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New data on ferriakasakaite-(La) and related minerals extending the compositional field of the epidote supergroup

Nikita V. Chukanov[1,2,*], Natalia V. Zubkova[2], Christof Schäfer[3], Dmitry A. Varlamov[1,4], Vera N. Ermolaeva[5], Yury S. Polekhovsky[5], Simeon Jančev[6], Igor V. Pekov[2] and Dmitry Yu. Pushcharovsky[2]

[1] Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow region 142432, Russia
*Corresponding author, e-mail: chukanov@icp.ac.ru
[2] Faculty of Geology, Moscow State University, Vorobievy Gory, Moscow 119991, Russia
[3] Südwestdeutsche Salzwerke AG, Salzgrund 67, 74076 Heilbronn, Germany
[4] Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia
[5] Department of Mineral Deposits, Faculty of Geology, St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg 199034, Russia
[6] Faculty of Technology and Metallurgy, Saints Cyril and Methodius University, Ruger Boskovic 16, 1000 Skopje, Republic of Macedonia

Abstract: Detailed studies of ferriakasakaite-(La) including determination of chemical composition and crystal structure, infrared spectroscopy, optical characteristics in reflected light and micro-indentation hardness have been carried out on a non-metamict sample from young nosean-bearing sanidinite from the Laach Lake volcanic complex, Eifel, Germany. The chemical composition is (electron microprobe, Fe^{2+}: Fe^{3+} determined from structural data, wt%): CaO 6.74, La_2O_3 13.35, Ce_2O_3 10.58, Pr_2O_3 0.42, Nd_2O_3 0.49, Sm_2O_3, 0.34, Eu_2O_3 0.18, Gd_2O_3 0.20, ThO_2 0.43, UO_2 0.10, MgO 0.89, MnO 9.98, Al_2O_3 11.47, Fe_2O_3 7.39, FeO 4.04, TiO_2 1.32, SiO_2 29.80, H_2O (calc.) 1.49, total 99.22. The empirical formula is $(Ca_{0.68}Mn^{2+}_{0.32})_{\Sigma 1.00}(La_{0.49}Ce_{0.39}Pr_{0.02}Nd_{0.02}Sm_{0.01}Eu_{0.01}Gd_{0.01}Th_{0.01}Ca_{0.04})_{\Sigma 1.00}(Fe^{3+}_{0.52}Fe^{2+}_{0.04}Al_{0.34}Ti^{4+}_{0.10})_{\Sigma 1.00}Al_{1.00}(Mn^{2+}_{0.53}Fe^{2+}_{0.34}Mg_{0.13})_{\Sigma 1.00}(Si_{2.98}Al_{0.02})_{\Sigma 3.00}O_{12.00}(OH)$. The crystal structure was solved by direct methods and refined to $R = 0.018$ based on 1259 unique reflections with $I > 2\sigma(I)$. The H atom was located. The mineral is monoclinic, space group $P2_1/m$, $a = 8.9054(1)$, $b = 5.7545(1)$, $c = 10.1037(2)$ Å, $\beta = 114.103(2)°$, $V = 472.63(1)$ Å^3. The IR spectrum confirms the presence of OH groups. Reflectance spectra of ferriakasakaite-(La) obtained in the visible range show reflectance minima at the wavelength of ~590 nm. Various epidote-supergroup minerals including ferriakasakaite-(La), allanite-(Ce), Al-dominant (at the *M*1 site) analogue of ferriakasakaite-(Ce), piemontite, piemontite-(Pb), as well as Pb-, Zn- and Cu-bearing varieties of Fe^{3+}-dominant (at the *M*1 site) analogues of piemontite and piemontite-(Pb), have been discovered in sulfide-free metasomatic rocks containing oxide/oxysalt compounds of chalcophile elements (Zn, Cu, Sb, and Pb), within the Pelagonian massif, Republic of Macedonia. Crystal chemical regularities of these minerals are discussed.

Key-words: epidote supergroup; allanite group; ferriakasakaite-(La); crystal structure; Laach Lake volcanic complex; Germany; Nežilovo; Pelagonian massif; Macedonia.

1. Introduction

Epidote-supergroup minerals rich in rare-earth elements (*REE*) are common accessory components of igneous, metamorphic and metasomatic rocks. Most *REE*-dominant epidote-supergroup minerals belong to the allanite group, which includes 15 species. Allanite-group minerals (or 'allanites' in the following) are monoclinic neso-soro silicates with the general formula $A1A2M1M2M3(Si_2O_7)(SiO_4)O(OH)$ where $A1 = Ca$, Mn^{2+} (sometimes with minor Na); $A2 = REE^{3+}$ (sometimes with subordinate or minor Ca, Pb^{2+}, Sr, Ba, Th^{4+}, U^{4+}); $M1,2 = Al$, Fe^{3+}, Mn^{3+}, V^{3+} (sometimes with subordinate or minor Cr^{3+}, Ti^{4+}, Sn^{4+}); $M3 = Fe^{2+}$, Mg, Mn^{2+} (sometimes with subordinate or minor amounts of trivalent cations, such as Fe^{3+} and/or Mn^{3+}) (Armbruster *et al.*, 2006; Mills *et al.*, 2009). The *M*1–3 cations have octahedral coordination. In all known 'allanites' the *M*2 site is Al-dominant, whereas the sites *A*1, *A*2, *M*1, and *M*3 show wide compositional variations.

The presumed Mn^{2+}-dominant analogue of ferriallanite-(La) was discovered by us in 2010 in the course of investigations of the new mineral species piemontite-(Pb)

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from the Pelagonian massif, Republic of Macedonia (Chukanov *et al.*, 2012a). Piemontite-(Pb) was approved by the IMA CNMNC in 2011, but complete investigations of the Mn^{2+} analogue of ferriallanite-(La) could not be carried out because of the small grain size and insufficient material amount. We anticipated that this mineral could also exist in late parageneses related to sanidinite of the Laach Lake volcanic complex, Eifel, Germany which is the type locality of ferriallanite-(La) (Kolitsch *et al.*, 2012), because the so-called "nosean sanidinites" of the Laach Lake volcano are enriched in Mn [the main minerals concentrating this element are rhodonite, spessartine, tephroite, amphiboles, pyroxenes, mendigite, laachite, and members of the spinel group]. Attempts to find the Mn^{2+} analogue of ferriallanite-(La) in this association were unsuccessful until 2016, but at that time the mineral had already been described elsewhere and approved with the name ferriakasakaite-(La) (Nagashima *et al.*, 2015). However, taking into account significant chemical differences between samples of this mineral from different localities, as well as wide compositional variations found in epidote-supergroup minerals from the Pelagonian massif, we report them jointly here as they extend knowledge about the main regularities of isomorphic substitutions in epidote-supergroup minerals.

