

Perbøeite-(Ce) and alnaperbøeite-(Ce), two new members of the epidote-törnebohmite polysomatic series: Chemistry, structure, dehydrogenation, and clue for a sodian epidote end-member

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ABSTRACT

In yttrian fluorite from pegmatites of the Tysfjord granite, Norway, grayish-green to very pale green gatelite-like crystals occur along with millimeter-size aggregates of Y-silicates as a late primary phase; they are associated with allanite-(Ce), bastnäsite-(Ce), and intimately inter- or overgrown by törnebohmite-(Ce). Sub- to euhedral crystals, up to 400 µm in size, are chemically zoned between two near-end-member compositions that imply the existence of two new members of the polysomatic gatelite group, in which *ET* polysomes are composed of *E* modules with epidote-type structure alternating with *T* modules of törnebohmite-type structure. The two new minerals form a continuous solid-solution series, along which two crystals of intermediate compositions served for species definition. Their electron-microprobe analyses yield the empirical formulas $(\text{Ca}_{1.00}\text{Mn}_{0.03}\text{Na}_{0.08}\text{La}_{0.51}\text{Ce}_{1.30}\text{Pr}_{0.16}\text{Nd}_{0.62}\text{Sm}_{0.10}\text{Gd}_{0.06}\text{Dy}_{0.03}\text{Er}_{0.01}\text{Y}_{0.06}\text{Th}_{0.01})_{\Sigma 3.97}(\text{Al}_{3.21}\text{Fe}^{2+}_{0.79})_{\Sigma 4.00}\text{Si}_{5.01}\text{O}_{20}(\text{OH})_2$ for perbøeite-(Ce) [IMA 2011-55] and $(\text{Ca}_{1.10}\text{Mn}_{0.03}\text{Na}_{0.20}\text{La}_{0.42}\text{Ce}_{1.14}\text{Pr}_{0.16}\text{Nd}_{0.60}\text{Sm}_{0.13}\text{Gd}_{0.07}\text{Dy}_{0.03}\text{Er}_{0.01}\text{Yb}_{0.01}\text{Y}_{0.12}\text{Th}_{0.02})_{\Sigma 4.04}(\text{Al}_{3.54}\text{Fe}^{2+}_{0.40}\text{Mg}_{0.02})_{\Sigma 3.96}\text{Si}_{4.99}\text{O}_{20}(\text{OH})_2$ for alnaperbøeite-(Ce) [IMA 2012-54]. The respective end-member formulas are $^{\text{A}}(\text{Ce}_3\text{Ca})^{\text{M}}(\text{Al}_3\text{Fe}^{2+})\text{Si}_2\text{O}_7(\text{SiO}_4)_3\text{O}(\text{OH})_2$, which requires Ce_2O_3 45.10, CaO 5.14, FeO 6.58, Al_2O_3 14.01, SiO_2 27.52, H_2O 1.65, total 100.00 wt%; and $^{\text{A}}(\text{Ce}_{2.5}\text{CaNa}_{0.5})^{\text{M}}(\text{Al}_4)\text{Si}_2\text{O}_7(\text{SiO}_4)_3\text{O}(\text{OH})_2$, which requires Ce_2O_3 40.86, CaO 5.58, Na_2O 1.54, Al_2O_3 20.31, SiO_2 29.92, H_2O 1.79, total 100.00 wt%. Cell parameters of perbøeite-(Ce) and alnaperbøeite-(Ce) for these crystals are $a = 8.9277(6)$ and $8.9110(4)$, $b = 5.6548(6)$ and $5.6866(2)$, $c = 17.587(1)$ and $17.5252(7)$ Å, $\beta = 116.475(8)$ and $116.300(5)^\circ$, $V = 794.8(1)$ and $796.13(7)$ Å³, respectively. Members of the perbøeite-(Ce)-alnaperbøeite-(Ce) solid solution are topologically identical to the minerals gatelite-(Ce) and västmanlandite-(Ce). Structural data (space group $P2_1/m$) were obtained for the holotype crystals and for several crystals with intermediate composition. Structural refinements of a crystal annealed step-wise in air confirm that most of Fe in M3 is divalent before heating and show that oxidation/dehydrogenation takes place mostly in the *E* module (M3 and H1). Perbøeite-(Ce) derives from gatelite-(Ce) by the homovalent substitution $[\text{M}^3\text{Fe}^{2+} \rightarrow \text{M}^3\text{Mg}]$. Alnaperbøeite-(Ce) derives from perbøeite-(Ce) or gatelite-(Ce) by the coupled heterovalent substitutions $[\text{A}\text{Na}^+ + 2\text{M}^3\text{Al}^{3+} \rightarrow \text{A}\text{REE} + 2\text{M}^3(\text{Fe}^{2+} \text{ or } \text{Mg})]$.

Törnebohmite-(Ce) associated with alnaperbøeite-(Ce) is Na-free, whereas coexisting allanite is Na-bearing and shows the same coupled substitution between A and M sites as the one relating perbøeite-(Ce) and alnaperbøeite-(Ce) ($\text{Na}_{0.5}\text{Al} \leftrightarrow \text{REE}_{0.5}\text{Fe}^{2+}$). This could suggest, although crystallographic evidence is inconclusive, that Na incorporation in the *ET* polysome occurs in the *E* module alone (A2 or A1 sites), leading to the sodian *E* end-member $^{\text{A}}(\text{CaREE}_{0.5}\text{Na}_{0.5})^{\text{M}}(\text{Al}_3)\text{Si}_2\text{O}_7(\text{SiO}_4)_3\text{O}(\text{OH})$. In any event, this new epidote end-member is needed to account for up to ca. 10 mol% of the composition of allanite-group minerals, in which Na_2O contents may reach 0.3 wt%. Sodium must be analyzed in epidote-supergrout and gatelite-group minerals.

Keywords: New mineral, perbøeite-(Ce), alnaperbøeite-(Ce), Tysfjord granite (Norway), polysomatic series, epidote supergrout, crystal structure, chemical composition, gatelite group

INTRODUCTION

Minerals belonging to the gatelite group, i.e., gatelite-(Ce) (Bonazzi et al. 2003) and västmanlandite-(Ce) (Holtstam et al. 2005), can be regarded as iso-topological *ET* type polysomes within a polysomatic series having epidote and törnebohmite

as end-members. Their structure (Fig. 1) is a regular alternating stacking of (001) slabs of epidote-type structure (*E*) and ($\bar{1}02$) slabs of törnebohmite-type structure (*T*) (Shen and Moore 1982). The *T* modules in both minerals have the same composition as the mineral törnebohmite, $(\text{Ce},\text{La})_2\text{Al}[\text{SiO}_4]_2(\text{OH})$, whereas the chemical variability of the *E* module characterizes the mineral, even if all the *E* modules known so far belong to the allanite

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group. Specifically, the *E* module is of dissakisite-(Ce) composition, $\text{CaCeAl}_2\text{MgSi}_2\text{O}_7(\text{SiO}_4)\text{O}(\text{OH})$ (Grew et al. 1991; Rouse and Peacor 1993) in gatelite-(Ce) and of dollaseite-(Ce) composition, $\text{CaCeAlMg}_2\text{Si}_2\text{O}_7(\text{SiO}_4)\text{F}(\text{OH})$ (Peacor and Dunn 1988) in västmanlandite-(Ce). Moreover, the gatelite-like minerals from the Bergslagen mining region of south-central Sweden characterized by Holtstam and Andersson (2007) can be essentially described as members of the solid-solution between västmanlandite-(Ce) and an unnamed mineral having the *E* module of ferriallanite-(Ce) composition, $\text{CaCeFe}^{3+}\text{AlFe}^{2+}\text{Si}_2\text{O}_7(\text{SiO}_4)\text{O}(\text{OH})$ (Kartashov et al. 2002; Kolitsch et al. 2012).

The recent finding of two new *ET* type polysomes extending the range of known compositions led to the definition of two new species, perbøeite-(Ce) and alnaperbøeite-(Ce), approved by the Commission on New Minerals, Nomenclature and Classification, IMA (2011-055 and 2012-054, respectively). Their definition is based on the analytical evidence of a continuous solid solution between two near-end-member compositions of new *ET* polysomes, and on the structure refinement of crystals of intermediate compositions, by lack of homogeneous crystals of near-end-member composition. In addition, the analysis of the structural variations observed on a crystal heated in air offers the opportunity to explore possible differences in response to the induced oxidation-dehydrogenation reaction within *E* and *T* modules.

Holotype material is deposited in the collections of the Museo di Storia Naturale, Sezione di Mineralogia e Litologia, Università di Firenze, Italy, under catalog number 3110/I [perbøeite-(Ce)] and 3114/I [alnaperbøeite-(Ce)].

GEOLOGICAL SETTING, OCCURRENCE, AND PARAGENESIS

Hundholmen, Stetind, and Nedre Eivollen pegmatites belong to a series of quartz-microcline pegmatites of the niobium-yttrium-fluorine family found in the Tysfjord granite (Norway), a ca. 1742 ± 46 Ma old granitic gneiss deformed during the Caledonian orogeny (Andresen and Tull 1986). Main accessory minerals in these pegmatites include allanite-(Ce), fergusonite-(Y), columbite-(Fe), beryl, various sulfides (pyrite, pyrrhotite, arsenopyrite) and fluorite, particularly an yttrium-rich variety, yttrian fluorite, with abundant inclusions of various REE-minerals (Husdal 2008). The new species hundholmenite-(Y) (Raade et al.

2007), stetindite (Schlüter et al. 2009), fluorbritholite-(Y) (Pekov et al. 2011), atelisite-(Y) (Malcherek et al. 2012), bastnäsite-(Nd) (IMA 2011-062), cayalsite-(Y) (IMA 2011-094), and schlüterite-(Y) (IMA 2012-015) were found in yttrian fluorite masses.

Both perbøeite-(Ce) and alnaperbøeite-(Ce) occur as isolated or loosely aggregated, sub- to euhedral crystals, up to 400 μm in size within white yttrian fluorite. Crystals have a stout prismatic morphology elongated along [010]. Perbøeite-(Ce) and alnaperbøeite-(Ce) appear very similar to each other: they are transparent with vitreous luster and their color ranges from pale grayish-green [perbøeite-(Ce)] to very pale green [alnaperbøeite-(Ce)].

At Hundholmen [type-locality for perbøeite-(Ce)] and Stetind [type-locality for alnaperbøeite-(Ce)] these minerals [and törnebohmite-(Ce)] occur both as inclusions in the fluorite groundmass and, along with some isolated crystals of allanite-(Ce) and bastnäsite-(Ce), within millimeter-size aggregates of one or several Y-silicates [fluorthalénite-(Y)/thalénite-(Y), kuliokite-(Y), hundholmenite-(Y)], also included in yttrian fluorite (Supplementary Fig. 1¹). In the Hundholmen material pyrite was also observed as accessory mineral; in the Stetind material, vyuntspakhkite-(Y) and thorite with zircon inclusions. Material from Nedre Eivollen shows a somewhat different texture, in which subhedral perbøeite-(Ce)/alnaperbøeite-(Ce) associated with thalénite-(Y)/fluorthalénite-(Y) [and minor allanite-(Ce), törnebohmite-(Ce), bastnäsite-(Ce), and fluorbritholite-(Y)] fill or line millimeter-size interstices and voids in the fluorite groundmass [with bastnäsite-(Ce) and fluocerite-(Ce) inclusions], the remaining void spaces being ultimately filled by massive albite. Perbøeite-(Ce)/alnaperbøeite-(Ce) therefore appear as late primary minerals in the pegmatite evolution. They are relatively abundant in the material studied, whereas allanite-(Ce), although commonly reported there, is subordinate.

