

**THE CRYSTAL STRUCTURE OF ILÍMAUSSITE-(Ce),  
(Ba,Na)<sub>10</sub>K<sub>3</sub>Na<sub>4.5</sub>Ce<sub>5</sub>(Nb,Ti)<sub>6</sub>[Si<sub>12</sub>O<sub>36</sub>][Si<sub>9</sub>O<sub>18</sub>(O,OH)<sub>24</sub>]O<sub>6</sub>,  
AND THE "ILÍMAUSSITE" PROBLEM**

GIOVANNI FERRARIS<sup>§</sup> AND ANGELA GULA

*Dipartimento di Scienze Mineralogiche e Petrologiche, Università di Torino, and Istituto di Geoscienze e Georisorse,  
CNR, Via Valperga Caluso, 35, I-10125, Torino, Italy*

NATALIA V. ZUBKOVA, DMITRY YU. PUSHCHAROVSKY, ELENA R. GOBETCHIYA AND IGOR V. PEKOV

*Faculty of Geology, Moscow State University, Vorobievsky Gory, RU-119899 Moscow, Russia*

KNUT ELDJARN

*SERO AS, Stasjonsveien 44, N-1375 Billingstad, Norway*

ABSTRACT

The crystal structure of ilímaussite-(Ce), (Ba,Na)<sub>10</sub>K<sub>3</sub>Na<sub>4.5</sub>Ce<sub>5</sub>(Nb,Ti)<sub>6</sub>[Si<sub>12</sub>O<sub>36</sub>][Si<sub>9</sub>O<sub>18</sub>(O,OH)<sub>24</sub>]O<sub>6</sub>, from the type locality, the Ilímaussaq alkaline complex, South Greenland, has been solved and refined to  $R = 0.11$  for 1663 observed reflections collected from a very poor crystal [ $a$  10.770(3),  $c$  61.05(2) Å; space group  $R32$ ,  $Z = 3$ ; MoK $\alpha$  radiation; Nonius Kappa CCD X-ray diffractometer]. The structure consists of three pairs of (001) silicate sheets. These sheets sandwich: CeO<sub>6</sub> trigonal prisms and Na cations ( $A$  layer), NbO<sub>6</sub> octahedra, Ba, and K ( $O$  layer), and CeO<sub>6</sub> trigonal prisms ( $A'$  layer). The layers are stacked according to the sequence  $AOA'O$ ; the tetrahedral sites in  $A'$  are only 50% occupied by Si, with consequent disorder of the basal oxygen atoms. Overall, the ratio of (Si + Al) to other cations is about 0.8. In the similar structure of a Ti-dominant analogue of ilímaussite-(Ce), to be compared with diversilite-(Ce), the same sites have been reported as being one-third occupied; in this case, the ratio of (Si + Al) to other cations is about 1.2. New chemical data are reported for diversilite-(Ce), in which the ratio of (Si + Al) to other cations is about 0.9. There is possibly a family of phases of "ilímaussite" type with compositions in the range  $21 \leq \text{Si} \leq 24$  apfu, with polytypism related to the disorder in the  $A'$  layer.

*Keywords:* ilímaussite-(Ce), crystal structure, diversilite-(Ce), polytypism, Ilímaussaq complex, Greenland.

