7)	4.6(8)	9.9(8)	0.0	3.3(5)	0.0
M2	8.3(8)	4.4(10)	10.0(9)	0.0	2.8(7)	0.0
M3	8.5(6)	8.4(7)	9.0(6)	0.0	0.9(4)	0.0
Si1	10.1(8)	6.2(9)	9.8(8)	0.0	2.6(7)	0.0
Si2	10.3(8)	6.4(9)	9.6(8)	0.0	3.9(7)	0.0
Si3	8.6(8)	8.7(10)	9.4(8)	0.0	4.5(7)	0.0

which is very low for piemontites. Such a high Fe content was also observed in other REE-bearing piemontites (BONAZZI et al., 1992) and is best interpreted as a solid solution between allanite and piemontite. There is no essential zonation of Si, Al, Mg, Zn and Fe content within one grain.

Structure refinement

Fractional coordinates and displacement parameters are shown in table 2. Selected distances and angles are given in table 3. Only Ca was assumed on A1, however small substitutions of Mn^{2+} and/

or Fe^{2+} can not be excluded. The refined Mn concentration on M1 and M3 corresponds to the transition metals Mn, Fe, Zn whereas Al represents Al and Mg. The maximum Al + Mg concentration of 1.71 p.f.u. measured by electron microprobe analyses corresponds well with the unconstrained Al + Mg concentration of 1.76(2) p.f.u. obtained by structure refinement.

Discussion

The cation distribution in the Pb- and REE-rich piemontite is very similar to that of ordinary piemontites (DOLLASE, 1969). The REE content and the Mn/(Mn + Fe) ratio resembles analyses of REE-bearing piemontite from Alpi Apuane (BONAZZI et al., 1992). In the Pb- and REE-rich piemontite studied here the La_2O_3/Ce_2O_3 ratio varies within a wide range between 0.7 and 4.2 which is probably a result of variable oxidation potential during the crystallization.

The Pb- and REE-rich piemontite from Nezilovo shows some peculiarities due to its high Pb concentration. The Pb-rich member of the epidote group is hancockite but according to the more recent analyses (DUNN, 1985; HOLTSTAM and LANGHOF, 1994) its formula approximates CaPb $Al_2Fe(Si_2O_7)(SiO_4)(O,OH)_2$. However, the Pb-rich epidote mineral from the Nezilovo area is Mn-rich and thus corresponds to piemontite.

Tab 3   Selected interatomic distances (Å) and angles (°) in Pb-rich piemontite.

A2-O7		2.273(6)	A1-O7		2.268(7)
A2-O2	2×	2.679(4)	A1-O3	2×	2.298(4)
A2-O10		2.614(5)	A1-O1	2×	2.413(5)
A2-O2'	2×	2.597(4)	A1-O5		2.514(7)
A2-O3	2×	2.782(5)	A1-O6		2.945(5)
A2-O8	2×	2.987(2)	A1-O9	2×	3.055(2)
mean		2.698	mean		2.584
M1-O1	2×	1.995(4)	M2-O3	2×	1.871(3)
M1-O4	2×	1.862(3)	M2-O6	2×	1.920(5)
M1-O5	2×	2.006(4)	M2-O10	2×	1.877(4)
mean		1.954	mean		1.889
M3-O1	2×	2.256(4)			
M3-O2	2×	2.054(4)			
M3-O4		1.967(5)			
M3-O8		1.904(6)			
mean		2.082			
Si1-O1	2×	1.643(5)	Si2-O3	2×	1.617(4)
Si1-O7		1.575(5)	Si2-O8		1.615(9)
Si1-O9		1.633(8)	Si2-O9		1.618(7)
mean		1.623	mean		1.617
Si3-O2	2×	1.625(4)			
Si3-O5		1.660(5)			
Si3-O6		1.638(7)			
mean		1.637			
Si1-O9-Si2	148.8(4)°				