In the holotype sample of ferriakasakaite-(La), ideally $CaLaFe^{3+}AlMn^{2+}(Si_2O_7)(SiO_4)O(OH)$, the *A*1 site contains 0.46 Mn^{2+} atoms per formula unit (*apfu*), the *M*1 site contains 0.34 V^{3+} *apfu*, and the Mn^{2+}-dominant *M*3 site contains only 0.50 Mn *apfu* (Nagashima *et al.*, 2015). Our recent find of non-metamict, vanadium-free ferriakasakaite-(La) in young sanidinite from the Laach Lake volcanic complex provided the opportunity of a thorough characterization of this mineral, including structure refinement to $R = 0.018$ with localization of the H atom, as well as the IR spectrum and reflectance spectrum in the visible range. The other new findings of ferriakasakaite-(La) and related members of the epidote supergroup in the Pelagonian massif, Republic of Macedonia reveal important crystal-chemical features of these minerals.

2. Occurrences and general appearance

Perfect crystals of ferriakasakaite-(La) (Fig. 1) were found in a sanidinite ejectum (eruptive rock fragment) collected by one of the authors (C.S.) in the In den Dellen pumice quarry, Niedermendig, Mendig, Laach Lake volcanic complex, Eifel, Rhineland-Palatinate, Germany in association with nosean and/or haüyne, Mn-bearing biotite, magnetite, ilmenite–pyrophanite series members, Mn-bearing zirconolite, and secondary jarosite. The origin of nosean syenite rocks from the Laach Lake paleovolcano was discussed earlier (Chukanov *et al.*, 2014). Most probably, it is cogenetic with the phonolitic host magma, and the crystallization took place in an intrusive syenite–carbonatite complex at temperatures below 700 °C in the host rock surrounding the top of the magma chamber. Considering the zoned structure of some "nosean sanidinite" ejecta, we proposed that Mn was mobilized from hosting Mn-bearing metamorphic rocks (Chukanov *et al.*, 2012b, 2014). The last eruption of the residual phonolite magma took place about 12.9 ka ago (Litt *et al.*, 2001; Schmitt *et al.*, 2010). As a result, all Th- and U-bearing accessory minerals from this rock are non-metamict and demonstrate perfect crystal structures.

Fig. 1. Crystal of ferriakasakaite-(La) on sanidinite. Laach Lake volcanic complex. Field width 1.2 mm. Photograph: M. Burkhardt.

Crystals of ferriakasakaite-(La) from the Laach Lake complex have thick-tabular habit. The main crystal form is {1 0 0} and the subordinate forms are {0 0 1}, {1 0 1}, {0 1 1}, {1 1 0}, {1 1 1}, and {2 0 1}. The mineral is brittle; the mean VHN hardness determined by micro-indentation (load 100 g) is 847 kg/mm^2 (range 794–861 kg/mm^2) which corresponds to a Mohs' hardness *ca.* 6½. Its colour is black, and the streak is brown. The density calculated using the empirical formula is 4.216 g/cm^3.

Various epidote-supergroup minerals, including ferriakasakaite-(La), allanite-(Ce), epidote, piemontite, piemontite-(Pb), as well as Fe^{3+}-dominant (at the *M*1 site) analogues of piemontite and piemontite-(Pb) occur in metasomatic rocks at the contact of meta-rhyolites and dolomitic marbles belonging to the metamorphic "Mixed Series" situated in the Pelagonian massif near the Nežilovo village, about 25 km WSW of the city of Veles, Republic of Macedonia (41°41′ N, 21°25′ E), in association with pyrochlore-supergroup minerals (hydroxyplumboroméite, Pb-bearing hydroxyroméite, fluorroméite, and hydroxyplumbobetafite), Zn spinels and their tetragonal polymorphs (gahnite, franklinite, franklinite tetragonal analogue, zincochromite, and hetaerolite), Zn-bearing silicates (talc, phlogopite, amphiboles), *etc.* (*e.g.*, Bermanec *et al.*, 1994, 1996; Chukanov *et al.*, 2012b, 2015; Ermolaeva *et al.*, 2016; Varlamov *et al.*, 2017). A specific feature of these rocks is the concentration of chalcophile elements (S, As, Sb,

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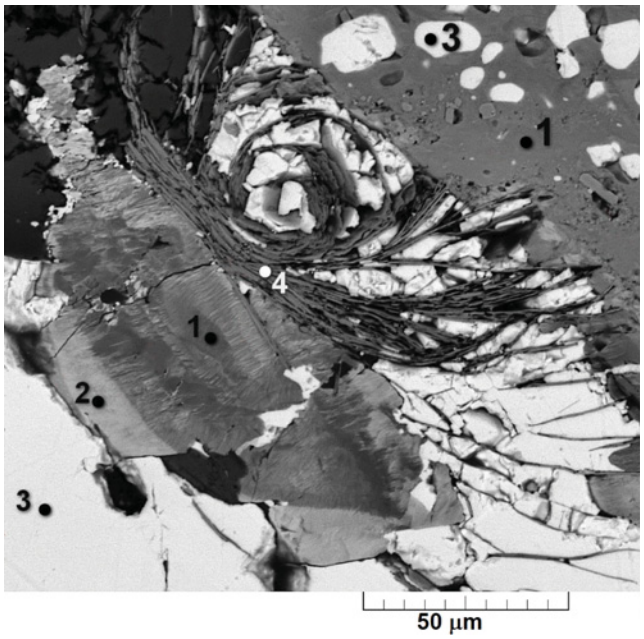

Fig. 2. Zoned crystal containing piemontite (1) and piemontite-(Pb) (2) zones in association with baryte (3) and zincovelesite-6*N*6*S* (4). Polished section. SEM (BSE) image.

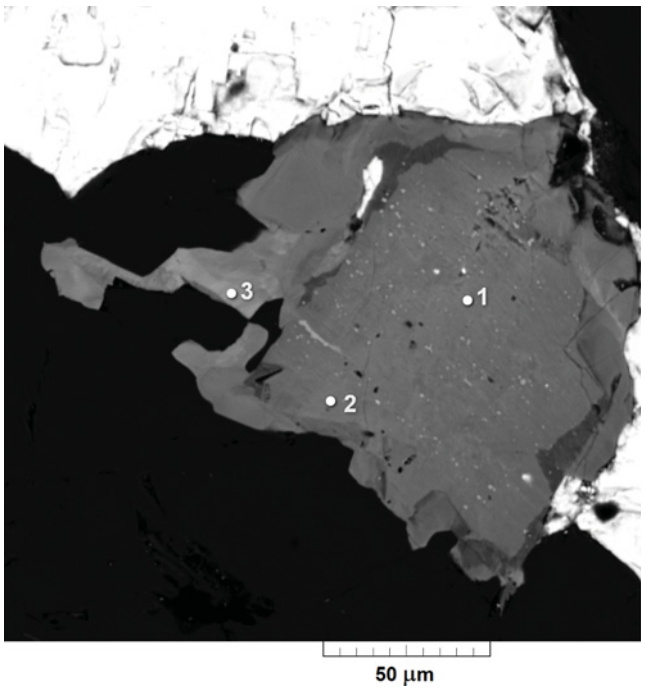

Fig. 3. Piemontite grain (1) with peripheral zones corresponding to allanite-(Ce) (2) and "ferripiemontite-(Pb)" (3), ideally CaPb-$Fe^{3+}AlMn^{3+}Si_3O_{12}(OH)$, in association with baryte (white) and Zn-rich amphibole of the glaucophane–magnesio-riebeckite series (black). Polished section. SEM (BSE) image.