SOMMAIRE

Nous avons résolu la structure cristalline de l'ilímaussite-(Ce), (Ba,Na)<sub>10</sub>K<sub>3</sub>Na<sub>4.5</sub>Ce<sub>5</sub>(Nb,Ti)<sub>6</sub>[Si<sub>12</sub>O<sub>36</sub>][Si<sub>9</sub>O<sub>18</sub>(O,OH)<sub>24</sub>]O<sub>6</sub>, provenant de la localité-type, le complexe alcalin d'Ilímaussaq, dans le sud du Groënland, et nous l'avons affiné jusqu'à un résidu  $R$  de 0.11 pour 1663 réflexions observées, prélevées sur un cristal de bien piètre qualité [ $a$  10.770(3),  $c$  61.05(2) Å; groupe spatial  $R32$ ,  $Z = 3$ ; rayonnement MoK $\alpha$ ; diffractomètre Nonius Kappa CCD]. La structure est faite de trois paires de feuillets silicatés. En intercalation entre ces feuillets (001) sont: des prismes trigonaux CeO<sub>6</sub> et des cations Na (feuillelet  $A$ ), des octaèdres NbO<sub>6</sub>, Ba, et K (feuillelet  $O$ ), et des prismes trigonaux CeO<sub>6</sub> (feuillelet  $A'$ ). Les feuillets sont empilés selon la séquence  $AOA'O$ . Les sites tétraédriques du feuillelet  $A'$  ne seraient que 50% remplis par le Si, et par conséquent, il y a un désordre dans les atomes d'oxygène à la base. En tout, le rapport de (Si + Al) aux autres cations est égal à 0.8 environ. Dans la structure semblable d'un analogue à dominance de Ti de l'ilímaussite-(Ce), à comparer à la diversilite-(Ce), les mêmes sites ont été décrits avec un taux d'occupation de 1/3; dans ce cas, le rapport de (Si + Al) aux autres cations est égal à 1.2 environ. Nous présentons de nouvelles données chimiques décrivant la diversilite-(Ce), dans laquelle le rapport de (Si + Al) aux autres cations est égal à 0.9 environ. Il est possible qu'il y ait une famille de phases de type "ilímaussite" ayant des compositions dans l'intervalle  $21 \leq \text{Si} \leq 24$  apfu, avec un polytypisme lié au désordre dans le feuillelet  $A'$ .

(Traduit par la Rédaction)

*Mots-clés:* ilímaussite-(Ce), structure cristalline, diversilite-(Ce), polytypisme, complexe d'Ilímaussaq, Groënland.

<sup>§</sup> E-mail address: giovanni.ferraris@unito.it

## INTRODUCTION

Ilímaussite-(Ce), a hydrous silicate of Na, K, Ba, REE and Nb, was described by Semenov *et al.* (1968) from an analcime–ussingite pegmatite situated on the Taseq slope in the northern part of the Ilímaussaq alkaline complex, South Greenland. It was found as a  $15 \times 10 \times 3$  mm cluster consisting of brownish yellow lamellae with a resinous luster and associated with chkalovite and epistolite. The simplified formula of ilímaussite-(Ce),  $\text{Na}_4\text{Ba}_2\text{CeFeNb}_2\text{Si}_8\text{O}_{28} \cdot 5\text{H}_2\text{O}$ , was calculated on the basis of results of a wet-chemical analysis. An X-ray single-crystal study revealed hexagonal symmetry with  $a$  10.80(4),  $c$  20.31(7) Å and possible space groups  $P6_3/mcm$ ,  $P6_3cm$  or  $P\bar{6}c2$ .

In 2001, one of the authors (K.E.) found a specimen of ilímaussite-(Ce) in the same pegmatite at the Taseq slope, Ilímaussaq, in which the holotype was discovered in 1964 by E.I. Semenov. This discovery led us to study the yet unknown crystal structure of ilímaussite-(Ce), and the results obtained are presented in this paper. Results published for related samples are discussed. With the support of new chemical data, we show that in ilímaussite-like minerals, the (Si+Al)/(other cations) ratio is variable, which has consequences on details of the crystal structure.

## REVIEW OF RELATED RESULTS

Sokolova *et al.* (1968), Khomyakov (1995), Yakovenchuk *et al.* (1999), Rastsvetaeva *et al.* (2003), and Krivovichev *et al.* (2003) have studied samples of an ilímaussite-like mineral collected from several pegmatites at the Mt. Yukspor (Khibiny massif, Kola Peninsula, Russia), and with Ti dominating over Nb. In particular, while our research was in progress, a Ti-dominant analogue of ilímaussite-(Ce) from Mt. Yukspor (Khibiny massif), corresponding to the unnamed mineral M30 in Khomyakov (1995), was defined as the mineral species diversilite-(Ce) (Khomyakov *et al.* 2003). At the same time, Rastsvetaeva *et al.* (2003) (hereafter KhibR; sample M30) and Krivovichev *et al.* (2003) (hereafter KhibK) independently determined two different crystal structures using Ti-dominant samples from different pegmatites from Mt. Yukspor. Krivovichev *et al.* (2003) studied a sample from a pegmatite situated on the northwestern slope of Mount Yukspor (Yakovenchuk *et al.* 1999). They found  $a$  10.708,  $c$  60.073 Å and space group  $R32$  for KhibR and maintain that the crystal structure published by Rastsvetaeva *et al.* (2003) ( $a$  10.713,  $c$  60.77 Å, space group  $R\bar{3}$ ) for KhibR is substantially wrong. In particular, mixed-tetrahedron complexes formed by three-membered rings  $\text{Si}_3\text{O}_9$  and isolated  $\text{SiO}_4$  tetrahedra described for the  $R\bar{3}$  model are replaced by six-membered  $\text{Si}_6\text{O}_{18}$  rings in the  $R32$  model.