At the three localities, both new minerals are consistently intergrown with and/or overgrown by lamellae of törnebohmite-(Ce), or exhibit minute irregular intergrowths with törnebohmite-(Ce) (Fig. 2). As also revealed by high-contrast backscattered electron imaging of polished sections, especially in the Stetind material, crystals are more or less concentrically zoned, with lower-mass cores and higher-mass rims, overgrowths and fillings of cracks or of dissolution embayments in the crystal (Supplementary Figs. 2 and 3¹).

EXPERIMENTAL METHODS

X-ray data collection

Several single crystals were mounted on a CCD-equipped Oxford Diffraction Excalibur 3 diffractometer. The unit-cell dimensions of 12 examined crystals are in the range $a = 8.90\text{--}8.95$, $b = 5.65\text{--}5.69$, $c = 17.50\text{--}17.65$ Å, $\beta = 116.2\text{--}116.7^\circ$ (Table 1), without any evidence of doubling of the translation unit along the *a*-axis. Although the crystals were examined with long exposure times, neither superstructure reflections such as in gatelite-(Ce) nor the weak, continuous streaking as in västmanlandite-(Ce) were detected. One crystal (ST2_02) was annealed for 48 h at selected temperatures ranging from 350 to 750 °C in a Carbolite CWF1200 furnace allowing the crystal to cool slowly in the furnace down to room temperature.

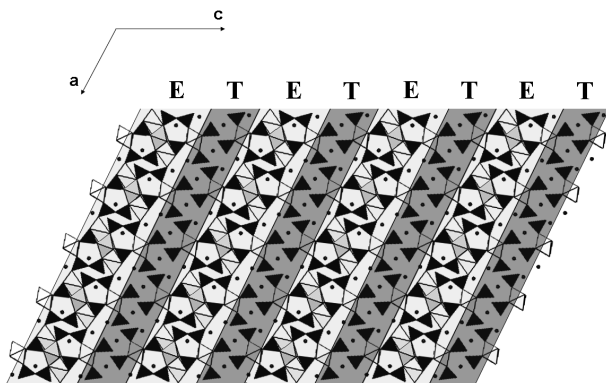


FIGURE 1. Schematic representation of the structure ([010] projection) of gatelite-group minerals in terms of *E*-type and *T*-type modules.

¹ Deposit item AM-14-102, Tables 3, 4, and 7, Supplemental Figures 1, 2, and 3, and CIF. Deposit items are stored on the MSA web site and available via the *American Mineralogist* Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam.org), and then click on the deposit link.

Intensity data for natural and heat-treated crystals were collected with an Oxford Diffraction Xcalibur 3 diffractometer with a monochromatized MoK α X-radiation, equipped with a Sapphire 2 CCD detector (see Table 1 for details). Intensity integration and standard Lorentz-polarization correction were performed with the CrysAlis RED (Oxford Diffraction 2006) software package. The program ABSPACK in CrysAlis RED (Oxford Diffraction 2006) was used for the absorption correction.

Structure refinement

Given the absence of superstructure hkl reflections with $h = 2n + 1$, like in the case of västmanlandite-(Ce) the structure was refined in the $P2_1/m$ space group, instead of $P2_1/a$ like in gatelite-(Ce). The atomic parameters of gatelite-(Ce)

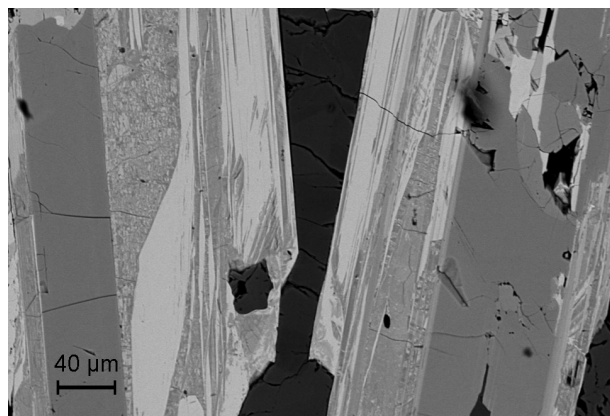


FIGURE 2. Backscattered electron image of perbøeite-(Ce) (medium gray) and törnebohmité-(Ce) (light gray) intergrowths within a matrix of yttrian fluorite (dark gray). Sample ST4, Stetind.

(transformed in the $P2_1/m$ setting) were used as starting model. The full-matrix least-squares program SHELXL-97 (Sheldrick 2008) was used for the refinement of the structure. One oxygen atom (O15) was found to be located out of the mirror plane (O15-O15 in the range 0.72–0.80 Å) and partially occupied (50%). In most cases three-dimensional difference Fourier synthesis yielded the position of two H atoms, close to O11 (H1) and O10 (H2). Nonetheless, in most of the investigated crystals the diffraction quality allowed the refinement of the atomic parameters of H1 alone.

The site population of all the metal positions was allowed to vary using different couples of scattering factors for ionized species as follows: Ca $^{2+}$ vs. Ce $^{3+}$ (A sites), Al $^{3+}$ vs. Fe $^{3+}$ (M1 and M2), Al $^{3+}$ vs. Fe $^{2+}$ (M3). Both scattering curves and $\Delta f'$, $\Delta f''$ coefficients were taken from the *International Tables for X-ray Crystallography*, volume C (Wilson and Prince 1999). Details of the anisotropic refinements are summarized in Table 1.

In analogy with the epidote-supergroup* members, M3 is the key-site to discriminate a new mineral species (Armbruster et al. 2006) in gatelite-like minerals. Two of the studied crystals, one showing aluminum dominance (ST4_11, M3 = Al $_{0.69}$ Fe $_{0.40}$) and one iron dominance (HU_02, M3 = Fe $_{0.69}$ Al $_{0.40}$), were thus selected to characterize the two new mineral species alnaperbøeite-(Ce) and perbøeite-(Ce).

Fractional atomic coordinates and equivalent isotropic-displacement parameters of ST4_11 and HU_02 are reported in Table 2. Table 3¹ reports the atom coordinates and the ADPs of the other studied crystals. Table 4¹ lists the observed and calculated structure factors for all the investigated crystals. (CIF¹ files are available online and from the corresponding author.)

The X-ray powder diffraction pattern was collected with an automated Philips PV110 diffractometer using Ni-filtered CuK α radiation by selecting grayish green crystals from sample ST2 in which perbøeite-(Ce) prevails on alnaperbøeite-(Ce). However, the unit cell obtained by least-squares refinement of 25 measured reflections [$a = 8.9120(7)$, $b = 5.6691(3)$, $c = 17.473(1)$ Å, $\beta = 116.147(6)^\circ$, $V = 792.45(8)$ Å ^{3}] and a comparison with calculated X-ray powder patterns (Table 5) reveals a likely admixture with Al-rich grains.

* According to the recent standardization of mineral group hierarchies (Mills et al. 2009), the terms “group” and “subgroup” used by Armbruster et al. (2006) for the epidote nomenclature have been changed to “supergroup” and “group”, respectively.

TABLE 1. Experimental details for the selected crystals

	ST4_11	ST4_09	ST3_01	NE_01	ST4_10	ST4_02	ST2_01	ST2_03	HU_02
<i>a</i> (Å)	8.9277(6)	8.9310(5)	8.9205(4)	8.9546(8)	8.9222(4)	8.9165(4)	8.9327(4)	8.9313(9)	8.9110(4)
<i>b</i> (Å)	5.6548(6)	5.6574(3)	5.6573(3)	5.6675(5)	5.6650(2)	5.6754(2)	5.6817(2)	5.6608(6)	5.6866(2)
<i>c</i> (Å)	17.587(1)	17.6000(9)	17.5715(9)	17.652(2)	17.569(1)	17.5253(7)	17.5807(7)	17.549(2)	17.5252(7)
β (°)	116.475(8)	116.517(4)	116.500(4)	116.677(7)	116.470(5)	116.321(3)	116.465(3)	116.396(8)	116.300(5)
<i>V</i> (Å ^{3})	794.8(1)	795.71(8)	793.59(7)	800.5(1)	794.92(7)	794.92(6)	798.77(6)	794.8(2)	796.13(7)
Data collection									
$\theta_{\max}$ (°)	35.68	33.30	33.25	34.23	34.82	28.86	33.79	32.34	34.92
Total refl. collected	8111	6562	6816	7140	7589	3598	7953	6861	7576
Unique refl. (R_{int})	3705 (4.01)	3040 (4.43)	3030 (4.29)	3313 (7.00)	3417 (4.02)	1968 (2.46)	3209 (3.84)	2829 (4.48)	3460 (3.57)
Refl. with $F > 4\sigma(F)$	2637	1942	1995	1546	2224	1593	2269	1830	2679
Structure refinement									
Number of parameters	202	206	206	206	206	206	206	206	206
R_1 [$F > 4\sigma(F)$]	5.19	4.57	4.28	5.08	3.94	2.76	3.60	3.77	4.14
R_1 all	8.19	8.15	7.25	12.41	7.34	3.79	6.05	7.04	6.12
Max ΔF peak ($e^-/\text{\AA}^3$)	3.06	2.23	2.87	2.50	2.61	0.98	2.50	2.14	2.09
Min ΔF peak ($e^-/\text{\AA}^3$)	-2.17	-1.66	-2.84	-1.28	-1.72	-0.90	-1.74	-1.77	-2.50
	ST2_04	HU_01	ST2_02	ST2_02-350	ST2_02-450	ST2_02-550	ST2_02-650	ST2_02-750	
<i>a</i> (Å)	8.8996(4)	8.8950(4)	8.9039(3)	8.9044(3)	8.9002(3)	8.9031(3)	8.8979(4)	8.8936(4)	
<i>b</i> (Å)	5.6759(4)	5.6827(2)	5.6785(2)	5.6650(2)	5.6304(2)	5.6290(1)	5.6235(2)	5.6189(2)	
<i>c</i> (Å)	17.5154(9)	17.5044(7)	17.5039(6)	17.5261(7)	17.7324(6)	17.7392(6)	17.731(1)	17.7550(7)	
β (°)	116.221(4)	116.240(3)	116.301(4)	116.399(5)	116.710(3)	116.752(4)	116.815(5)	116.952(5)	
<i>V</i> (Å ^{3})	793.71(8)	793.63(6)	793.39(5)	791.88(6)	793.78(5)	793.85(5)	791.81(7)	790.89(7)	
Data collection									
$\theta_{\max}$ (°)	35.00	34.88	32.53	34.67	33.01	34.96	34.95	34.87	
Total refl. collected	7621	7722	8188	7535	6736	7926	7630	7709	
Unique refl. (R_{int} %)	3432 (4.23)	3475 (7.44)	2848 (3.07)	3413 (2.79)	3043 (2.87)	3424 (2.57)	3431 (3.84)	3449 (3.29)	
Refl. with $F > 4\sigma(F)$	2405	1712	2280	2739	2433	2722	2643	2718	
Structure refinement									
Number of parameters	206	203	206	206	203	203	203	203	
R_1 [$F > 4\sigma(F)$] (%)	4.57	4.47	2.97	3.62	3.04	3.05	3.48	3.47	
R_1 all (%)	7.21	11.47	4.22	4.94	4.16	4.26	5.06	4.87	
Max ΔF peak ($e^-/\text{\AA}^3$)	4.54	1.95	1.66	2.27	1.57	2.71	2.28	2.85	
Min ΔF peak ($e^-/\text{\AA}^3$)	-2.62	-1.62	-2.03	-3.04	-2.71	-3.43	-3.15	-4.31	

Notes: Crystals labeled ST, NE, and HU come from Stetind, Nedre Eivollen, and Hundholmen pegmatites, respectively. The ST_02 crystal was annealed for 48 h at 350, 450, 550, 650, and 750 °C.