Zn, and Pb) mainly in the form of oxides and oxysalts, whereas sulfides and sulfosalts are present only in trace amounts.

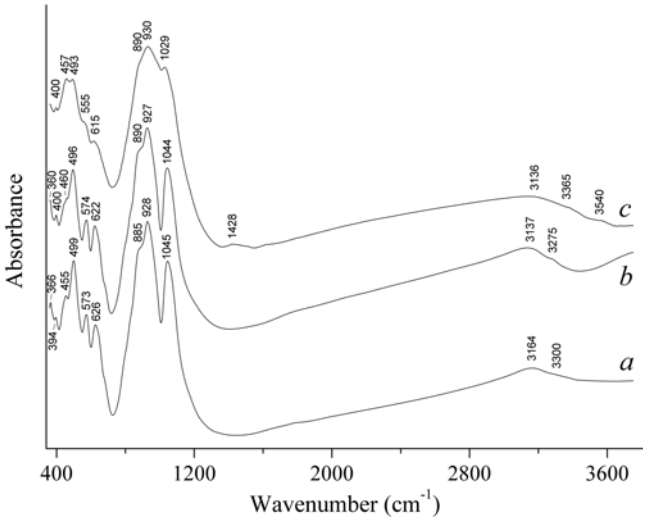

Fig. 4. IR spectra of (*a*) ferriakasakaite-(La), (*b*) non-metamict ferriallanite-(La) $Ca_{1.02}(La_{0.49}Ce_{0.39}Nd_{0.05}Pr_{0.03})(Fe_{0.63}Al_{0.30}Ti_{0.07})Al(Fe_{0.68}Mn_{0.28}Mg_{0.04})(Si_{2.99}Al_{0.01})O_{12}(OH)$ from the Laach Lake volcanic complex (Chukanov & Chervonnyi, 2016), and (*c*) partly metamict ferriallanite-(Ce) $(Ca_{0.91}Mn_{0.09})[(Ce_{0.43}La_{0.25}Nd_{0.11}Pr_{0.07}\ldots)Ca_{0.08}](Fe_{0.59}Al_{0.41})Al(Fe_{0.92}Mg_{0.08})Si_{3.00}O_{12}(OH)$ from the Håkonhals quarry, Finnøy, Hamarøy, Nordland, Norway (Chukanov & Chervonnyi, 2016).

Two generations of epidote-supergroup members can be distinguished in the Nežilovo ores: *REE*-poor minerals [mainly piemontite-(Pb) and Pb-bearing piemontite] belong to the first generation and form purple to red imperfect prismatic crystals up to 0.5×2 mm in size (Fig. 2) and random aggregates up to 2 mm across, whereas *REE*-dominant ones ('allanites') form outer zones of piemontite-(Pb) and piemontite crystals (Fig. 3) and anhedral grains up to 20 μm across in interstices between grains of earlier formed minerals.

3. Infrared spectroscopy

In order to obtain IR absorption spectra of 'allanites' (Fig. 4), powdered samples were mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm^{-1}; 16 scans were collected. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

The IR absorption bands of ferriakasakaite-(La) from the complex and Laach Lake volcanic their assignments are (cm^{-1}, s – strong band, sh – shoulder): 3300sh, 3164 (O–H – stretching vibrations), 1045s, 928s, 885sh (Si–O – stretching vibrations), 626, 573, 499s (O–Si–O bending and Al–O – stretching vibrations), 455, 394, 366 (lattice modes involving Si–O–Si bending and *M*…O stretching vibrations where *M* = Mn, Fe, Ca). The IR spectrum of ferriakasakaite-(La) is similar to the spectra of other 'allanites' given for comparison in Fig. 4. The weak band at 1428 cm^{-1} in the IR spectrum of partly metamict ferriallanite-(Ce) corresponds to a minor admixture of bastnäsite-(Ce).

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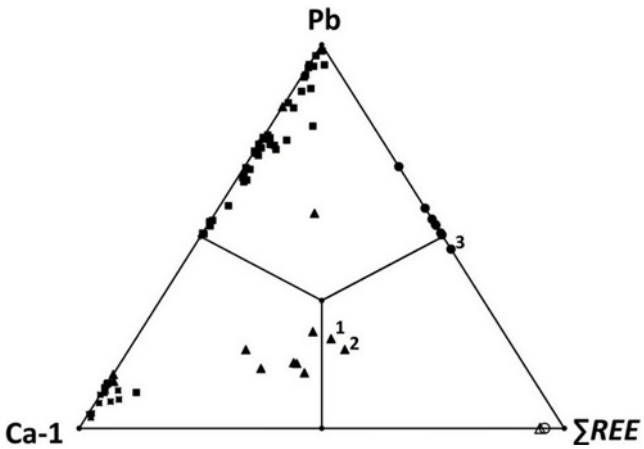

Fig. 5. Relations between Ca, Pb and Σ*REE* in the *A*2 site in epidote-supergroup minerals from the Pelagonian massif: samples from baryte–amphibole–clinopyroxene rock (black triangles), from massive baryte (black circles) and from baryte–phlogopite aggregates with subordinate Pb-Zn-Fe-Mn oxides (black squares). The figures correspond to the allanite-(La)–ferriakasakaite-(La) intermediate member (1), Zn,Mn-rich allanite-(Ce) (2), and ferriakasakaite-(La) (3). Open circle: holotype ferriakasakaite-(La) from Japan. Open triangle: ferriakasakaite-(La) from the Laach Lake volcanic complex.

Table 1. Chemical composition of ferriakasakaite-(La) from the Laach Lake volcanic complex.