Ca on A1 is the prevailing cation. However, we can not exclude that minor Mn^{2+} and/or Fe^{2+} replaces Ca on this 9-coordinated site. On the A2 site Ca is strongly replaced by REE and Pb. According to the structural refinement about 44% of this site is occupied by Pb and REE. We assume that preferentially Mn enters M3 as two-valent cation, because M3-O distances are longer than in examples where only trivalent cations (Mn^{3+} and Fe^{3+}) occupy M3 (strontiopiemontite with about Mn^{3+} + Fe^{3+} = 98% and 2% Al has a mean M3-O distance of 2.06 Å (BONAZZI et al., 1991). In our Nezilovo piemontite with Fe + Mn = 88% and 12% Al, the average M3-O distance is 2.082(4) Å. In addition, for Mn^{3+} the Jahn-Teller distortion on M3 (Tab. 3) would be expected to be more prominent.

In this refinement model, no vacancies are assumed in spite of the high concentrations of trivalent REE. This assumption is in agreement with the electron microprobe analyses which yield rather constant 3 Si p.f.u. when standardized on 8 cations. Charge balance is achieved by M^{2+} cations, mainly on M3 as already proposed by PEACOR and DUNN (1988) for dollaseite-Ce and

SOKOLOVA et al. (1991) for an unnamed new member of the epidote group. For additional charge balance of REE^{3+}, SOKOLOVA et al. (1991) assumed that there are also vacancies on A1. However, our population refinements for the Nezilovo sample indicate A1 to be completely occupied.

The average distances for A and M sites are within the range of average distances for the other minerals from the epidote group and very close to strontian piemontite (FERRARIS et al., 1989; CATTI et al., 1988) and strontiopiemontite (BONAZZI et al., 1990).

It is striking that the disilicate angle Si1-O9-Si2 varies significantly in this mineral group, between 138° for REE-rich piemontite (SOKOLOVA et al., 1991) and 164° for clinozoisite (DOLLASE, 1968). With increasing Si1-O9-Si2 angle, the bridging Si-O9 distance decreases which is in agreement with theory (GIBBS, 1982). In REE-epidote (SOKOLOVA et al., 1991) with Si1-O9-Si2 = 137.8° the bridging Si-O9 distance is 1.647 Å, whereas in clinozoisite (DOLLASE, 1968) with Si1-O9-Si2 = 164.3° the bridging Si-O9 distance is 1.627 Å. This Si1-O9-Si2 variation seems to be mainly affected by the

Tab. 4   Randomly selected examples of known structures of epidote, piemontite, allanite and hancockite used in figure 1 and figure 2.