TABLE 2. Refined site occupancy, fractional atomic coordinates, and equivalent isotropic displacement parameters ($\text{\AA}^2$) for alnaperbøite-(Ce) (ST4_11 crystal) and perbøite-(Ce) (HU_02 crystal)

Atom	Occupancy	x	y	z	U_{iso}
A1	$\text{Ca}_{0.942(4)}\text{Ce}_{0.056}$	0.7322(2)	1/4	0.4097(1)	0.0229(5)
	$\text{Ca}_{0.958(2)}\text{Ce}_{0.042}$	0.7322(2)		0.40998(8)	0.0182(4)
A2	$\text{Ce}_{0.896(6)}\text{Ca}_{0.104}$	0.88965(6)	1/4	0.24991(3)	0.0198(2)
	$\text{Ce}_{0.978(4)}\text{Ca}_{0.022}$	0.89185(5)		0.24954(2)	0.0154(1)
A3	$\text{Ce}_{0.888(6)}\text{Ca}_{0.112}$	0.73978(8)	1/4	0.01013(4)	0.0375(2)
	$\text{Ce}_{0.958(4)}\text{Ca}_{0.042}$	0.73949(6)		0.00968(3)	0.0311(2)
A4	$\text{Ce}_{0.858(6)}\text{Ca}_{0.142}$	0.08128(6)	3/4	0.16453(3)	0.0198(2)
	$\text{Ce}_{0.950(4)}\text{Ca}_{0.050}$	0.07839(5)		0.16574(2)	0.0148(1)
M1	$\text{Al}_{1.000}$	1/2	1/2	1/2	0.0137(4)
	$\text{Al}_{0.992(7)}\text{Fe}_{0.008}$			0.0112(6)	
M2	$\text{Al}_{0.973(8)}\text{Fe}_{0.027}$	0.4827(1)	-0.0005(3)	0.2051(1)	0.0132(5)
	$\text{Al}_{0.973(6)}\text{Fe}_{0.027}$	0.4813(1)	0.0005(2)	0.20530(8)	0.0113(4)
M3	$\text{Al}_{0.598(9)}\text{Fe}_{0.402}$	0.1988(2)	3/4	0.3756(1)	0.0207(6)
	$\text{Fe}_{0.716(7)}\text{Al}_{0.284}$	0.1950(1)		0.37640(7)	0.0139(3)
Si1		0.1627(2)	1/4	0.4755(1)	0.0135(4)
		0.1625(2)		0.4774(1)	0.0107(3)
Si2		0.8084(2)	3/4	0.3374(1)	0.0128(4)
		0.8055(2)		0.3357(1)	0.0104(3)
Si3		0.3072(2)	1/4	0.3136(1)	0.0122(4)
		0.3050(2)		0.3126(1)	0.0095(3)
Si4		0.6723(2)	3/4	0.1043(2)	0.0160(4)
		0.6697(2)		0.1030(1)	0.0118(4)
Si5		0.1564(2)	1/4	0.0773(1)	0.0119(4)
		0.1553(2)		0.0776(1)	0.0092(3)
O1		0.2668(5)	0.4926(7)	0.4783(3)	0.0224(9)
		0.2674(4)	0.4901(5)	0.4824(2)	0.0165(7)
O2		0.1837(5)	0.4802(7)	0.2924(3)	0.0217(8)
		0.1793(4)	0.4750(5)	0.2897(2)	0.0163(7)
O3		0.6982(5)	0.9864(6)	0.2969(3)	0.0189(8)
		0.6943(4)	-0.0130(5)	0.2980(2)	0.0148(7)
O4		0.4413(6)	3/4	0.4240(4)	0.016(1)
		0.4421(5)		0.4248(3)	0.0124(9)
O5		0.4525(7)	1/4	0.4140(3)	0.015(1)
		0.4496(5)		0.4129(3)	0.0133(9)
O6		0.4193(6)	1/4	0.2603(4)	0.015(1)
		0.4188(5)		0.2601(3)	0.0126(9)
O7		-0.0172(7)	1/4	0.3969(4)	0.022(1)
		-0.0166(5)		0.3967(3)	0.0152(9)
O8		-0.0311(9)	3/4	0.3207(6)	0.038(2)
		-0.0435(7)		0.3114(4)	0.029(1)
O9		0.8654(9)	3/4	0.4391(4)	0.034(2)
		0.8723(6)		0.4386(3)	0.023(1)
O10		0.5579(6)	1/4	0.1632(4)	0.015(1)
		0.5581(5)		0.1624(3)	0.0105(8)
O11		0.4065(7)	3/4	0.2482(4)	0.018(1)
		0.4037(5)		0.2484(3)	0.0117(9)
O12		0.5396(6)	3/4	0.1471(4)	0.014(1)
		0.5391(5)		0.1474(3)	0.0112(9)
O13		0.2702(5)	0.4905(7)	0.1104(3)	0.0195(8)
		0.2685(4)	0.4907(5)	0.1104(2)	0.0157(7)
O14		0.7958(5)	0.5232(7)	0.1334(3)	0.027(1)
		0.7942(4)	0.5243(6)	0.1321(2)	0.0200(8)
O15	$\text{O}_{0.50}$	0.555(1)	0.817(1)	0.0047(5)	0.031(2)
	$\text{O}_{0.50}$	0.5496(8)	0.818(1)	0.0033(4)	0.022(2)
O16		0.063(1)	1/4	-0.0232(5)	0.056(2)
		0.0613(8)		-0.0229(4)	0.042(2)
O17		0.0235(9)	1/4	0.1163(5)	0.043(2)
		0.0233(6)		0.1164(4)	0.029(1)
H1		-	3/4	-	-
		0.434(8)		0.325(4)	0.01(2)

Note: For each atom, the first row refers to alnaperbøite-(Ce), the second one to perbøite-(Ce).

Chemical analyses

The two holotype crystals and the crystal ST2_02 were embedded in epoxy and polished for electron microprobe analysis (EMPA). Additional EMPA data for alnaperbøite-(Ce) and perbøite-(Ce) solid solution and coexisting minerals were obtained on polished rock samples from Stetind (ST2 and ST4) and Nedre Eivollen (NE) and on a minute fragment from Hundholmen. Analyses were performed using Cameca SX100 and SXFive electron microprobes at Centre Camparis, Paris, in wavelength-dispersive mode at 15 kV, 15 nA beam current, 2 μm beam diameter, 5 to

TABLE 5. X-ray powder diffraction data

(1)		(2)		(3)		h	k	l
alnaperbøite-(Ce)		perbøite-(Ce)		ST2				
l_{calc}	d_{calc}	l_{calc}	d_{calc}	l_{obs}	d_{obs}			
91.88	15.7426	91.34	15.7111	75	15.7	0	0	1
13.68	7.9914	18.32	7.9886	15	7.98	1	0	0
12.21	7.5326	16.21	7.5051	15	7.49	1	0	2
6.91	4.7739	6.24	4.7900	-	-	1	1	1
9.60	4.6639	9.94	4.6628	-	-	1	0	2
29.90	4.6160	33.18	4.6327	30	4.62	1	1	0
8.96	4.5925	7.21	4.6063	-	-	0	1	2
6.65	4.3908	5.88	4.3749	-	-	1	0	4
7.13	4.1504	7.39	4.1629	-	-	1	1	1
6.17	3.9357	6.67	3.9278	-	-	0	0	4
41.60	3.4986	43.95	3.5014	40	3.489	2	1	2
17.94	3.4681	17.67	3.4675	15	3.461	1	1	4
5.87	3.3768	5.30	3.3767	-	-	2	1	3
12.41	3.2633	13.09	3.2686	10	3.268	2	1	0
18.63	3.0553	17.77	3.0553	15	3.061	2	0	2
100.00	2.9831	100.00	2.9805	100	2.971	1	1	5
7.86	2.9688	6.40	2.9625	-	-	3	0	3
7.10	2.8815	6.28	2.8733	-	-	3	0	4
47.37	2.8274	48.13	2.8433	50	2.828	0	2	0
32.33	2.7509	31.31	2.7503	30	2.739	0	1	5
7.67	2.6881	6.37	2.6914	-	-	2	1	2
17.24	2.6655	18.05	2.6787	15	2.667	1	2	0
22.82	2.6587	23.32	2.6584	20	2.660	2	0	3
10.29	2.6286	9.72	2.6273	-	-	3	1	3
56.54	2.6188	58.50	2.6190	60	2.619	3	1	2
5.43	2.4891	5.11	2.4988	-	-	0	2	3
16.52	2.4488	14.60	2.4447	15	2.442	3	1	5
6.11	2.2953	7.19	2.2865	-	-	3	0	7
11.42	2.2612	10.49	2.2662	10	2.262	2	2	4
14.59	2.1823	15.29	2.1799	15	2.181	4	0	2
25.80	2.1431	25.46	2.1464	25	2.140	2	2	5
9.91	2.1037	10.20	2.1083	10	2.101	0	2	5
7.04	2.0812	6.36	2.0828	-	-	3	1	2
18.18	2.0752	16.95	2.0814	15	2.078	2	2	2
5.31	2.0656	5.24	2.0648	-	-	2	0	5
17.26	1.9369	18.37	1.9418	20	1.940	2	2	3
11.11	1.9164	11.26	1.9176	10	1.921	3	1	3
6.81	1.8692	6.26	1.8698	-	-	2	2	7
12.70	1.8435	11.99	1.8426	10	1.842	1	1	7
6.00	1.7276	6.47	1.7300	-	-	4	2	2
8.11	1.6945	7.60	1.6899	-	-	1	0	10
12.41	1.6608	12.52	1.6668	-	-	1	3	5
7.02	1.6484	6.06	1.6479	-	-	5	1	2
12.21	1.6332	13.37	1.6325	-	-	4	2	7
10.31	1.5891	11.00	1.5948	10	1.591	3	3	2
5.42	1.4916	5.45	1.4902	-	-	2	2	10
12.34	1.4137	11.98	1.4217	10	1.419	0	4	0

Notes: In columns 1 and 2 are reported the calculated powder pattern for alnaperbøite-(Ce) and perbøite-(Ce), obtained using atomic parameters of the crystals ST4_11 and HU2_02, respectively. Column 3 is experimental powder pattern for the solid solution in ST2.

30 s counting time on both peak and background, using the following standards: apatite (F and P $K\alpha$), albite (Na $K\alpha$), diopside (Mg, Si, and Ca $K\alpha$), orthoclase (Al and K $K\alpha$), MnTiO₃ (Ti and Mn $K\alpha$), hematite (Fe $K\alpha$), SrSiO₃ (Sr $L\alpha$), BaSO₄ (Ba $L\alpha$), monazite (Ce $L\alpha$, Th $M\alpha$), La₃ReO₈ (La $L\alpha$), NdCu (Nd $L\beta$), Sm₃ReO₈ (Sm $L\beta$), and REE-bearing glasses (Pr, Gd, Dy, Ho, and Er $L\beta$, Yb and Y $L\alpha$), with due consideration of possible interferences and $\phi\rho Z$ data reduction (PAP, Pouchou and Pichoir 1984). Table 6 reports chemical analyses and atomic ratios for the three single crystals investigated. Chemical analyses obtained along the solid-solution series on zoned crystals are listed in Table 7¹, whereas Table 8 reports the analyses of coexisting minerals in Stetind (ST) and Nedre Eivollen (NE). The relatively low analytical totals obtained for the REE-rich minerals may reflect the difficulty in analyzing accurately all the REEs.