Constituent	wt%	Range	Standard deviation	Probe standard
CaO	6.74	6.24–7.21	0.44	wollastonite
La_2O_3	13.35	12.48–14.49	0.82	$LaPO_4$
Ce_2O_3	10.58	9.76–11.19	0.60	$CePO_4$
Pr_2O_3	0.42	0.35–0.62	0.10	$PrPO_4$
Nd_2O_3	0.49	0.28–0.60	0.12	$NdPO_4$
Sm_2O_3	0.34	0–1.18	0.51	$SmPO_4$
Eu_2O_3	0.18	0–0.72	0.29	$EuPO_4$
Gd_2O_3	0.20	0–0.53	0.25	$GdPO_4$
ThO_2	0.43	0–0.77	0.25	ThO_2
UO_2	0.10	0–0.44	0.18	UO_2
MgO	0.89	0.57–1.15	0.22	MgO
MnO*	9.98	9.31–10.39	0.43	Mn
Al_2O_3	11.47	10.87–12.21	0.49	Al_2O_3
Fe_2O_3	7.39	11.36–12.47**	0.46**	Fe_2O_3
FeO	4.04			
TiO_2	1.32	1.07–1.51	0.15	Ti
SiO_2	29.80	28.63–31.32	0.89	SiO_2
H_2O_{calc}***	1.49	–	–	–
Total	99.22	–	–	–

Note: Total iron (corresponding to measured 11.88 wt% Fe_2O_3) was apportioned between 4.04 wt% FeO and 7.39 wt% Fe_2O_3 in accordance with structural data.
* According to structural data, manganese is considered as Mn^{2+}.
** For total iron considered as Fe_2O_3.
*** Calculated for $(OH)_{1.00}$ *pfu*.

4. Optical properties in reflected light

Reflectance measurements for ferriakasakaite-(La) from the Laach Lake volcanic complex were carried out in air using a MSF-21 micro-spectrophotometer (LOMO public limited company, St. Petersburg) with the monochromator slit width of 0.4 mm and beam diameter of 0.1 mm; SiC (Reflection standard 474251, No. 545, Germany) was used as a standard.

The results are given in Fig. S1 and Table S1 of the supplementary Material, linked to this article and freely available on the GSW website of the journal: https://pubs.geoscienceworld.org/eurjmin). Ferriakasakaite-(La) is weakly anisotropic, with $\Delta R_{589} = 0.3\%$. The colour in reflected light is dark grey, without internal reflections.

5. Chemical data

Six analyses of ferriakasakaite-(La) from the Laach Lake volcanic complex were obtained using a digital scanning electron microscope Tescan VEGA-II XMU with wave-length-dispersive spectrometer (WDS) Oxford INCA Wave 700 (WDS mode, at an accelerating voltage of 20 kV, current of absorbed electrons on the studied polished sample 1 nA, 900 nm beam «spot» diameter and size of "excitation" zone 4–5 μm). The results of the microanalysis were processed by means of a software package of INCA Energy 300 (with an option accounting for matrix effects in WDS analysis). Analytical data are given in Table 1. Contents of other elements with atomic numbers >8 are below detection limits. H_2O was calculated from structural data.

Chemical analyses of epidote-supergroup minerals from the Pelagonian massif (Table 2), as well as their backscattered electron (BSE) images were obtained using the same Tescan VEGA-II XMU instrument but with energy-dispersive spectrometer (EDS) INCA Energy 450 with semiconducting Si (Li) detector Link INCA Energy (EDS mode, 20 kV, absorption current 350–400 pA, 164 nm beam «spot» diameter). In all cases the standards used were MgF_2 for F, albite for Na, MgO for Mg, Al_2O_3 for Al, SiO_2 for Si, $LaPO_4$ for P, wollastonite for Ca, SrF_2 for Sr, BaF_2 for Ba, synthetic *REE* monophosphates for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Yb, PbTe for Pb, ThO_2 for Th, UO_2 for U, and pure Ti, V, Cr, Mn, Fe, Cu, Zn, and Y for corresponding elements.

According to the rules of formula calculation for epidote-supergroup minerals (Armbruster *et al.*, 2006), the charge-balanced empirical formula of ferriakasakaite-(La) from the Laach Lake volcanic complex based on $\Sigma(A+M+T)=8$ and $O_{12}(OH)$ is $(Ca_{0.68}Mn^{2+}_{0.32})_{\Sigma 1.00}(La_{0.49}Ce_{0.39}Pr_{0.02}Nd_{0.02}Sm_{0.01}Eu_{0.01}Gd_{0.01}Th_{0.01}Ca_{0.04})_{\Sigma 1.00}(Fe^{3+}_{0.52}Fe^{2+}_{0.04}Al_{0.34}Ti^{4+}_{0.10})_{\Sigma 1.00}Al_{1.00}(Mn^{2+}_{0.53}Fe^{2+}_{0.34}Mg_{0.13})_{\Sigma 1.00}(Si_{2.98}Al_{0.02})_{\Sigma 3.00}O_{12}(OH)$. However, the crystal structure analysis shows minor Fe^{3+} at the *M*2 site and somewhat lower Fe^{3+}:Al ratio at the *M*1 site.

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Table 2. Representative chemical data for epidote-supergroup minerals from the Pelagonian massif.

Components	Pb-rich piemontite	Piemontite-(Pb)	"Ferri-piemontite"	"Ferri-piemontite-(Pb)"	Mn,Zn,Pb-rich epidote	Pb,Zn,Cu-rich allanite-(Ce)	Ferriaka-sakaite-(La)
wt%							
CaO	15.15	12.01	13.96	9.92	14.59	12.89	6.82
MgO	bdl	bdl	1.25	0.75	bdl	bdl	0.43
PbO	14.61	23.40	5.70	30.58	6.84	9.07	15.63
CuO	0.03	bdl	1.59	bdl	0.74	1.96	bdl
ZnO	bdl	bdl	1.74	0.50	2.86	3.33	0.87
Fe_2O_3	10.02	11.74	6.58	11.49	10.44	9.49	8.32
Mn_2O_3	10.42	8.96	9.59	7.87	6.67	4.74	13.67
La_2O_3	bdl	bdl	7.85	bdl	6.04	3.30	4.87
Ce_2O_3	0.83	0.89	bdl	bdl	bdl	3.97	4.49
Pr_2O_3	bdl	bdl	0.91	bdl	bdl	0.64	1.39
Nd_2O_3	bdl	bdl	3.41	bdl	1.31	2.79	2.40
Sm_2O_3	bdl	bdl	bdl	bdl	bdl	0.97	bdl
Al_2O_3	15.37	13.98	13.22	11.11	15.29	15.71	10.34
SiO_2	31.94	30.70	32.99	28.70	31.71	31.32	28.89
TiO_2	bdl	bdl	0.11	bdl	bdl	0.73	0.28
Total	98.37	101.68	98.91	100.91	96.50	100.88	98.40
Formula coefficients (*apfu*) calculated on the basis of 8 cations							
Ca	1.51	1.25	1.45	1.18	1.46	1.36	0.77
Mg	0	0	0.17	0.11	0	0	0.07
Pb	0.37	0.61	0.14	0.85	0.17	0.23	0.45
Cu	0	0	0.11	0	0.05	0.14	0
Zn	0	0	0.12	0.04	0.20	0.23	0.07
Fe	0.70	0.86	0.45	0.89	0.74	0.66	0.66
Mn	0.74	0.66	0.67	0.62	0.48	0.33	1.10
La	0	0	0.27	0	0.21	0.11	0.19
Ce	0.03	0.03	0	0	0	0.14	0.18
Pr	0	0	0.03	0	0	0.02	0.05
Nd	0	0	0.11	0	0.04	0.09	0.09
Sm	0	0	0	0	0	0.03	0
Al	1.69	1.60	1.43	1.35	1.68	1.71	1.29
Si	2.97	2.98	3.04	2.96	2.97	2.90	3.06
Ti	0	0	0.01	0	0	0.05	0.02

Note: bdl means that the content of the relevant component is below its detection limit. The F content is below its detection limit in all analyzed samples.