## EXPERIMENTAL

The new specimen of ilímaussite-(Ce) mentioned above is a large (3 cm) cluster with the same morphology and associated minerals as in the holotype specimen. The identity between the two samples was confirmed by comparison of the chemical composition (Table 1) and the X-ray powder-diffraction pattern (RKD 57.3 mm camera,  $\text{CuK}\alpha$  radiation, Ni filter; Table 2).

Chemical analyses of the new sample of ilímaussite-(Ce) from Ilímaussaq, including the crystal used for the collection of X-ray-diffraction data, were carried out by means of wavelength-dispersion and energy-dispersion spectrometry (WDS, EDS) with an electron microprobe and are reported in Table 1, together with two new datasets for diversilite-(Ce), and information on the experimental procedure. Following the results of the wet-chemical data published by Semenov *et al.* (1968), all Fe is given as  $\text{Fe}^{3+}$ . The deficiency of the sum from 100% compares with the weight loss reported by the same authors and is assigned to  $\text{H}_2\text{O}$ , also on the basis of the IR spectrum, kindly provided by N.V. Chukanov. It shows a very broad absorption band centered around  $3400 \text{ cm}^{-1}$ . Relative to the holotype, our sample has a slightly higher content of REE and Ti and slightly less Na and Nb; it shows some variability, particularly for the Si, Ti and Nb contents.

Single-crystal X-ray data have been collected at room temperature on a Nonius Kappa CCD diffractometer at the Institute of Mineralogy and Crystallography, University of Vienna, equipped with an X-ray capillary optics collimator, using graphite-monochromatized  $\text{MoK}\alpha$  radiation. All tested fragments showed broad, streaked and commonly split diffraction-maxima. In particular, only  $hkl$  diffraction-maxima with  $l = 3n$  are strong and quite sharp; all other diffraction-maxima are diffuse and by far weaker, as already noted by Sokolova *et al.* (1968) for Ti-dominant samples. The poor crystallinity of the material is presumably due to both metamictization-induced damage caused by the thorium content and stacking disorder related to polytypism (see below).

The complete Ewald sphere was explored up to  $2\theta = 55^\circ$  ( $1.5^\circ \omega$  scan width); the crystal-to-detector distance was 50 mm. Data processing, including an absorption correction based on multiple-frame measured reflections (Otwinowski & Minor 1997) and the refinement of the lattice parameters [ $a$  10.770(3),  $c$  61.05(2)], were performed with the Nonius program DENZO-SMN. A total of 6542 reflections resulted from the data processing, corresponding to 3353 independent ones in the point group 32 and 1663 observed ones with  $|F_o| > 4\sigma(|F_o|)$ . Details of collection of the single-crystal X-ray data and the structure refinement of ilímaussite-(Ce) are given in Table 3.

TABLE 1. CHEMICAL COMPOSITION OF ILÍMAUSSITE-(Ce) FROM THE ILÍMAUSSAQ COMPLEX AND DIVERSILITE-(Ce) FROM THE Khibiny COMPLEX