1. Epidote, (BELOV and RUMANOVA, 1953)
$Ca_2Al_2FeSi_3O_{12}(OH)$
2. Epidote, (KVICK et al., 1988)
$Ca_2Al_{2.2}Fe_{0.8}Si_3O_{13}H$
3. New REE-rich piemontite, (SOKOLOVA et al., 1991)
$(Ca_{0.6}La_{0.2})(Ce_{0.5}La_{0.12}Nd_{0.15}Dy_{0.10}Pr_{0.05}Sm_{0.02})(Mg_{0.40}Fe_{0.15}Cr_{0.12}Ti_{0.12}V_{0.09}Al_{0.12})Al_{1.00}Mn_{1.00}Si_3O_{11}(OH)(F_{0.63}O_{0.37})$
4. Piemontite, (FERRARIS et al., 1989)
$Ca(Ca_{0.84}Sr_{0.16})(Al_{0.81}Mn_{0.17}Fe_{0.02})Al(Al_{0.06}Mn_{0.61}Fe_{0.33})Si_{3.00}O_{12}(OH)$
5. Strontiopiemontite, (BONAZZI et al., 1990)
$(Ca_{0.78}Mn_{0.22})(Sr_{0.73}Ca_{0.27})(Al_{0.78}Fe_{0.08}Mn_{0.14})Al_{1.00}(Fe_{0.36}Mn_{0.62}Al_{0.02})Si_3O_{12}OH$
6. Strontiopiemontite, (BONAZZI et al., 1990)
$(Ca_{0.97}Sr_{0.03})(Sr_{0.59}Ca_{0.41})(Al_{0.72}Fe_{0.10}Mn_{0.18})Al_{1.00}(Fe_{0.37}Mn_{0.61}Al_{0.02})Si_3O_{12}OH$
7. REE-bearing piemontite, (BONAZZI et al., 1992)
$(Ca_{0.78}Mn_{0.22})(Ca_{0.69}La_{0.28}Sr_{0.03})(Al_{0.61}Mg_{0.08}Mn_{0.20}Fe_{0.11})Al_{1.00}(Fe_{0.29}Mn_{0.57}Al_{0.14})Si_3O_{12}OH$
8. REE-bearing piemontite, (BONAZZI et al., 1992)
$(Ca_{0.80}Mn_{0.20})(Ca_{0.91}La_{0.05}Sr_{0.04})(Al_{0.77}Mg_{0.01}Mn_{0.12}Fe_{0.10})Al_{1.00}(Fe_{0.40}Mn_{0.49}Al_{0.11})Si_3O_{12}OH$
9. Piemontite, (DOLLASE, 1969)
$Ca_{1.87}Sr_{0.13}Mn_{0.72}Fe_{0.31}Al_{1.97}Si_{3.00}O_{12}OH$
10. Allanite, (DOLLASE, 1971)
$Ca_{1.00}(REE_{0.74}Ca_{0.26})(Al_{0.66}Fe_{0.34})Al_{1.00}(Al_{0.17}Fe_{0.83})Si_{3.00}O_{13}H$
11. Allanite, (RUMANOVA and NIKOLEVA, 1959)
$Ca_{1.00}Ce_{1.00}Al_{2.00}Fe_{1.00}Si_{3.00}O_{13}H$
12. Hancockite, (DOLLASE, 1971)
$Ca_{1.00}(Pb_{0.50}Ca_{0.25}Sr_{0.25})(Al_{0.86}Fe_{0.14})Al_{1.00}(Al_{0.16}Fe_{0.84})Si_{3.00}O_{13}H$
13. Clinozoisite, (DOLLASE, 1968)
$Ca_{2.00}Al_{3.00}Si_{3.00}O_{13}H$
14. Dollaseite, (PEACOR and DUNN, 1988)
$(Ca_{0.91}REE^{3+}_{1.08})(Mg_{1.81}Fe_{0.25})Al_{0.97}Si_3O_{10.99}(OH)_{1.25}F_{0.88}$
15. Pb- and REE-bearing piemontite,
$Ca_{1.56}REE_{0.25}Pb_{0.19}(Mn+Fe)_{1.24}Al_{1.76}Si_{3.00}O_{13}H$

substitutions on M1 and M3 which share one octahedral edge on the opposite ends of the disilicate group (M3-O8 and M1-O1). M3 is the most deformed octahedral site in this structure thus the M3 bond length distortion was calculated to be 0.056 for the Nezilovo sample in terms of the distortion index DI proposed by BAUR (1974), where: DI = $1/(6R_{av})$ $|R_i-R_{av}|$. R_i is a distance between M and O and R_{av} is the average M-O distance in the octahedron. Corresponding M3 distortion indices were also calculated for randomly selected structures of epidote, piemontite, allanite and hancockite (Tab. 4). FERRARIS et al. (1989) considered the deformation of M3 and M1 octahedra as a function of cation substitution for these sites. They accomplished that such a deformation index is not useful for consistent conclusions as far as the contents of M sites are concerned, because the deformation depends on more variables than someone can control. The reason is that various cations can enter this position: Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{3+}, Mg^{2+}, V^{3+}. If DI for M3 is plotted vs the corresponding Si1-O9-Si2 angle it becomes obvious that epidote minerals can be
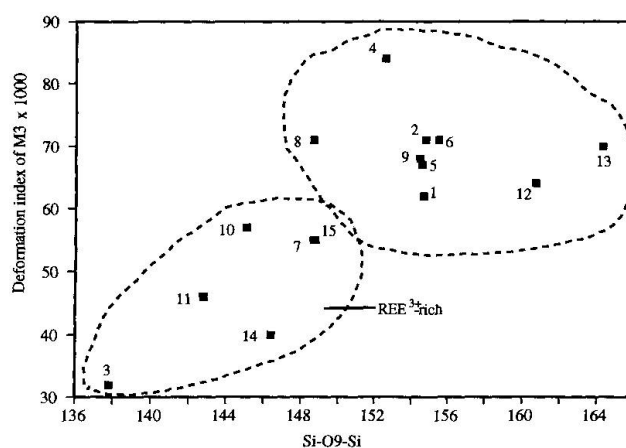