The idealized formula, $CaLaFe^{3+}AlMn^{2+}(Si_2O_7)(SiO_4)O(OH)$, corresponds to the ferriakasakaite-(La) end-member. Unlike ferriakasakaite-(La) holotype, $(Ca_{0.54}Mn^{2+}_{0.46})(La_{0.48}Ce_{0.20}Pr_{0.07}Nd_{0.18}Gd_{0.02}Ca_{0.05})(Fe^{3+}_{0.42}V^{3+}_{0.34}Al_{0.18}Ti^{4+}_{0.06})(Al_{0.96}Fe^{3+}_{0.04})(Mn^{2+}_{0.50}Fe^{2+}_{0.43}Mg_{0.07})Si_{3.00}O_{12}(OH)$ (Nagashima *et al.*, 2015), the mineral from the Laach Lake volcanic complex does not contain vanadium and is closer to the end-member composition.

Representative chemical data for epidote-supergroup minerals from the "Mixed Series" of the Pelagonian massif are given in Table 2. Figure 5 shows relations between main components in the *A*2 site of these minerals. The analyses show wide compositional diversity and correspond to epidote, piemontite, piemontite-(Pb), the potentially new species "ferripiemontite" [ideally $Ca_2Fe^{3+}AlMn^{3+}Si_3O_{12}(OH)$] and "ferripiemontite-(Pb)" [ideally $CaPbFe^{3+}AlMn^{3+}Si_3O_{12}(OH)$], as well as various allanite-group minerals.

Ferriakasakaite-(La) from this locality is enriched in Pb and has the empirical formula $(Ca_{0.73}Mn^{2+}_{0.27})[(La_{0.19}Ce_{0.18}Pr_{0.05}Nd_{0.09})_{\Sigma 0.51}Pb_{0.45}Ca_{0.04}](Fe^{3+}_{0.66}Al_{0.29}Ti_{0.06})Al(Mn_{0.83}Zn_{0.07}Mg_{0.07})Si_{3.06}O_{12}(OH,O)$. The small size prevented determination of the crystal structure and of the Mn^{2+}: Mn^{3+} ratio.

6. Single-crystal X-ray diffraction data and crystal structure

Single-crystal X-ray studies of ferriakasakaite-(La) from the Laach Lake volcanic complex were carried out using an Xcalibur S diffractometer equipped with a CCD detector. A full sphere of three-dimensional data was collected. Data reduction was performed using CrysAlisPro Version 1.171.37.35 (Agilent Technologies, 2014). The data were corrected for Lorentz factor and polarization effects. Ferriakasakaite-(La) is monoclinic, space group $P2_1/m$ and unit-cell dimensions $a = 8.9054(1)$, $b = 5.7545(1)$, $c = 10.1037(2)$ Å, $\beta = 114.103(2)°$ and $V = 472.63(1)$ Å^3. The crystal structure was solved by direct methods and refined using the SHELX-97 software package (Sheldrick, 2008) to $R = 0.0182$ for 1259 unique reflections with $I > 2\sigma$

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Table 3. Crystal data, data collection information and structure refinement details for ferriakasakaite-(La).

Formula	$(Ca_{0.70}Mn_{0.30})(La_{0.55}Ce_{0.40}Nd_{0.05})(Fe_{0.48}Al_{0.42}Ti_{0.10})$ $(Al_{0.93}Fe_{0.07})(Mn_{0.53}Fe_{0.34}Mg_{0.13})$ $(SiO_4)(Si_2O_7)O(OH_{0.90}O_{0.10})$
Formula weight, g/mol	600.65
Temperature, K	293(2)
Radiation and wavelength, Å	Mo*K*α; 0.71073
Crystal system, space group, *Z*	Monoclinic, $P2_1/m$, 2
Unit-cell dimensions	$a = 8.9054(1)$ Å, $b = 5.7545(1)$ Å, $c = 10.1037(2)$, $\beta = 114.103(2)°$
V, Å^3	472.63(1)
Absorption coefficient μ, mm^{-1}	8.120
F_{000}	567
Crystal size, mm	0.12 × 0.15 × 0.21
Diffractometer	Xcalibur S CCD
Absorption correction	GaussianNumerical absorption correction based on Gaussian integration over a multifaceted crystal model. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm
θ range, °	3.96–28.28
Index ranges	$-11 \le h \le 11$, $-7 \le k \le 7$, $-13 \le l \le 13$
Reflections collected	8584
Unique reflections	1283 ($R_{int} = 0.0266$)
Unique reflections with $I > 2\sigma(I)$	1259
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
Number of refined parameters	121
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.018$, $wR2^* = 0.047$
R indices (all data)	$R1 = 0.019$, $wR2^* = 0.0475$
GoF	1.141
Largest diff. peak and hole, e/Å^3	1.08 and −0.70

* $w = 1/[\sigma^2(F_0^2) + (0.0187P)^2 + 1.9180P]$, $P = [(\text{max of } 0 \text{ or } F_0^2) + 2F_c^2]/3$.

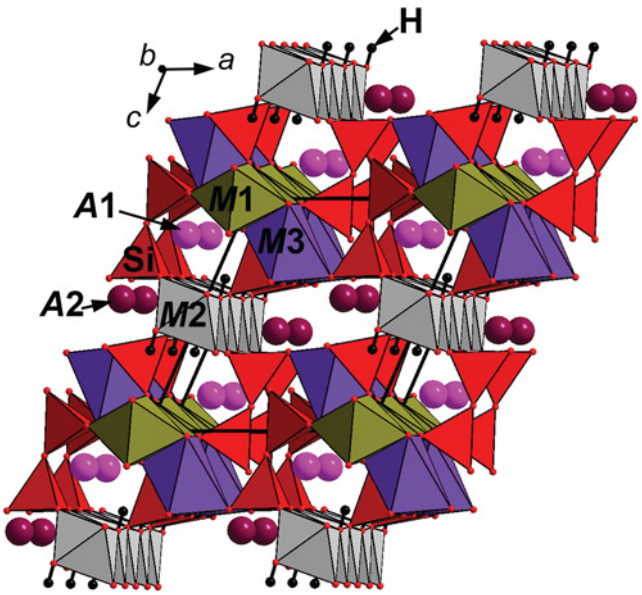

Fig. 6. The crystal structure of ferriakasakaite-(La). The unit cell is outlined.