PHYSICAL PROPERTIES

Both minerals are brittle, with a good {100} and an imperfect {001} cleavage. Crystals are elongated along *b*, with the main forms {101}, {100}, and {001}. They are transparent, biaxial, optically positive with pleochroism from absent in alnaperbøite-

TABLE 6. Electron-microprobe analyses (mean and range of number point-analyses, in wt%) and atomic ratios on a $O_{20}(OH)_2$ basis for the selected crystals of perbøite and alnaperbøite

No.	ST4_11 15	Range	HU2_02 5	Range	ST2_02 4	Range
Na ₂ O	0.56	0.84–0.54	0.22	0.21–0.23	0.26	0.24–0.27
CaO	5.74	5.76–5.25	5.00	4.94–5.06	5.07	5.11–5.04
MnO ^a	0.18	0.00–0.24	0.20	0.16–0.24	0.18	0.12–0.29
BaO	0.04	0.00–0.10	0.04	0.00–0.08	0.05	0.02–0.09
La ₂ O ₃	6.29	4.87–6.41	7.43	7.27–5.52	6.67	6.65–6.69
Ce ₂ O ₃	17.29	15.63–17.40	19.07	18.52–19.48	18.35	18.28–18.42
Pr ₂ O ₃	2.52	2.33–2.68	2.43	2.30–2.50	2.38	2.30–2.46
Nd ₂ O ₃	9.31	8.40–11.74	9.41	9.04–10.02	11.25	11.16–11.34
Sm ₂ O ₃	2.02	1.91–2.29	1.62	1.52–1.68	1.97	1.78–2.16
Gd ₂ O ₃	1.13	0.83–1.34	0.91	0.87–0.95	0.78	0.77–0.79
Dy ₂ O ₃	0.56	0.09–0.57	0.49	0.34–0.72	0.13	0.02–0.24
Ho ₂ O ₃	0.04	0.00–0.18	0.00	0.00–0.00	0.13	0.11–0.16
Er ₂ O ₃	0.12	0.00–0.30	0.18	0.01–0.27	0.35	0.27–0.44
Yb ₂ O ₃	0.12	0.05–0.15	0.03	0.00–0.10	0.08	0.00–0.16
Y ₂ O ₃	1.29	1.00–1.57	0.60	0.56–0.65	0.75	0.68–0.81
ThO ₂	0.37	0.16–0.50	0.17	0.14–0.22	0.12	0.10–0.14
MgO	0.09	0.02–0.12	0.01	0.00–0.01	0.11	0.10–0.13
FeO ^a	2.67	0.95–3.06	5.05	4.87–5.25	5.05	5.02–5.09
Al ₂ O ₃	16.71	16.48–19.08	14.67	14.49–14.88	14.29	14.17–14.41
SiO ₂	27.79	27.50–27.83	26.95	26.50–27.04	26.98	26.79–27.16
Total	94.84	94.00–95.70	94.48	93.93–94.87	94.95	94.79–95.19
Na	0.20		0.08		0.09	
Ca	1.10		1.00		1.01	
Mn ²⁺	0.03		0.03		0.03	
Ba	0.00		0.00		0.00	
La	0.42		0.51		0.46	
Ce	1.14		1.30		1.25	
Pr	0.16		0.16		0.16	
Nd	0.60		0.62		0.75	
Sm	0.13		0.10		0.13	
Gd	0.07		0.06		0.05	
Dy	0.03		0.03		0.01	
Ho	0.00		0.00		0.01	
Er	0.01		0.01		0.02	
Yb	0.01		0.00		0.00	
Y	0.12		0.06		0.07	
Th	0.02		0.01		0.01	
ΣREE+Th	2.71		2.86		2.92	
Σ(A cat)	4.04		3.97		4.05	
Mg	0.02		0.00		0.03	
Fe ²⁺	0.40		0.79		0.79	
Al	3.54		3.21		3.13	
Σ(M cat)	3.96		4.00		3.95	
Si	4.99		5.01		5.02	
Total	12.98		12.99		13.01	

^a = Mn and Fe assumed as divalent.

(Ce) to very weak in perbøite-(Ce) (Table 9). There is no evidence of metamictization. Density could not be measured due to the zoned nature of the crystals and to the presence of lamellae of törnebohmité-(Ce) within them. The calculated values of density, obtained using the empirical formulas of single crystals used for the structural study, and the mean refractive indices, calculated according to the Gladstone-Dale relationship (Mandarino 1976), are reported in Table 9.

MINERAL CHEMISTRY

Major elements in the *E*, *T*, and *ET* phases

There is no P and Pb, virtually no F, Ti, Sr, Ba, and U in the coexisting *E*, *T*, and *ET* compounds. Mg is minor in allanite, even more so in perbøite-(Ce), and absent in törnebohmité-(Ce), showing a partitioning similar to Fe among these phases. The situation is different for Mn, which is substantial only in some allanite-(Ce) crystals, whereas it is minor to trace in gatelite-type phases and a trace in törnebohmité-(Ce). Its behavior is not

related to that of Fe. The significant presence of Na is a major new feature, with Na₂O contents increasing up to 0.84 wt% from perbøite-(Ce) to alnaperbøite-(Ce), variable in allanite-(Ce) (up to 0.29 wt%), and as traces in törnebohmité-(Ce). Light REE are dominant over heavy ones in all four phases, but clearly less so in törnebohmité-(Ce), and marginally less in alnaperbøite-(Ce) than in perbøite-(Ce). Yttrium is present in the four phases, with average oxide contents of 0.3 wt% in allanite-(Ce), 2.2 wt% in törnebohmité-(Ce) and, in the *ET* phases, Y₂O₃ contents ranging between 0.3 and ca. 1.0 wt% in perbøite-(Ce) and ca. 1.0 to 2.0 wt% in alnaperbøite-(Ce), grossly correlated with Al and Na contents. Thorium is minor to trace: very low in allanite-(Ce), variable (up to 0.5 wt% ThO₂) in törnebohmité-(Ce) and, although with much scatter, clearly increasing up to this value from perbøite-(Ce) to alnaperbøite-(Ce).

On the basis of crystallographic knowledge, structural formulas were first tentatively calculated on the same basis of nine tetrahedral + octahedral cations (Si+P+Al+Ti+Fe+Mg) for all the phases of the polysomatic series, i.e., allanite-(Ce), törnebohmité-(Ce), and perbøite-(Ce)/alnaperbøite-(Ce) (Table 7). The advantages are (1) to spread the analytical uncertainty on several elements rather than tying it to Si alone, (2) there is no assumption on Fe and Mn valence states nor on the A-site occupancy, and (3) if some REEs are not analyzed, the results for the other elements are unaffected. The only assumption made is that Mn and Y are assigned to the A sites.

This preliminary calculation showed that, for the simpler compound törnebohmité-(Ce), the mean and standard deviation values were Si = 5.99(2) and Al = 3.00(2) atoms per chosen formula unit (apfu) for all the analyses (n = 8). Likewise, for all perbøite-(Ce)/alnaperbøite-(Ce) analyses (n = 54), Si = 5.00(5) apfu and the sum of M and A cations [Σ(M+A)] was 7.96(8) apfu. This indicated the reliability of Si and Al analysis and that there is very little A vacancy, if any, in the new gatelite-type phases (see below). The case of allanite was more subtle, with a mean Si = 4.55(3) instead of the ideal 4.50 atoms for this calculation basis. Scrutiny of analyses showed that the Si excess was directly linked to high Mn values. Therefore, the assumption of all Mn in the A site does not hold for these allanites, and the allanite formulas were recalculated on a Si = 3 basis, yielding a mean [Σ(M+A)] = 4.98(3) apfu for all allanite analyses (n = 10), with on average one third of the total Mn content in octahedral position.

Considering that REEs are difficult to analyze and that some were not analyzed, the question arises as to whether the slight deficit in A+M cations is real. Indeed, such a deficit increases from allanite-(Ce) (0.4%) to gatelite-type (0.5%) to törnebohmité-(Ce) (0.9%), i.e., as a function of the REE amounts in the mineral. The slightly low mean analytical totals [97.3, 95.9, and 95.3 wt% for allanite-(Ce), gatelite-type, and törnebohmité-(Ce), respectively] may hint to the same conclusion, namely that the slight deficit of A+M cations reflects an analytical deficit in REE and is therefore essentially an *apparent* A-site deficit. This can also account for the low mean refractive indices calculated on the basis of the analyses, as compared to the measured one (Table 9).

On this firm ground, formulas were then calculated and are presented here on the basis of O₂₀(OH)₂ for gatelite-type phases, O₁₂(OH) for allanite-(Ce), and O₈(OH) for törnebohmité-(Ce), assuming divalent iron and manganese. The dominantly divalent

TABLE 8a. Electron-microprobe analyses of allanite (A) and törnebohmité (T) coexisting with perbøeite/alnaperbøeite in Stetind (ST) and Nedre Eivollen (NE)

Sample No.	Allanite-(Ce)				Törnebohmité-(Ce)			
	NE 1	NE 1	ST2 8	range	ST2 5	range	ST4 3	range
Na ₂ O	0.28	0.29	0.12	(0.06–0.18)	0.01	(0.00–0.02)	0.02	(0.01–0.04)
CaO	9.08	9.65	7.61	(6.31–8.48)	0.20	(0.17–0.25)	0.14	(0.09–0.20)
MnO	0.50	0.58	2.58	(0.73–4.83)	0.00	(0.00–0.00)	0.00	(0.00–0.00)
SrO	0.00	0.02	0.01	(0.00–0.07)	0.02	(0.00–0.09)	0.01	(0.00–0.03)
BaO	0.00	0.00	0.02	(0.00–0.09)	0.08	(0.02–0.14)	0.04	(0.00–0.08)
La ₂ O ₃	2.99	2.66	3.24	(2.68–3.84)	6.53	(5.55–8.26)	4.57	(2.64–6.34)
Ce ₂ O ₃	11.38	10.62	11.63	(11.08–12.30)	22.17	(18.26–25.61)	18.35	(12.08–23.08)
Pr ₂ O ₃	1.88	1.75	1.84	(1.70–1.96)	3.84	(3.51–4.02)	3.43	(3.28–3.63)
Nd ₂ O ₃	7.46	7.96	8.38	(7.25–9.20)	19.33	(16.81–20.53)	21.03	(17.68–26.39)
Sm ₂ O ₃	1.73	1.62	1.51	(1.19–1.76)	4.49	(3.12–5.72)	6.47	(4.89–7.77)
Gd ₂ O ₃	0.65	0.89	0.49	(0.00–0.85)	2.22	(1.69–3.32)	3.33	(2.59–3.88)
Dy ₂ O ₃	0.11	0.00	0.13	(0.00–0.33)	0.85	(0.44–1.30)	1.56	(1.24–1.75)
Ho ₂ O ₃	0.03	0.00	0.05	(0.00–0.23)	0.21	(0.00–0.44)	0.20	(0.11–0.34)
Er ₂ O ₃	0.22	0.09	0.16	(0.00–0.36)	0.00	(0.00–0.00)	0.43	(0.28–0.53)
Yb ₂ O ₃	0.10	0.03	0.05	(0.00–0.08)	0.14	(0.00–0.22)	0.19	(0.15–0.21)
Y ₂ O ₃	0.34	0.34	0.29	(0.17–0.38)	1.74	(0.97–2.76)	2.14	(2.02–2.24)
ThO ₂	0.00	0.04	0.04	(0.00–0.17)	0.21	(0.00–0.56)	0.07	(0.00–0.20)
MgO	0.03	0.07	0.15	(0.10–0.21)	0.00	(0.00–0.02)	0.00	(0.00–0.00)
MnO	0.50	0.58	2.58	(0.73–4.83)	0.00	(0.00–0.00)	0.00	(0.00–0.00)
FeO tot.	10.78	9.96	11.90	(11.33–12.73)	0.04	(0.00–0.08)	0.00	(0.00–0.00)
Al ₂ O ₃	18.47	19.16	16.55	(15.01–16.86)	9.77	(9.37–10.10)	9.87	(9.74–10.10)
SiO ₂	30.99	31.24	30.35	(29.77–30.81)	22.87	(22.02–23.54)	23.35	(22.95–23.90)
Total	97.02	96.97	97.10	(96.31–98.11)	94.72	(92.44–96.02)	95.20	(94.85–95.51)
Basis	25 charges	25 charges	25 charges		17 charges		17 charges	
Na	0.053	0.054	0.023		0.002		0.003	
Ca	0.945	0.994	0.811		0.019		0.013	
Mn	0.041	0.047	0.217		0.000		0.000	
Sr	0.000	0.001	0.001		0.001		0.001	
Ba	0.000	0.000	0.001		0.003		0.001	
La	0.107	0.094	0.119		0.211		0.146	
Ce	0.404	0.374	0.423		0.711		0.583	
Pr	0.067	0.061	0.067		0.123		0.108	
Nd	0.259	0.273	0.298		0.605		0.652	
Sm	0.058	0.054	0.052		0.136		0.193	
Gd	0.021	0.028	0.016		0.064		0.096	
Dy	0.003	0.000	0.004		0.024		0.044	
Ho	0.001	0.000	0.002		0.006		0.006	
Er	0.007	0.003	0.005		0.000		0.012	
Yb	0.003	0.001	0.002		0.004		0.005	
Y	0.018	0.017	0.015		0.081		0.099	
Th	0.000	0.001	0.001		0.004		0.001	
REE + Th	0.948	0.906	1.004		1.969		1.945	
Σ(A cat)	1.987	2.002	2.057		1.994		1.963	
Mg	0.004	0.010	0.022		0.000		0.000	
Fe ²⁺	0.875	0.801	0.989		0.003		0.000	
Al	2.113	2.170	1.939		1.009		1.009	
Σ(M cat)	2.992	2.981	2.950		1.012		1.009	
Si	3.009	3.002	3.017		2.003		2.026	
Σcat	7.987	7.986	8.023		5.007		4.998	