	1	2	3	4	5	6	7	8	9		1	2	3	4		6	7	8	9
Na <sub>2</sub> O wt%	7.00	5.56	5.19	5.16	5.07–5.33	2.76	1.32	1.33	1.75	Na <i>apfu</i>	9.11	6.79	7.02	6.69		3.96	1.55	2.03	2.50
K <sub>2</sub> O	3.80	3.03	3.98	4.26	3.90–4.05	5.81	3.33	4.11	6.17	K	3.25	2.43	3.54	3.64		5.48	2.56	4.14	5.80
CaO		b.d.l.	b.d.l.	b.d.l.		0.10	1.01	0.85	0.15	Ca	-	-	-	-		0.08	0.65	0.72	0.12
SrO		b.d.l.	0.07	b.d.l.	0.00–0.17	0.42	0.64	b.d.l.	b.d.l.	Sr	-	-	0.03	-		0.18	0.22	-	-
BaO	23.62	24.06	24.97	26.20	24.22–25.89	24.85	22.17	23.47	22.69	Ba	6.21	5.94	6.83	6.87		7.20	5.24	7.25	6.55
MnO		0.21	0.30	b.d.l.	0.26–0.37	1.09	0.05	b.d.l.	1.18	Y	-	-	-	-		-	-	-	-
FeO						3.10				La	0.62	0.95	0.81	0.87		1.32	0.64	1.34	0.75
Y <sub>2</sub> O <sub>3</sub>		b.d.l.	b.d.l.	b.d.l.				0.65	b.d.l.	Ce	1.43	1.82	2.04	2.12		1.82	1.39	1.77	2.01
La <sub>2</sub> O <sub>3</sub>	2.5	4.08	3.16	3.54	2.66–3.53	4.84	2.89	4.62	2.76	Pr	0.17	0.26	0.13	0.11		0.20		0.26	0.12
Ce <sub>2</sub> O <sub>3</sub>	5.8	7.90	7.97	8.65	7.79–8.13	6.72	6.59	6.13	7.47	Nd	0.38	0.18	0.31	0.33		0.32	0.18	0.40	0.46
Pr <sub>2</sub> O <sub>3</sub>	0.7	1.13	0.50	0.46	0.32–0.85	0.74		0.91	0.44	Sm	-	-	0.03	0.12		0.04	0.02	0.04	-
Nd <sub>2</sub> O <sub>3</sub>	1.6	0.81	1.25	1.38	1.06–1.45	1.21	0.84	1.41	1.74	ΣREE	2.60	3.21	3.32	3.55		3.70	2.23	3.81	3.34
Sm <sub>2</sub> O <sub>3</sub>		n.d.	0.11	0.50	0.00–0.34	0.16	0.12	0.16	b.d.l.	Th			0.19	0.16		0.27	0.49	0.79	-
ΣREE <sub>2</sub> O <sub>3</sub>	10.60	13.92	12.99	14.53		13.67	10.37	13.88	12.41	U			-	-				0.05	-
Fe <sub>2</sub> O <sub>3</sub>	3.18	2.13	1.99	2.02	1.94–2.05	1.63	2.59	3.21		Mn		0.11	0.18	-		0.68	0.03	-	0.74
Al <sub>2</sub> O <sub>3</sub>		0.62	0.39	0.34	0.20–0.48			0.24	0.13	Fe	1.61	1.01	1.04	1.02		1.92	0.74	1.54	1.78
SiO <sub>2</sub>	31.28	32.61	29.64	30.96	29.33–30.05	32.46	39.78	30.15	32.44	Ti	0.83	1.10	1.87	1.58		5.10	4.91	5.08	4.99
TiO <sub>2</sub>	1.64	2.32	3.56	3.14	3.07–4.10	9.17	10.82	8.57	9.01	Nb	4.01	3.33	3.42	2.87		0.54	0.69	1.06	0.42
ThO <sub>2</sub>		n.d.	1.20	1.03	1.16–1.27		2.00	2.73	4.70	Σcations	27.62	23.92	27.44	26.38		28.84	19.09	26.44	27.03
UO <sub>2</sub>		n.d.	b.d.l.	n.d.				0.27	b.d.l.	Al			0.46	0.32	0.27			0.22	0.11
Nb <sub>2</sub> O <sub>5</sub>	13.20	11.69	10.83	9.47	9.99–11.67	1.62	2.52	2.96	1.27	Si	21.00	20.54	20.68	20.73		24.00	24.00	23.78	23.89
H <sub>2</sub> O						6.15		n.d.	n.d.	(Si+Al)/ other cations	0.76	0.88	0.76	0.80		0.83	1.26	0.91	0.89
F		n.d.	0.53	b.d.l.	0.40–0.78			n.d.	n.d.	OH	28.82					30.72			
-O=F <sub>2</sub>										F			1.17	-					
LOI	6.43	n.d.	n.d.				n.d.	n.d.											
Total	100.75	96.15	95.42	97.11		101.20	95.71	91.15	95.11										