(*I*). The H atom was located from the difference Fourier synthesis and its position was fixed during the refinement. The occupancies of *A*(1–2) and *M*(1–3) cation sites were set in keeping the chemical composition of the studied sample and all cation sites were refined assuming their full occupancy. In the cases of *A*(1) and *M*(2) sites, Mn *vs*. Ca and Al *vs.* Fe, respectively, were refined. All *REE* were assumed to be located in the *A*(2) site. Occupancy factors of *M*(1) and *M*(3) sites were refined using Fe and Mn scattering curves, respectively, and then fixed as $(Fe_{0.48}Al_{0.42}Ti_{0.10})$ for *M*(1) and $(Mn_{0.53}Fe_{0.34}Mg_{0.13})$ for *M*(3) according to chemical data and the refined number of electrons, taking interatomic distances into account. The crystal data and the experimental details are presented in Table 3, atom coordinates, thermal displacement parameters and site occupancies in Table 4, selected interatomic distances in Table 5 and bond valence calculations in Table 6.

The crystal structure of ferriakasakaite-(La) (Fig. 6) is typical of the members of the epidote supergroup (Dollase, 1968). It contains two types of chains of edge-sharing octahedra running along the *b* axis: the single chain formed by *M*(2) octahedra and the triple chain where *M*(1) octahedra build the central row and *M*(3) octahedra are linked to the row from both sides. The chains are linked by isolated SiO_4 tetrahedra and Si_2O_7 groups to form a pseudo-framework with cavities hosting the *A*(1) and *A*(2) cations.

Like other epidote-supergroup minerals, in ferriakasakaite-(La) Al is preferably concentrated in *M*(2) which is the electron-poorest site centering the smallest octahedron with a mean *M*(2)–O distance (⟨*M*(2)–O⟩) of 1.903 Å. The *M*(1)-centered octahedron is slightly larger (⟨*M*(1)–O⟩ = 1.976 Å) and is occupied by Fe^{3+} with subordinate Al and minor Ti^{4+} admixture. The largest *M*(3) octahedron (⟨*M*

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Table 4. Atom coordinates and thermal displacement parameters (U_{eq}, in Å^2), site occupancy factors (s.o.f.) for ferriakasakaite-(La).

Site	x	y	z	U_{eq}	s.o.f.
A(1)	0.75934(10)	0.75	0.15284(8)	0.0099(2)	$Ca_{0.695(14)}Mn_{0.305(14)}$
A(2)	0.59366(3)	0.75	0.42838(2)	0.00815(9)	$La_{0.55}Ce_{0.40}Nd_{0.05}$
M(1)	0.0	0.0	0.0	0.00807(16)	$Fe^{3+}_{0.48}Al_{0.42}Ti_{0.10}$
M(2)	0.0	0.0	0.5	0.0054(4)	$Al_{0.929(6)}\ Fe^{3+}_{0.071(6)}$
M(3)	0.30671(7)	0.25	0.21038(7)	0.00536(14)	$Mn_{0.53}Fe^{2+}_{0.34}Mg_{0.13}$
Si(1)	0.34111(13)	0.75	0.03447(11)	0.0042(2)	1
Si(2)	0.68929(13)	0.25	0.28194(11)	0.0040(2)	1
Si(3)	0.18869(12)	0.75	0.32306(11)	0.0035(2)	1
O(1)	0.2366(2)	0.9887(4)	0.0240(2)	0.0088(4)	1
O(2)	0.3125(2)	0.9714(4)	0.3625(2)0	0.0069(4)	1
O(3)	0.7982(2)	0.0133(4)	0.3356(2)	0.0082(4)	1
O(4)	0.0560(3)	0.25	0.1318(3)	0.0070(5)	1
O(5)	0.0500(3)	0.75	0.1529(3)	0.0072(5)	1
O(6)	0.0715(3)	0.75	0.4138(3)	0.0064(5)	1
O(7)	0.5101(4)	0.75	0.1760(3)	0.0092(6)	1
O(8)	0.5476(4)	0.25	0.3404(3)	0.0134(6)	1
O(9)	0.6079(4)	0.25	0.1042(3)	0.0112(6)	1
O(10)*	0.0863(3)	0.25	0.4292(3)	0.0060(5)	1
H	0.0724**	0.25	0.3454**	0.050**,***	0.90**

* Oxygen atom of the OH group.
** Fixed during the refinement.
*** U_{iso}.

Table 5. Selected interatomic distances (Å) and angles (°) in the structure of ferriakasakaite-(La).

A(1)–O(3)	2.303(2) × 2	A(2)–O(7)	2.347(3)
A(1)–O(7)	2.325(3)	A(2)–O(2)	2.508(2) × 2
A(1)–O(1)	2.347(2) × 2	A(2)–O(10)	2.616(3)
A(1)–O(5)	2.588(3)	A(2)–O(2)	2.641(2) × 2
A(1)–O(6)	2.948(3)	A(2)–O(3)	2.808(2) × 2
⟨A(1)–O⟩	2.452	A(2)–O(8)	2.9900(8) × 2
		A(2)–O(8)	3.073(3)
M(1)–O(4)	1.8838(18) × 2	⟨A(2)–O⟩	2.721
M(1)–O(1)	2.021(2) × 2		
M(1)–O(5)	2.023(2) × 2	M(2)–O(3)	1.8859(19) × 2
⟨M(1)–O⟩	1.976		1.9031(18) × 2
			1.9202(18) × 2
M(3)–O(8)	2.006(3)	⟨M(2)–O⟩	1.903
M(3)–O(4)	2.041(3)		
M(3)–O(2)	2.207(2) × 2	Si(2)–O(8)	1.597(3) ×
M(3)–O(1)	2.289(2) × 2	Si(2)–O(3)	1.631(2) × 2
⟨M(3)–O⟩	2.173	Si(2)–O(9)	1.639(3)
		⟨Si(2)–O⟩	1.625
Si(1)–O(7)	1.597(3)		
Si(1)–O(1)	1.638(2) × 2	Si(3)–O(2)	1.624(2) ×
Si(1)–O(9)	1.640(3)	Si(3)–O(6)	1.646(3)
⟨Si(1)–O⟩	1.628	Si(3)–O(5)	1.657(3)
		⟨Si(3)–O⟩	1.638
Si(2)–O(9)–Si(1)	141.5(2)	O(10)–H–O(4)	175.5
O(10)–H	0.80	O(10) ··· O(4)	2.905

(3)–O⟩ = 2.173 Å) is dominantly occupied by Mn^{2+} cations with subordinate Fe^{2+} and minor Mg, in good agreement with earlier data. For example, in holotype samples of ferriakasakaite-(La) and ferriandrosite-(La) (Nagashima *et al.*, 2015), khristovite-(Ce) (Sokolova *et al.*, 1991), manganiandrosite-(La) (Bonazzi *et al.*, 1996), vanadoandrosite-(Ce) and manganiandrosite-(Ce) (Cenki-Tok *et al.*, 2006), this site is dominantly or completely occupied by Mn^{2+}.