Notes: Ti and P below detection limit. No. = number of point analyses.

state of iron is confirmed by crystallographic data and makes the presence of trivalent manganese unlikely.

Two new *ET* phases

The empirical formulas calculated from the EMP analyses of the three single crystals investigated (Table 6) are:

$(\text{Ca}_{1.10}\text{Mn}_{0.03}\text{Na}_{0.08}\text{La}_{0.42}\text{Ce}_{1.14}\text{Pr}_{0.16}\text{Nd}_{0.60}\text{Sm}_{0.13}\text{Gd}_{0.07}\text{Dy}_{0.03}\text{Er}_{0.01}\text{Yb}_{0.01}\text{Y}_{0.12}\text{Th}_{0.02})_{\Sigma 4.04}(\text{Al}_{3.54}\text{Fe}_{0.40}^{2+}\text{Mg}_{0.02})_{\Sigma 3.96}\text{Si}_{4.99}\text{O}_{20}(\text{OH})_2$ for ST4_11,

$(\text{Ca}_{1.00}\text{Mn}_{0.03}\text{Na}_{0.08}\text{La}_{0.51}\text{Ce}_{1.30}\text{Pr}_{0.16}\text{Nd}_{0.62}\text{Sm}_{0.10}\text{Gd}_{0.06}\text{Dy}_{0.03}\text{Er}_{0.01}\text{Yb}_{0.01}\text{Th}_{0.01})_{\Sigma 3.97}(\text{Al}_{3.21}\text{Fe}_{0.79}^{2+}\text{Si}_{5.01}\text{O}_{20}(\text{OH})_2$ for HU_02, and

$(\text{Ca}_{1.01}\text{Mn}_{0.03}\text{Na}_{0.09}\text{La}_{0.46}\text{Ce}_{1.25}\text{Pr}_{0.16}\text{Nd}_{0.75}\text{Sm}_{0.13}\text{Gd}_{0.05}\text{Dy}_{0.01}\text{Ho}_{0.01}\text{Er}_{0.02}\text{Y}_{0.07}\text{Th}_{0.01})_{\Sigma 4.05}(\text{Al}_{3.13}\text{Fe}_{0.79}^{2+}\text{Mg}_{0.03})_{\Sigma 3.95}\text{Si}_{5.02}\text{O}_{20}(\text{OH})_2$ for ST2_02 (before heating).

The total electron number ($e_A^- + e_M^-$) calculated on the basis of the chemical formulas derived from microprobe data (239.5, 251.0 and 254.3 for ST4_11, HU_02, and ST2_02, respectively) is in satisfactory accord with that obtained by the structure refinements (240.5, 253.6, and 252.2, respectively). In HU_2 and ST2_02, the M-sites cation content ($\text{Al}_{3.21}\text{Fe}_{0.79}^{2+}$ and $\text{Al}_{3.13}\text{Fe}_{0.79}^{2+}\text{Mg}_{0.03}$, respectively) suggests Fe-dominance in M3, as confirmed by the structure refinements, and, given the classical population of the A sites, point to an *E* module dominantly of allanite-(Ce) composition.

This composition is new among the *ET* polysomes (cf. Introduction) and is the basis for the definition of the new species perbøeite-(Ce). The end-member formula of perbøeite-(Ce) is therefore $^A(\text{Ce}_3\text{Ca})(\text{Al}_3\text{Fe}^{2+})\text{Si}_2\text{O}_7(\text{SiO}_4)_3\text{O}(\text{OH})_2$, which requires Ce_2O_3 45.10, CaO 5.14, Al_2O_3 14.01, FeO 6.58, SiO_2 27.52, H_2O 1.65, total 100.00 wt%.

TABLE 8b. Electron-microprobe analyses of minerals coexisting with perbøite/alnaperbøite in Stetind (ST) and Nedre Eivollen (NE)

Sample	Fluorite NE	Fluorite ST2	Kuliokite ST4	Hundhol. ST2	F-thalenite NE	Thalenite NE	F-brithol NE
Na ₂ O	0.32	0.22	0.01	0.20	0.01	0.00	0.11
CaO	52.53	58.65	0.70	5.43	0.07	0.18	9.89
SrO	0.08	0.00	0.00	0.00	0.03	0.00	0.02
BaO	0.00	0.04	0.06	0.00	0.00	0.03	0.00
La ₂ O ₃	0.64	0.30	0.04	2.74	0.19	0.80	1.32
Ce ₂ O ₃	1.97	0.85	0.11	9.42	1.19	5.12	7.63
Pr ₂ O ₃	0.33	0.13	0.19	1.43	0.42	1.45	1.51
Nd ₂ O ₃	1.42	1.00	2.07	11.31	3.51	8.19	10.40
Sm ₂ O ₃	0.70	0.30	2.12	5.23	3.05	4.43	4.95
Gd ₂ O ₃	0.71	0.39	5.83	5.42	5.42	5.40	5.23
Dy ₂ O ₃	1.08	0.76	6.57	4.01	7.50	6.59	5.87
Ho ₂ O ₃	0.34	0.19	0.91	0.39	0.92	0.93	0.67
Er ₂ O ₃	0.89	0.57	6.03	2.95	7.35	5.76	3.91
Yb ₂ O ₃	1.09	0.57	3.69	1.69	6.63	5.39	2.92
Y ₂ O ₃	14.93	11.09	39.62	18.85	28.53	23.21	16.57
ThO ₂	0.00	0.01	0.00	0.02	0.00	0.13	0.20
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MnO	0.00	0.00	0.00	0.02	0.00	0.00	0.30
FeO tot.	0.00	0.00	0.00	0.41	0.00	0.00	0.25
Al ₂ O ₃	0.00	0.00	6.85	1.33	0.00	0.00	0.00
SiO ₂	0.00	0.00	15.53	14.35	28.20	28.19	21.77
F	44.20	46.94	11.76	6.86	3.06	0.10	2.53
-F=O	-18.61	-19.77	-4.95	-2.89	-1.29	-0.04	-1.07
Total	102.62	102.24	97.14	89.17	94.79	95.86	94.98
Basis	1 cation	1 cation	23 charges	Si = 7 pfu	21 charges	21 charges	25 charges
Na	0.009	0.006	0.003	0.189	0.002	0.000	0.029
Ca	0.827	0.886	0.097	2.838	0.008	0.021	1.458
Sr	0.001	0.000	0.000	0.000	0.002	0.000	0.002
Ba	0.000	0.000	0.003	0.000	0.000	0.001	0.000
La	0.003	0.002	0.002	0.493	0.008	0.032	0.067
Ce	0.011	0.004	0.005	1.682	0.047	0.202	0.384
Pr	0.002	0.001	0.009	0.254	0.017	0.057	0.076
Nd	0.007	0.005	0.096	1.970	0.136	0.315	0.511
Sm	0.004	0.001	0.094	0.879	0.114	0.165	0.235
Gd	0.003	0.002	0.250	0.876	0.195	0.193	0.239
Dy	0.005	0.003	0.273	0.630	0.262	0.229	0.260
Ho	0.002	0.001	0.037	0.061	0.032	0.032	0.029
Er	0.004	0.003	0.245	0.452	0.250	0.195	0.169
Yb	0.005	0.002	0.145	0.251	0.219	0.177	0.123
Y	0.117	0.083	2.724	4.893	1.644	1.332	1.213
Th	0.000	0.000	0.000	0.002	0.000	0.003	0.006
REE + Th	0.163	0.107	3.881	12.445	2.921	2.932	3.312
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.000	0.000	0.000	0.008	0.000	0.000	0.035
Fe ²⁺	0.000	0.000	0.000	0.167	0.000	0.000	0.029
Al	0.000	0.000	1.043	0.765	0.000	0.000	0.000
Si	0.000	0.000	2.007	7.000	3.053	3.039	2.995
F	2.055	2.094	4.805	10.583	1.048	0.034	1.101
Σcat	1.000	1.000	7.033	23.413	5.987	5.993	7.860

Note: Ti and P below detection limit, also for fluor-britholite-(Y).

The analysis of ST4_11 implies Al dominance in all M sites, M3 included, therefore pointing to a novel *ET* compound that, unlike all others, has a trivalent cation in M3. Charge balance is achieved in the A sites by substitution of trivalent REEs by divalent Ca to some extent but, essentially, by monovalent Na. The resulting composition is necessarily new among the *ET* phases and thus the basis for the definition of the new species alnaperbøite-(Ce). The end-member formula of alnaperbøite-(Ce) is $^A(\text{Ce}_{2.5}\text{CaNa}_{0.5})^M(\text{Al}_4)\text{Si}_2\text{O}_7(\text{SiO}_4)_3\text{O}(\text{OH})_2$, which requires Ce₂O₃ 40.86, CaO 5.58, Na₂O 1.54, Al₂O₃ 20.31, SiO₂ 29.92, H₂O 1.79, total 100.00 wt%.

Compositional variations: A solid-solution series

A first-order feature is the continuity of the chemical trends between near-end-member values as shown in Figure 3, where the calculated atomic contents are plotted as a function of the number of Al apfu, which varies between 3 [as in end-member

perbøite-(Ce)] and 4 [as in end-member alnaperbøite-(Ce)]. Typical crystal-core compositions are near 3.8–3.7 Al apfu in samples ST4 and NE and may grade within the same crystal to rim compositions of 3.2–3.1 Al, whereas they evolve from 3.4 (cores) to 3.0 Al (rims) in sample ST2. The continuity across the series is evidence for a continuous solid solution between the two new minerals, with a divide between the two species at the 50:50 boundary (i.e., 3.5 Al apfu) in the case of a pure binary system. Figure 3 illustrates the main substitutions acting across the series: with decreasing Al, a near 1/1 increase of Fe (substitution in M3), coupled to a clear decrease of Na and increase of REEs (substitution in A sites) to reach an extreme composition for Al = 3 that has nearly exact end-member perbøite-(Ce) stoichiometry. For the more Al-rich compositions the departure of Ca contents from unity (>1) reveals that the analyzed solid solution is not purely binary between the perbøite-(Ce) and alnaperbøite-(Ce) end-members, but ternary with some contribution (about 10 mol%)

of an *ET* polysome having clinozoisite as *E* module.