Fig. 1   Dependence of the deformation index DI = $1/(6)$ $|R_i-R_{av}|$ for M3 (BAUR, 1974) on the disilicate Si1-O9-Si2 angle. Numbers at the symbols characterize the samples from table 4.

roughly distinguished on the basis of M3 deformation (Fig. 1). Those samples with high REE^{3+} concentrations on A2 and thus high M^{2+} concentrations on M3 display low deformation indices and low Si1-O9-Si2 angles. There is the trend that with
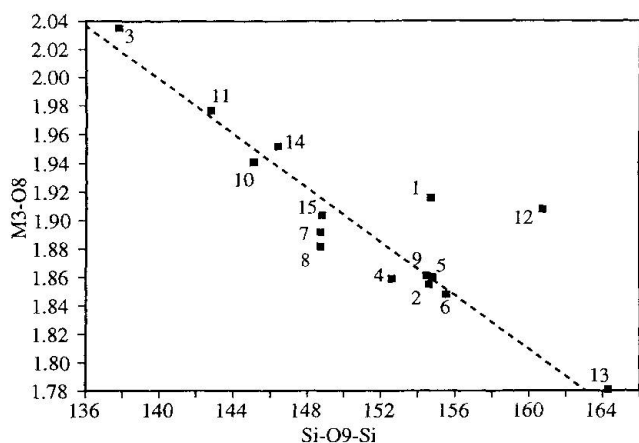
Fig. 2 Correlation between the M3-O8 distances and the disilicate Si1-O9-Si2 angle. Numbers at symbols as in figure 1. Samples #1 and #12 were not considered in the least square regression analysis shown as dashed line.

increasing bond length distortion, Si1-O9-Si2 also increases. It is surprizing that minerals with high octahedral Mn^{3+} content (piemontites) do not show stronger deformation due to Jahn-Teller distortion than epidotes and clinozoisite. FERRARIS et al. (1989) argue that the distortion of the M sites tends to be independent from the contents of these sites (for REE-poor samples). This is confirmed by figure 1 where DI is fairly constant for REE-poor samples. REE^{3+}-poor piemontites, epidotes and hancockite have distortion indices between 0.6 and 0.85. In figure 2, the Si1-O9-Si2 angle is plotted versus the M3-O8 distance, yielding a strong negative linear relationship (R^2 = 0.94) between these parameters. Hancockite, for unknown reasons except maybe due to low quality of the crystal used for the refinement (DOLLASE, 1971), violates this relation. One epidote (#1) also does not fit the general trend. This could be because of poor refinement (BELOV and RUMANOVA, 1953). Another epidote (#2) with similar composition (KVICK et al., 1988) fits excellently to the other samples. A corresponding dependance between Si1-O9-Si2 angle and the M1-O1 distance could be also assumed but a significant trend was not found. The reason is that M1-O1 distances vary in a narrow range between 1.92 Å and 2.06 Å (actually, only #3 and #14 both characterized by high Mg^{2+} and Mn^{2+} concentrations are above 2 Å); in contrast, M3-O8 distances vary between 1.78 Å and 2.04 Å. The isotropic displacement parameters (Ueq in Tab. 2) for O8 and O9 are significantly higher than other oxygen displacement parameters in this piemontite. We believe that the existence of short (Al,Fe^{3+},Mn^{3+})-O and long (Fe^{2+},Mn^{2+})-O distances around M3 are re-

sponsible for the increased Ueq of O8. In turn, this disorder is also reflected by locally varying Si1-O9-Si2 angles which cause high displacements for O9.

Acknowledgement

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