7. Discussion

There are minor discrepancies between the empirical formulae calculated following the rules suggested by Armbruster *et al.* (2006) and the formulae obtained as a result of crystal structure refinement. In particular, according to the rules of assignment of ionic species to the various key sites, "if there is sufficient Al the M2 site is fully occupied by Al". However, the structural data for ferriakasakaite-(La) from the Laach Lake volcanic complex (this paper), as well as ferriakasakaite-(La) and ferriandrosite-(La) from Shobu area, Japan (Nagashima *et al.*, 2015), show the presence of minor Fe^{3+} in the M2 site.

According to the rules of cation assignment to key sites (Armbruster *et al.*, 2006), Ti is to be assigned to the octahedral site that is preferably occupied by Mn^{2+} and Fe^{2+} (*i.e.* the M3 site in the allanite group). However, only in the structure of ferriallanite-(La) (Kolitsch *et al.*, 2012) Ti cations have been assigned to the M(3) site due to its highly distorted octahedral coordination. The distortion of the M(3)-centered octahedron which shares edges with distorted *REE*-bearing A(2) polyhedra is typical for epidote-supergroup minerals, including Ti-free ones. Moreover, the M(3)-centered octahedron is unusually large for Ti^{4+} and its distortion is almost independent of the composition (Ferraris & Ivaldi, 1989). The presence of Ti in the M(1) site was reported for most 'allanites', including holotype ferriakasakaite-(La) and ferriandrosite-(La) from Ise, Mie Prefecture, Japan (Nagashima *et al.*, 2015), khristovite-(Ce)

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Table 6. Bond valence calculations for ferriakasakaite-(La). Parameters were taken from Brese & O'Keeffe (1991) and from Ferraris & Ivaldi (1988).

	A(1)	*A*(2)	*M*(1)	*M*(2)	*M*(3)	Si(1)	Si(2)	Si(3)	Σ	H-bonding	Σ
O(1)	0.32 ×2↓		0.46 ×2↓		0.25 ×2↓	0.96 ×2↓			1.99		1.99
O(2)		0.39 ×2↓									
0.27 ×2↓			0.29 ×2↓			1.00 ×2↓	1.95		1.95		
O(3)	0.36 ×2↓	0.18 ×2↓		0.55 ×2↓			0.98 ×2↓		2.07		2.07
O(4)			0.66 ×2↓x2→		0.47				1.79	+0.15(O(10))	1.94
O(5)	0.17		0.45 ×2↓ ×2→					0.91	1.98		1.98
O(6)	0.06			0.49 ×2↓ ×2→				0.94	1.98		1.98
O(7)	0.33	0.61				1.08			2.02		2.02
O(8)		0.10 ×2↓ ×2→									
0.08			0.51		1.08		1.87		1.87		
O(9)						0.96	0.96		1.92		1.92
O(10)		0.29		0.52 ×2↓ ×2→					1.33	–0.15 (O(4))	1.18
Σ	1.92	2.86	3.14	3.12	2.06	3.96	4.00	3.85			

(Sokolova *et al.*, 1991), ferriallanite-(Ce) (Kartashov *et al.*, 2002), dissakisite-(Ce) (Rouse & Peacor, 1993), allanite-(Ce) (Hoshino *et al.*, 2005), and manganiandrosite-(Ce) (Cenki-Tok *et al.*, 2006). In the structure model for ferriakasakaite-(La) from the Laach Lake volcanic complex, we assume that Ti occupies the *M*(1) site which also has irregular octahedral coordination.

The cation distribution for ferriakasakaite-(La) from the Laach Lake volcanic complex determined based on the crystal structure refinement is close to that reported for the mineral from Japan (Nagashima *et al.*, 2015). The crystal-chemical formula of the ferriakasakaite-(La) from Japan is $^{A1}(Ca_{0.54}Mn^{2+}_{0.46})^{A2}(La_{0.48}Ce_{0.20}Pr_{0.07}Nd_{0.18}Gd_{0.02}\ Ca_{0.05})^{M1}(Fe^{3+}_{0.42}V^{3+}_{0.34}Al_{0.18}Ti^{4+}_{0.06})^{M2}(Al_{0.96}Fe^{3+}_{0.04})^{M3}(Mn^{2+}_{0.50}Fe^{2+}_{0.43}Mg_{0.07})(SiO_4)(Si_2O_7)O(OH)$.

The formula of the vanadium-free ferriakasakaite-(La) from the Laach Lake volcanic complex investigated in this work is $^{A1}(Ca_{0.70}Mn^{2+}_{0.30})^{A2}(La_{0.55}Ce_{0.40}Nd_{0.05})^{M1}(Fe^{3+}_{0.48}Al_{0.42}Ti^{4+}_{0.10})^{M2}(Al_{0.93}Fe^{3+}_{0.07})^{M3}(Mn^{2+}_{0.53}Fe^{2+}_{0.34}Mg_{0.13})(SiO_4)(Si_2O_7)O(OH_{0.90}O_{0.10})$, which is closer to the end-member formula. The Mg cations (0.13 apfu) were assigned according to the assignment rules of Armbruster *et al.* (2006) and by analogy with holotype ferriakasakaite-(La) (Nagashima *et al.*, 2015) and other Mg-bearing representatives of the allanite group. The relationship between cation distributions and structural variations in epidote-supergroup minerals was previously reported (*e.g.* Nagashima *et al.*, 2015). According to these correlations, the β angle systematically decreases with increasing *REE* content at the *A*(2) site. In addition, the Mn^{2+} content at the *A*(1) site also strongly affects the β angle, with the systematic decrease of the latter with increasing Mn^{2+} content at *A*(1). This is in a good agreement with our data: relatively close values of *REE* content in *A*(2) [0.95 *apfu* in the ferriakasakaite-(La) from Japan and 1.00 *apfu* in our sample] and higher Mn^{2+} content in *A*(1) in the holotype sample (0.46 *apfu*) than in the Laach Lake volcanic complex sample (0.30 *apfu*) result in a smaller value of the β angle: 113.845° (Nagashima *et al.*, 2015) *vs*. 114.103°. A still higher value of the β angle (114.54°) was obtained for ferriallanite-(La) in which *A*(1) is Mn-free and *A*(2) contains 0.91 *REE apfu* (Kolitsch *et al.*, 2012).

All known samples of ferriakasakaite are La-dominant. Ferriakasakaite-(La) holotype material originates from a stratiform ferromanganese deposit characterized by a negative Ce anomaly and high La contents (Nagashima *et al.*, 2015). Enhanced contents of La in epidote-supergroup minerals from the Pelagonian massif and Laach Lake volcano may be due to oxidative formation conditions and partial oxidation of Ce^{3+} to Ce^{4+} to form cerianite-(Ce) (Chukanov *et al.*, 2012c).