The associated allanite crystals (Table 8a) reflect the compositional variations observed in the *ET* phases between samples: they are more Al-, Ca-, and Na-rich (up to 2.17 Al, 0.99 Ca, and 0.05 Na apfu) and show no Fe³⁺ in sample NE where alnaperbøite crystal cores are common; they are more Fe- (0 to 17% trivalent, 7% on average) and REE-rich and Al-, Ca-, and Na-poor in sample ST2 (from a locality where hematite occurs), in which *ET* crystals have only perbøite compositions. Obviously, the same coupled substitutions relating perbøite-(Ce) and alnaperbøite-(Ce) are also acting in coexisting allanite, to an extent discussed below in more detail.

In contrast, associated törnebohmite-(Ce) appears, with a nearly constant Si/Al ratio and at most 0.25 wt% CaO and 0.56

TABLE 9. Physical and optical properties of alnaperbøite-(Ce) and perbøite-(Ce)

	Alnaperbøite-(Ce)	Perbøite-(Ce)
Morphology	prismatic, elongated along [010]	prismatic, elongated along [010]
Color	grayish very pale green	grayish green
Streak	white	white
Luster	vitreous, transparent	vitreous, transparent
Hardness (Mohs)	6–7	6–7
Tenacity	brittle	brittle
Cleavage	{100} good, {001} imperfect	{100} good, {001} imperfect
Parting	none observed	none observed
Fracture	irregular	irregular
Calculated density (g/cm ³) ^a	4.308	4.474
Mean refractive index ^a	1.757	1.775
<i>n_x</i>	1.778(2) colorless	1.788(2) colorless
<i>n_y</i>	1.784(2) colorless	1.793(2) grayish blue
<i>n_z</i>	1.810(5) colorless	1.820(5) colorless
2 <i>V_z</i>	33.5(5)°	30.0(5)°
Optical plane	(010)	(010)
<i>Z</i> ∩ (001) [°]	30(3)°	17(1)°
Dispersion	inclined (slightly stronger)	inclined (very weak)

^a Calculated with the chemical analyses given in Table 6. The mean refractive index was obtained according to the Gladstone–Dale relationship (Mandarino 1976).

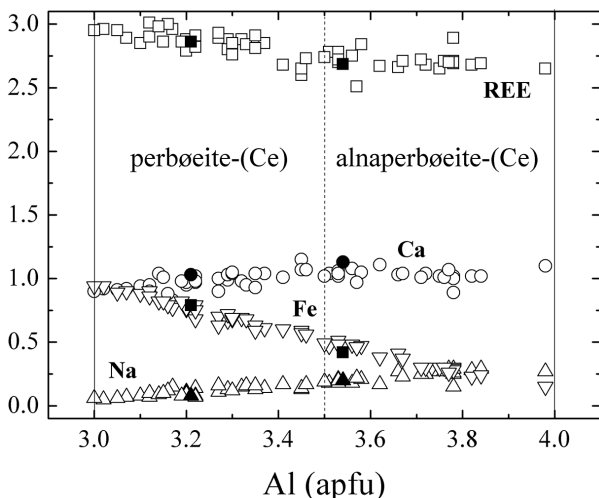


FIGURE 3. Chemical variations along the perbøite-(Ce)–alnaperbøite-(Ce) join. Element contents are given in atoms per formula unit (on the basis of Si+P+Al+Ti+Fe+Mg = 9); REE includes Y and Th; Ca includes Ba and Mn; Fe includes Mg. Empty symbols refer to chemical data reported in Table 7; black symbols represent perbøite-(Ce) and alnaperbøite-(Ce) single crystals (Table 6).

wt% ThO₂, as the least variable in composition among the *E*, *T*, and *ET* compounds, the only variations being among the REE (with up to 2.76 wt% Y₂O₃).

Description of the structure and cation distribution

Members of the perbøite-(Ce)–alnaperbøite-(Ce) solid solution are topologically identical to the minerals gatelite-(Ce) and västmanlandite-(Ce). Their structure consists of edge-sharing octahedral chains running along the *b* axis, cross-linked to each other by three non-equivalent SiO₄ isolated tetrahedra and one Si₂O₇ group. The large cavities are occupied by REE, Ca, and Na with Ca dominant at the A1 site and REE dominant at A2, A3, and A4 (Fig. 4). Three independent octahedral sites are present in the structure: M1 octahedra form branched chains with M3 octahedra alternately attached on opposite sides, whereas M2 octahedra form single chains. As in the case of gatelite-(Ce), the crystal-chemical details of the octahedral framework closely resemble those of the homologous sites in the structure of epidote-supergroup minerals, in particular in those belonging to the allanite group (Armbruster et al. 2006), and törnebohmite-(Ce) (Shen and Moore 1982), respectively. The M1 and M2 sites (<M1-O> = 1.924–1.930 Å and <M2-O> = 1.892–1.899 Å, Table 10) are occupied mainly by Al, whereas the cation population at the M3 octahedron, the largest and most distorted in the structure and the most suitable to incorporate divalent cations, differentiates perbøite-(Ce) from alnaperbøite-(Ce). In particular, in HU_02 perbøite-(Ce) crystal the <M3-O> distance (2.107 Å) is consistent with the dominance of Fe²⁺ at this site, whereas Al prevails over Fe²⁺ in ST4_11 alnaperbøite-(Ce) crystal (<M3-O> = 2.051 Å). Taking into account the refined site scattering (Table 10) and estimating the Fe³⁺ content on the basis of pure <M3-O> distances derived from known interatomic distances for members of the epidote supergroup (<Al-O>_{M3} = 1.968 Å, <Fe³⁺-O>_{M3} = 2.055 Å, <Fe²⁺-O>_{M3} = 2.175 Å; Bonazzi and Menchetti 1995), a cation population can be estimated. In particular, M3 = 0.64 Fe²⁺ + 0.08 Fe³⁺ + 0.28 Al and M3 = 0.60 Al + 0.40 Fe²⁺ for HU_02 and ST4_11, respectively. This empirical method to estimate the M3 site population suggests the presence of Fe³⁺ not only in HU_02 crystal but also in most of the investigated crystals wherein Fe³⁺ ranges from 0.00 to 0.17 apfu (Table 10). Site-scattering refinement also indicates that small amounts of Fe substitute for Al in M1 and M2 sites (up to 0.05 apfu in both sites), which, in keeping with the crystal chemical requirements of the epidote-supergroup minerals, should be assumed as Fe³⁺. When normalized on the basis of Σ(M+T) = 9 apfu, many of the chemical analyses (Tables 6 and 7) would lead to sums of posi-

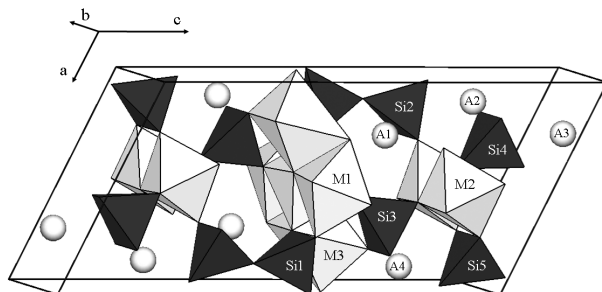


FIGURE 4. Unit-cell content in perbøite-(Ce)–alnaperbøite-(Ce).

TABLE 10. Selected structural parameters for the investigated crystals

	ST4_11	ST4_09	ST3_01	NE_01	ST4_10	ST4_02	ST2_01	ST2_03	HU_02
<A1-O> ^{vii}	2.487	2.488	2.481	2.487	2.481	2.477	2.480	2.474	2.470
no. e ⁻	22.2	22.0	22.0	23.1	22.4	21.1	22.1	22.1	21.6
<A2-O> ^{viii}	2.570	2.573	2.571	2.584	2.574	2.575	2.580	2.579	2.575
no. e ⁻	54.0	55.0	55.2	54.6	55.8	56.8	56.1	56.4	57.2
<A3-O> ^{viii}	2.598	2.603	2.601	2.610	2.597	2.596	2.603	2.598	2.595
no. e ⁻	53.7	54.7	55.0	55.0	55.7	56.2	55.6	55.9	56.4
<A4-O> ^x	2.653	2.650	2.646	2.658	2.623	2.652	2.656	2.652	2.676
no. e ⁻	52.6	53.7	53.7	53.3	54.4	55.9	55.3	55.4	56.1
<M1-O>	1.923	1.928	1.924	1.930	1.925	1.928	1.928	1.926	1.931
no. e ⁻	13.0	13.3	13.1	13.4	13.3	13.1	13.3	13.4	13.1
<M2-O>	1.895	1.894	1.893	1.898	1.895	1.897	1.897	1.897	1.899
no. e ⁻	13.4	13.6	13.4	13.7	13.3	13.2	13.5	13.5	13.4
<M3-O>	2.051	2.051	2.062	2.061	2.067	2.085	2.094	2.098	2.107
no. e ⁻	18.2	18.9	18.9	19.2	19.8	20.7	21.1	21.6	22.4
M ³ (Fe ³⁺) _{calc}	0.00	0.08	0.00	0.05	0.07	0.04	0.02	0.06	0.08
<Si1-O>	1.626	1.622	1.618	1.620	1.619	1.626	1.621	1.618	1.625
<Si2-O>	1.615	1.615	1.619	1.623	1.616	1.618	1.619	1.616	1.617
<Si3-O>	1.646	1.648	1.648	1.647	1.645	1.641	1.647	1.637	1.639
<Si4-O>	1.634	1.638	1.635	1.639	1.630	1.631	1.635	1.628	1.637
<Si5-O>	1.620	1.621	1.623	1.615	1.615	1.620	1.620	1.617	1.617
O11-O4	2.967(10)	2.975(9)	2.974(9)	2.99(1)	2.968(7)	2.945(7)	2.975(7)	2.965(8)	2.956(7)
O10-O15	2.689(10)	2.681(9)	2.66(1)	2.66(1)	2.661(7)	2.665(8)	2.686(7)	2.665(8)	2.653(8)

	ST2_04	HU_01	ST2_02	ST2_02-350	ST2_02-450	ST2_02-550	ST2_02-650	ST2_02-750
<A1-O> ^{vii}	2.466	2.469	2.471	2.472	2.481	2.484	2.481	2.483
no. e ⁻	22.2	21.4	21.1	21.1	21.5	21.1	21.1	20.8
<A2-O> ^{viii}	2.581	2.581	2.575	2.571	2.562	2.558	2.553	2.550
no. e ⁻	57.0	57.0	55.8	56.9	56.9	56.9	56.5	56.9
<A3-O> ^{viii}	2.599	2.594	2.594	2.593	2.588	2.588	2.581	2.578
no. e ⁻	55.9	56.2	56.1	56.1	56.1	56.1	56.5	56.9
<A4-O> ^x	2.647	2.650	2.649	2.645	2.646	2.645	2.641	2.637
no. e ⁻	55.9	55.9	55.8	55.7	55.7	55.7	56.1	56.1
<M1-O>	1.925	1.928	1.926	1.924	1.916	1.917	1.917	1.916
no. e ⁻	13.0	13.7	13.1	13.3	13.4	13.4	13.5	13.6
<M2-O>	1.892	1.898	1.893	1.893	1.896	1.897	1.898	1.897
no. e ⁻	13.4	13.4	13.4	13.3	13.5	13.4	13.3	13.5
<M3-O>	2.099	2.103	2.102	2.079	2.029	2.029	2.026	2.025
no. e ⁻	22.5	22.6	22.0	21.8	21.6	21.7	21.8	21.3
M ³ (Fe ³⁺) _{calc}	0.17	0.15	0.07	0.25	0.63	0.65	0.69	0.63
<Si1-O>	1.616	1.621	1.623	1.622	1.627	1.626	1.628	1.623
<Si2-O>	1.618	1.618	1.615	1.619	1.619	1.619	1.616	1.617
<Si3-O>	1.646	1.638	1.641	1.641	1.646	1.648	1.645	1.646
<Si4-O>	1.634	1.627	1.638	1.630	1.628	1.634	1.627	1.629
<Si5-O>	1.618	1.614	1.620	1.619	1.614	1.612	1.609	1.611
O11-O4	2.949(9)	2.939(9)	2.954(6)	2.972(7)	3.094(1)	3.113(6)	3.121(6)	3.134(6)
O10-O15	2.661(9)	2.672(9)	2.642(6)	2.670(7)	2.717(7)	2.728(6)	2.746(7)	2.752(7)

Notes: Distances are given in (Å); no. e⁻ = mean electron number obtained from occupancy refinement. Standard deviations for the individual metal-oxygen distances are in the 0.001–0.009 (Å) range; the highest values regard the distances involving the O15 atom.

tive charges slightly higher than those corresponding to O₂₀(OH)₂. Thus, the hypothesized presence of Fe³⁺ should involve in those cases a modest hydrogen deficiency.