A specific feature of epidote-supergroup minerals from the orogenic zone related to the "Mixed Series" of the Pelagonian massif is the occurrence of chalcophile elements mainly in oxygen-bearing minerals, which indicate high oxygen activity during the processes that accompany orogenesis. In particular, the presence of chalcophile elements Pb, Zn, and Cu is typical for epidote-supergroup minerals from this formation. For example, the empirical formula of presumed Pb, Zn, Cu-rich allanite-(Ce) (Table 2) is $Ca[(La_{0.11}Ce_{0.14}Pr_{0.02}Nd_{0.09}Sm_{0.03})_{\Sigma 0.39}Ca_{0.36}Pb_{0.23}Mn^{2+}_{0.02}](Al_{0.61}Fe^{3+}_{0.34}Ti_{0.05})Al(Fe_{0.32}Mn_{0.31}Zn_{0.23}Cu_{0.14})(Si_{2.90}\ Al_{0.10})O_{12}(OH, O)$. Based on previously reported data for Pb-bearing epidote-supergroup minerals and their crystal chemical features we assume that Pb cations in the sample of ferriakasakaite-(La) from the Pelagonian massif (Table 2) occupy the *A*(2) site. The role of the $6s^2$ electron pair in distorting the coordination polyhedron containing Pb^{2+} was discussed in numerous papers (*e.g.* Chukanov *et al.*, 2012a). We assume Zn and Cu^{2+} incorporation in the *M*(3) site based on close values of effective octahedral ionic radii of these cations and divalent Fe and Mn. Moreover, the presence of Cu^{2+} in the most tetragonally distorted $M(3)O_6$ octahedron susceptible to Jahn-Teller distortion was suggested for piemontite (Bonazzi *et al.*, 1996). High oxygen activity could result in oxidation of all Fe and most Mn to the trivalent state. Therefore one cannot exclude that 'allanites' from the Pelagonian massif are actually O-dominant in the O(10) site

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and, consequently, belong to the åskagenite group. Although the åskagenite group is not mentioned in the epidote-supergroup nomenclature approved by the IMA CNMNC (Armbruster *et al.*, 2006), it exists *de facto* after the discovery of its first representative åskagenite-(Nd), ideally $Mn^{2+}NdAl_2Fe^{3+}(Si_2O_7)(SiO_4)O_2$ (Chukanov *et al.*, 2010).

The tentative assignment of some minerals from the Pelagonian massif to potential new species "ferripiemontite" and "ferripiemontite-(Pb) " (Table 2) is based on the formula calculation made in accordance with rules suggested by Armbruster *et al.* (2006). According to these rules, in end-member piemontite the *M*1 and *M*2 sites are occupied by Al, and all Mn^{3+} occurs in the *M*3 site. In the allanite trends for the *A*2 site: samples from the earliest association with Zn-rich mainly at the latest group, all bivalent cations except those occurring in the *A*1 site are to be assigned to the *M*3 site. Unfortunately, the Mn^{2+}:Mn^{3+} and Fe^{2+}:Fe^{3+} ratios in the epidote-supergroup minerals from the Pelagonian phlogopite are *REE*-depleted, whereas samples from late massive baryte aggregates are rich in Pb and *REE* and do not contain Ca. These trends show that supply of Pb and *REE* occurred massif could not be determined. In the presence of Fe^{3+} the cation distribution between *M* sites cannot be unambiguously determined from chemical data. In particular, available structural and spectroscopic data show a stronger preference of Fe^{3+} for the more distorted *M*3 site compared to Mn^{3+} (Bonazzi & Menchetti, 2004).

Figure 5 shows that epidote-supergroup minerals from different assemblages of the Pelagonian massif show different compositionalstages of orogenesis, in agreement with our earlier observations (Ermolaeva *et al.*, 2016).

Bonazzi *et al.* (1992) and Bonazzi & Menchetti (2004) note that Mn^{3+}-rich epidote-supergroup minerals (including those from the Nežilovo area of the Pelagonian massif) exhibit anomalous depletion in *HREE*, usually with La>Ce. The chemical compositions of most samples from Nežilovo reported by Bermanec *et al.* (1994) correspond to Pb- and *REE*-bearing "ferripiemontite" with La > Ce and about 1 Mn^{3+} *apfu*. The deficit of Ce in Mn^{3+}-rich epidote-supergroup minerals can be explained by the high oxidation conditions of their formation which also favor a high Ce^{4+}/Ce^{3+} ratio.

In the Pelagonian massif, very unusual elements. In particular, cymrite is a rock-forming component of quartz–cymrite schists outcropping in the footwall of and complex sulfide-free mineral assemblages bearing chalcophile elements in the form of oxides and oxysalts were formed as a result of metasomatic replacement of dolomite marbles at their contacts with meta-rhyolites (Chukanov *et al.*, 2012b, 2015; Ermolaeva *et al.*, 2016; Varlamov *et al.*, 2017). This process occurred at high activities of barium and oxygen. Baryte is abundant in all associations, from the earliest to the latest. Excess barium (relative to sulfur) concentrated in cymrite. This mineral is common in the sulfide-free mineral assemblages bearing chalcophile the mentioned dolomitic marbles. Along with cymrite, these rocks contain other Ba-bearing silicates (hyalophane and sanbornite) as accessories (Chukanov *et al.*, 2015).

Taking into account that baryte is characterized by a very low solubility and mobility under hydrothermal conditions up to 300 °C and 1400 bars (Blount, 1977), the following mechanism explaining sulfur between $SO_4^{2-}$and S^{2-} shifts to the right. In an excess of barium, all sulfur is immobilized in the sulfate form. As a result, chalcophile elements (Zn, Cu, Sb, and Pb) form oxygen-bearing minerals (Zn-spinels, Zn- and Sb-rich members of the högbomite supergroup, nežilovite, ferricoronadite, piemontite-(Pb), almeidaite, hydroxyplumboroméite *etc.*) or immobilization and the absence of sulfides in the orogenic zone of the Pelagonian massif can be suggested: $S^{2-} + 2O_2 \leftrightarrow SO_4^{2-}$; $SO_4^{2-} + Ba^{2+} \rightarrow BaSO_4\downarrow$. As baryte crystallizes, the equilibrium occur as minor components of rock-forming silicates (micas, amphiboles, pyroxenes, epidote-group minerals).

The most probable source of barium was feldspar of metarhyolites. Post-magmatic fluids related to meta-rhyolites are considered as a possible source of a number of specific, ore and rare elements (Pb, Zn, Sb, As, Cu, Ba, *REE etc.*) in the contact-metasomatic rocks (Jančev, 1998; Ermolaeva *et al.*, 2016).

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