Looking at the crystal chemical formulas of HU_02 and ST4_11 (Table 6) and taking into consideration the chemical relationships along the alnaperbøite-(Ce)–perbøite-(Ce) join (Fig. 3), it is evident that all the heterovalent substitutions leading to a decrease of positive charge at the A sites, i.e., Na for Ca, Na for REE, or Ca for REE, involve a decrement of the mean electron number at the A sites. Indeed, it ranges from 191.3 e⁻ in HU_02 to 182.5 e⁻ in ST4_11 (Table 10). It is not possible, however, to determine with certainty at which site Na is incorporated. Taking into account the crystal with the highest Na content (ST4_11, 0.20 Na apfu), ordering of Na at one specific REE site (A2, A3, or A4) would involve a mean electron number <49 approximately, and can therefore be excluded on the basis of the mean electron number of these sites (Fig. 5). The monotonous decrease of the mean electron number observed as a function of the alnaperbøite component for A2, A3, and A4

but not for A1 (Fig. 5, Table 10) could be interpreted as due to Na incorporation at the A2, A3, and A4 sites, with Ca substituted by small, constant amounts of REE at A1 (22.2 e⁻). On the other hand, all Na could be ordered at A1, if a simultaneous entry of variable amounts of REE (approximately 0.10 apfu in ST4_11) masked the effect of Na on the site scattering. In this case, the replacement of Ca by an increasing (Na+REE) amount in A1 along the join alnaperbøite-(Ce)–perbøite-(Ce) would account for the decreasing site scattering at A2, A3, and A4.

The Si1 and Si2 tetrahedra, linked together to form a Si₂O₇ group, as well as the Si3 tetrahedron, are quite similar to the corresponding tetrahedra in epidotes (Franz and Liebscher 2004 and references therein); likewise, the Si4 and Si5 tetrahedra can be compared to the homologous ones in törnebohmite-(Ce). We can therefore reasonably assume that no substitution of Si by other cations occurs at these sites, as also implied by the mean number of 5.00(5) Si apfu for the 54 EMP analyses of the series.

As expected on the basis of the close structural relationship with gatelite-(Ce) (Bonazzi et al. 2003) and västmanlandite-

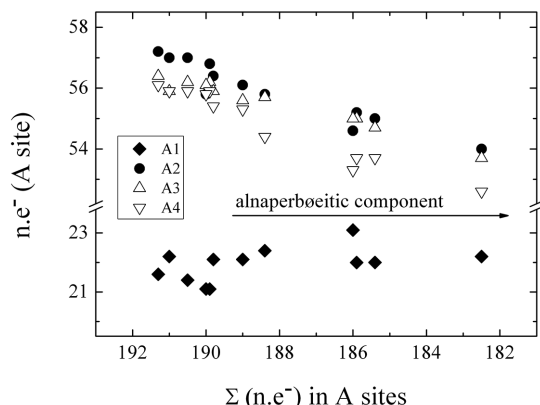


FIGURE 5. Variation of the mean electron number derived from the refined site scattering in each A site vs. their sum in the untreated crystals of the perbøite-(Ce) and alnaperbøite-(Ce) series. The monotonous decrease observed for A2, A3, and A4 as a function of the alnaperbøite component can be due to Na incorporation at A2, A3, and A4 sites with constant A1 population, or to Ca incorporation at A2, A3, and A4 with complete ordering into A1 of Na with enough REE to maintain site scattering (see text).

(Ce) (Holtstam et al. 2005), the two O-O contacts suitable for H-bonding (not polyhedral edges) are O11-O4 (2.939–2.990 Å) within the *E* module and O10-O15 (2.642–2.689 Å) within the *T* module, with O11 and O10 as donor O atoms.

Structure after heat treatments

All geometrical and structural variations induced by heating the crystal of perbøite-(Ce) in air indicate the development of an oxidation-dehydrogenation process, quite similar to that observed in allanite-group minerals (Bonazzi and Menchetti 1994; Bonazzi et al. 2009). As made evident by the shortening of the mean $\langle \text{M3-O} \rangle$ distance, the divalent iron ordered at the M3 octahedron oxidizes and the charge balance is maintained by concomitant H loss according to the reaction: $\text{M3}[\text{Fe}^{2+}] + \text{O}_{10,\text{O11}}[\text{OH}^-] \rightarrow \text{M3}[\text{Fe}^{3+}] + \text{O}_{10,\text{O11}}[\text{O}^{2-}] + \frac{1}{2}\text{H}_2$. After the annealing at 450 °C the $\langle \text{M3-O} \rangle$ distance approaches the values corresponding to those due to a site population of Fe^{3+} -Al alone (dotted line in Fig. 6) thus indicating that the process is almost complete at that temperature. As the divalent iron decreases, the M3 octahedron becomes more regular [λ values, calculated according to Robinson et al. (1971), decreasing from 1.037 to 1.025].

The loss of H compensating the oxidation of Fe^{2+} is indicated by the variation of the donor-acceptor distances (Table 10). In particular O11-O4 increases from 2.954(6) to 3.134(6) Å while O10-O15 increases more gradually, from 2.642(6) to 2.752(7) Å, suggesting loss of hydrogen mainly from the H1 position, i.e., in the *E* module.

The loss of positive charge on the donor O atoms (O11 and O10) due to partial dehydrogenation at H1 and H2, respectively, is balanced mainly by a pronounced shortening of the A4-O11 [from 2.605(3) to 2.403(4) Å] and a moderate shortening of A2-O10 [from 2.674(3) to 2.588(4) Å] distances. The oxygen O11 also approaches M2 [M2-O11 decreasing from 1.883(3) to 1.819(3) Å]. On the contrary, the M2-O10 bond distance, the shortest within the M2 octahedron, does not change

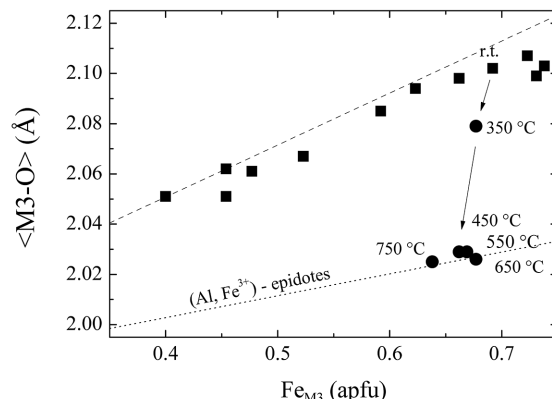


FIGURE 6. Variation of the $\langle \text{M3-O} \rangle$ octahedral distance as a function of the Fe content obtained by site-scattering refinement. Dotted line ($y = 1.968 + 0.087x$) refers to natural (Al, Fe^{3+})-epidotes and dashed line ($y = 1.968 + 0.207x$) is calculated for an (Al, Fe^{2+}) site population ($\langle \text{Fe}^{2+}\text{-O} \rangle = 2.175$ Å) (Bonazzi and Menchetti 1995). Black squares refer to the untreated crystals wherein Fe is present mainly as Fe^{2+} ; black circles refer to the perbøite-(Ce) crystal (ST2_02) heated in air at increasing temperatures. After the heating at 450 °C in air the $\langle \text{M3-O} \rangle$ distance approaches the values corresponding to those due to a site population of Fe^{3+} -Al alone.

significantly with heating.

With regard to the acceptor O atoms (O4 and O15), the loss of positive charge on the O4 oxygen is directly compensated by the oxidation of divalent iron at M3, as shown from the trend of the M3-O4 distance, which decreases from 1.973(3) to 1.892(4) Å, and, to a lesser extent, by the shortening of the M1-O4 distance [from 1.844(2) to 1.819(2) Å]; among the bond distances involving O15, which links Si4 and two A3, the longest A3-O15 is the only decreasing one [from 2.942(5) to 2.797(5) Å].

At the beginning of the heating process, the resulting empirical bond-valence sums on O11 and O10 are 1.29 and 1.28 v.u., respectively, while sums on O4 and O15 are 1.60 and 1.54 v.u., in keeping with the expected hydrogen-bonding system in these minerals. As the heating temperature increases, the total bond strength on the oxygen atoms involved in the O11-H1...O4 bond markedly increases, whereas only small variations are observed for O10-H2...O15 (Table 11), indicating severe dehydrogenation only at the H1 position. In particular, by combining the increase of bond strength on donor with that of acceptor oxygen, the estimated amount of hydrogen loss at H1 position is 0.63 apfu, while only 0.06 apfu appear to be lost at H2 position. On the other hand, the total Fe^{3+} in the crystal (estimated on the basis of the octahedral distances) changes from 0.14 apfu in the untreated crystal to 0.76 apfu after the annealing at 750 °C. The hydrogen loss compensating for the Fe^{2+} oxidation, therefore, seems to occur mainly within the *E* module, leaving the *T* module substantially unaffected.

With regard to the unit-cell parameters, the behavior is quite similar to that observed in heated REE-bearing epidote-supergroup minerals (Bonazzi and Menchetti 1994; Bonazzi et al. 2009). The contraction related to $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ oxidation results in a decrease of the $a\text{bsin}\beta$ parameter, whereas the relaxation of the O11-H1...O4 bond, which is approximately directed along [001], weakens the link between the M2 and the M1+M3 octahedral chains and results in a lengthening of *c* (Fig. 7).

TABLE 11. Bond-strengths (v.u.) on the four oxygen atoms involved in the hydrogen bonding system in the ST2_02 crystal before and after the heating in air at 750 °C

ST2_02	A2 Ce ³⁺ _{0.97} Ca _{0.03}	A3 Ce ³⁺ _{0.95} Ca _{0.05}	A4 Ce ³⁺ _{0.94} Ca _{0.06}	M1 Al _{0.99} Fe ³⁺ _{0.01}	M2 Al _{0.97} Fe ³⁺ _{0.03}	M3 Fe ²⁺ _{0.62} Al _{0.31} Fe ³⁺ _{0.07}	Si4 Si _{1.00}	Σ
O11			0.293		0.497 ^{x2}			1.29
O4				0.557 ^{x2}		0.483		1.60
O10	0.248				0.515 ^{x2}			1.28
O15		0.119 + 0.362					1.056	1.54
ST2_02-750 °C	A2 Ce _{0.97} Ca _{0.03}	A3 Ce _{0.97} Ca _{0.03}	A4 Ce _{0.95} Ca _{0.05}	M1 Al _{0.95} Fe ³⁺ _{0.05}	M2 Al _{0.96} Fe ³⁺ _{0.04}	M3 Fe ³⁺ _{0.63} Al _{0.36} Fe ²⁺ _{0.01}	Si4 Si _{1.00}	
O11			0.506		0.595 ^{x2}			1.70
O4				0.598 ^{x2}		0.619		1.82
O10	0.311				0.507 ^{x2}			1.32
O15		0.176 + 0.363					1.016	1.56

Note: Calculated from the bond-valence curves of Brese and O'Keeffe (1991).

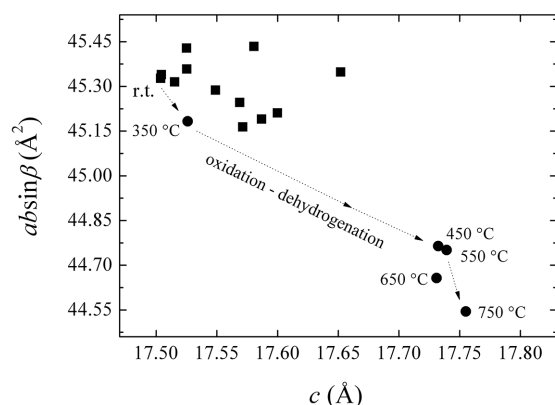


FIGURE 7. The $absin\beta$ value plotted against the c unit-cell parameter for ST2_02 crystal heated in air (black circles) and for the untreated crystals (black squares). As the heating temperature increases, the $Fe^{2+} \rightarrow Fe^{3+}$ oxidation causes a contraction of the M3-M1 octahedral chain mainly resulting in a decrease of the $absin\beta$ parameter; the relaxation of the O11-H1...O4 bond due to the hydrogen loss weakens the link between the M2 and the M1+M3 octahedral chains and results in a lengthening of c . In the absence of complete chemical characterization including Fe^{2+}/Fe^{3+} ratio or H determination, it is not easy to establish whether the spread of values observed for the untreated crystals is only due to the variation of the alnaperbøite-(Ce) component or whether a modest hydrogen deficiency also occurs.

Comparison with related structures

Perbøite-(Ce) derives from gatelite-(Ce) by the homovalent substitution $[M^3Fe^{2+} \rightarrow M^3Mg]$. Alnaperbøite-(Ce) derives from perbøite-(Ce) or gatelite-(Ce) by the coupled heterovalent substitutions $0.5[A^{Na+} \rightarrow A^{REE^{3+}}]$ and $[M^3Al^{3+} \rightarrow M^3(Fe^{2+} \text{ or } Mg)]$.

As concerns the unit-cell dimensions, alnaperbøite-(Ce) and perbøite-(Ce), as well as västmanlandite-(Ce), differ from gatelite-(Ce) for the lack of doubling of the translation unit along the a axis. The doubling of the translation unit along the a axis in gatelite-(Ce), where $a_{gat} \sim 2a_{epi} \sim [201]_{001}$, appears related to a small offset away from the (010) plane at $y = 1/4$ and $3/4$, which is a mirror in the epidote-supergroup minerals; as a consequence, the space group is $P2_1/a$ instead of $P2_1/m$. Such symmetry deviations are indeed very slight, so that the hkl reflections with $h = 2n+1$ are relatively weak. In a quite similar way, törnebohmit-(Ce) ($P2_1/c$) slightly deviates from the $P2_1/m$ symmetry and exhibits weak hkl reflections with $l = 2n+1$ leading to a doubling of the c

parameter (Shen and Moore 1982). In practice, the slight puckering of atomic planes present in törnebohmit-(Ce) and absent in epidotes persists when E and T modules are combined together in the gatelite-(Ce) structure. The larger the offset from the plane, or the higher the number of atoms deviating from the mirror symmetry, the stronger are the superstructure reflections. Indeed, the weak, continuous streaking at $a^*/2$ observed in västmanlandite-(Ce) (Holtstam et al. 2005) is due to the offset from the (010) mirror plane of two sites (A3 and O15, occupied by REE and oxygen, respectively), whereas in both alnaperbøite-(Ce) and perbøite-(Ce) only O15 exhibits an offset from the mirror plane.

Nomenclature remarks

In all members of the epidote-törnebohmit polysomatic series known so far the composition of the E module differentiates each member. For internal consistency, the same nomenclature rules as for epidote-supergroup minerals (Armbruster et al. 2006) are applied. Accordingly, the polysomes with $E =$ dissakisite, dollaseite, allanite, or a new Na-bearing REE epidote-composition deserve four different root names. The name perbøite-(Ce) is in honor of Per Bøe (b. 1937), a Norwegian geologist and Curator at the Tromsø Museum, who initiated the project that led to the discovery of this species; the name alnaperbøite-(Ce) emphasizes the chemical relationships with perbøite-(Ce), the dominance of Al in the M3 site and the role of Na to charge balance the dominance of a trivalent cation in the M3 site of the REE-epidote module.

In practice, the root name perbøite should apply to any ET polysome with the E module deserving the root name allanite (key-sites M3 = Fe^{2+} and A1 = Ca). The root name alnaperbøite should apply to any ET polysome composition in which (1) trivalent cations are dominant at the key-site M3 and aluminum is dominant among them and (2) the charge balance in A sites is dominantly achieved by substitution of Na for REE (rather than A^{2+} for REE). The writing of “alnaperbøite” without hyphen is deliberate: “al” and “na” are not intended as prefixes and, as for the epidote nomenclature, no prefix should be added to the root name if M1 = Al. Otherwise a proper prefix referring to homovalent substitution in M1 should be added. Thus, the unnamed mineral from the Bergslagen region (Holtstam et al. 2007) having M3 = Fe^{2+} and M1 = Fe^{3+} and reported as Fe^{3+} -analog of västmanlandite-(Ce) in the list of unnamed minerals (UM2007-35, Smith and Nickel 2007) is actually the Fe^{3+} -analog of perbøite-(Ce) and should be named ferriperbøite-(Ce).

The same name should be assigned to the mineral from eastern Siberia, Russia, described by Gurzhiy et al. (2010), which also exhibits an *E* module of ferriallanite-(Ce) composition.

A thermodynamic puzzle

An intriguing point is the occurrence at the three localities of the constituting *E* and *T* compounds also as single-phase crystals, along with the polysomatic *ET* phase. The absence of reaction textures among them raises the question of the stability of the ordered 1:1 polysome with respect to a mechanical mixture of *E* + *T*, whereby one would expect on thermodynamic grounds the occurrence of either *ET* + *E* or *ET* + *T*, depending on bulk chemistry (as commonly observed in the Bergslagen area for västmanlandite + dollaseite, Holtstam et al. 2005, and “ferriperbœite” + ferriallanite, Holtstam and Andersson 2007; but unlike Trimouns where gatelite occurs along with dissakisite and törnebohmite, Bonazzi et al. 2003). The complex texture observed in some perbœite crystals (Fig. 2) is reminiscent of an exsolution texture, but allanite has not been confirmed in it. The question is of very general bearing, namely that of the stability of any polysome with respect to the mechanical mixture of the end-members. The very same question is raised, for instance, by the coexistence of clinocllore with talc in the presence of kulkeite, the ordered 1:1 chlorite–talc mixed-layer (Schreyer et al. 1982), or the occurrence of paragonite with cookeite vs. that of their ordered 1:1 mixed-layer, salitote (Goffé et al. 1994).

IMPLICATIONS: A SODIAN EPIDOTE END-MEMBER

Solid solution toward the new alnaperbœite-(Ce) *ET* polysome end-member ${}^A(\text{REE}_{2.5}\text{CaNa}_{0.5})^M(\text{Al}_4)\text{Si}_2\text{O}_7(\text{SiO}_4)_3\text{O}(\text{OH})_2$ accounts for most of the compositional variation observed in crystals from Tysfjord granite pegmatites, as described above. Its very existence raises the question of the role of sodium in the *ET* polysome, in the *E* module and thus in epidote minerals in general, those of the allanite group in particular. Indeed, törnebohmite-(Ce) coexisting with alnaperbœite-(Ce) is Na-free, whereas coexisting allanite-(Ce) is Na-bearing and shows the same charge-compensating coupled substitutions between A and M sites as identified in alnaperbœite-(Ce) ($\text{Na}_{0.5}\text{Al} \leftrightarrow \text{REE}_{0.5}\text{Fe}^{2+}$), although to a much lesser extent (10 mol%). It is therefore extremely tempting to assign Na incorporation to the *E* module alone, i.e., into the A1 or A2 sites, leading to the sodian *E* end-member ${}^A(\text{CaREE}_{0.5}\text{Na}_{0.5})^M(\text{Al}_3)\text{Si}_2\text{O}_7(\text{SiO}_4)_3\text{O}(\text{OH})$. As shown above, crystallographic evidence is inconclusive as to Na site assignment, site scattering data allowing complete order of Na in A1, or disorder over A2, A3, and A4, or any combination thereof. In the latter two cases, both the *E* and *T* modules would be sodian and no longer be electrically neutral.

In any event, if one turns to the epidote-supergroup minerals, sodium is repeatedly reported as a very minor constituent (e.g., Franz and Liebscher 2004) that may become noteworthy only in REE-rich phases, essentially in the allanite group (survey by Gieré and Sorensen 2004). The extreme Na_2O values of 3.28 wt% (Coulson 1997), 1.38 wt% (Semenov et al. 1978), and 0.5 wt% (Bea 1996) reported in allanite can be discarded as due to contamination because the analyses cannot yield a plausible epidote formula. However, values between 0.2 and 0.3 wt% as found here are not uncommon in irrefragable allanite analyses

(e.g., Bea 1996, for allanites in granitoid rocks). What is their meaning? The 0.14 to 0.21 wt% Na_2O reported in dissakisite from UHP rocks (Yang and Enami 2003) may charge balance the Ti contents (0.54 to 0.62 wt% TiO_2), through the coupled substitution ${}^A\text{Na}^M\text{Ti} \leftrightarrow {}^A\text{Ca}^M\text{Al}$ as suggested by the authors, but as well ThO_2 contents (1.73 to 2.10 wt%) through the coupled substitution $\text{NaTh} \leftrightarrow 2\text{REE}$ in the A sites. However, alternative substitutions are possible and requested in the absence of Ti or Th, like ${}^A\text{Na}^M\text{Fe}^{3+} \leftrightarrow {}^A\text{Ca}^M\text{Fe}^{2+}$ (Yang and Enami 2003) or ${}^A\text{Na}^M\text{Al} \leftrightarrow {}^A\text{Ca}^M\text{Fe}^{2+}$ or ${}^A(\text{NaREE}) \leftrightarrow {}^A(2\text{Ca})$ (Gieré and Sorensen 2004). Actually, the combination of the latter two substitutions, i.e., $\text{Na}_{0.5}\text{Al} \leftrightarrow \text{REE}_{0.5}\text{Fe}^{2+}$, is the one that relates perbœite-(Ce) to alnaperbœite-(Ce) and that, in allanites, leads to the sodian end-member identified above as a tentative *E* module, namely $(\text{CaREE}_{0.5}\text{Na}_{0.5}\text{Al}_3\text{Si}_2\text{O}_7(\text{SiO}_4)_3\text{O}(\text{OH}))$. This new epidote end-member is obviously needed to account for the composition of allanite-group minerals (for up to ca. 10 mol%). This end-member is also needed to account for the chemistry of the *E* module of the new *ET* solid-solution series, even if it is still uncertain whether this electrically neutral formula reflects the actual partitioning of Na among the A sites of the *ET* phase. Clearly, the presence of sodium has to be carefully checked for a complete chemical characterization of the epidote-supergroup and gatelite-group minerals.

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