Columns 1–5: ilímaussite-(Ce); columns 6–9: diversilite-(Ce). 1: Holotype (wet-chemical analysis; Semenov *et al.* 1968); the lanthanide contents were established by X-ray fluorescence. 2–3: Average result of four point-analyses of the sample studied by EDS [2; Camebax MBX with Link AN 10000; 15 kV, 1–1.5 nA; standards: albite (Na, Al), orthoclase (K), SrSO<sub>4</sub> (Sr), BaSO<sub>4</sub> (Ba), Mn (Mn), LaPO<sub>4</sub> (La), CePO<sub>4</sub> (Ce), PrPO<sub>4</sub> (Pr), NdPO<sub>4</sub> (Nd), Fe (Fe), wollastonite (Si), Ti (Ti), Nb (Nb)] and WDS [3; Camebax MBX; 15 kV, 20 nA; standards: albite (Na), orthoclase (K, Al, Si), Sr-bearing glass (Sr), Ba-bearing glass (Ba), spessartine (Mn), LaPO<sub>4</sub> (La), CePO<sub>4</sub> (Ce), PrPO<sub>4</sub> (Pr), NdPO<sub>4</sub> (Nd), SmPO<sub>4</sub> (Sm), andradite (Fe), TiO<sub>2</sub> (Ti), ThO<sub>2</sub> (Th), LiNbO<sub>3</sub> (Nb), MgF<sub>2</sub> (F)]. In both cases, the beam was rastered over an area of 10 × 10 μm<sup>2</sup> to minimize damage. 4: Average result of 10 point-analyses determined on the crystal used for the structure determination (ARI–SEM-Q; 15 kV, 20 nA; standards: albite (Na), microcline (K), paracelsian (Si, Ba), ilmenite (Fe, Ti), anorthite (Al), ThO<sub>2</sub> (Th), Nb metal (Nb), CHGO glass REE3 (Nd, Sm), CHGO glass REE4 (La, Ce, Pr). 5: Range of analytical results given in 3. 6: KhibR, from Khomyakov *et al.* (2003). 7: KhibK, from Krivovichev *et al.* (2003). 8, 9: Results of our analyses for two samples of diversilite-(Ce): 8 from the same pegmatite of KhibK, and 9 from Mt. Yukspor; same instrumental conditions as for analysis 3, with the addition the standards diopside (Ca), garnet (Mn, Fe, Al), YPO<sub>4</sub> (Y) and UO<sub>2</sub> (U). The Yukspor sample (collected by I.V.P.) consists of spherulites (up to 2 mm) of pale-yellow lamellae within cavities of an aegirine – sodalite – microcline pegmatite; it occurs together with natrolite, pectolite, shcherbakovite, and magnesium astrophyllite. \* For our analyses, Mg, Zn, Cr, Zr, Ta, P, S, Cl, and lanthanides heavier than Sm are below detection limits (b.d.l.; n.d. = not detected). \*\* The compositions in atoms per formula unit (*apfu*) were calculated on the basis of 21 (Si + Al) for ilímaussite-(Ce) and 24 (Si + Al) for diversilite-(Ce). LOI: loss on ignition.

The structure was solved in the R32 space group by direct methods (SHELX–97 package; Sheldrick 1997). We obtained results corresponding to those published by Krivovichev *et al.* (2003) (KhibK) for the atom coordinates, but different for the site occupancies, in particular those of the Si and Ce sites, as discussed below. Owing to the poor quality of the diffraction data mentioned above, most of the atoms, in particular those connected with the disordered part of the structure (see below) could not be anisotropically refined. Thus, the refinement was isotropic for all atoms except Ce1, Ce2, Ba1, Ba2, Ba3, Nb, Si2, K1 and K2; it converged to  $R = 0.11$  for the 1663 observed reflections with  $|F_o| > 4\sigma(|F_o|)$ . The {001} twinning reported by Krivovichev

*et al.* (2003) for KhibK was not detected in our case. In Table 4, we report the atom coordinates, displacement parameters (temperature factors) and site occupancies obtained from the refinement; Table 5 lists the main bond-lengths. A table with  $F_o$  and  $F_c$  is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

## THE STRUCTURE

Following the description given by Krivovichev *et al.* (2003) for KhibK, the crystal structure of ilímaussite-(Ce) (Fig. 1) consists of (001) *A*, *A'* and *O* layers that are stacked according to the sequence *AOA'O*.

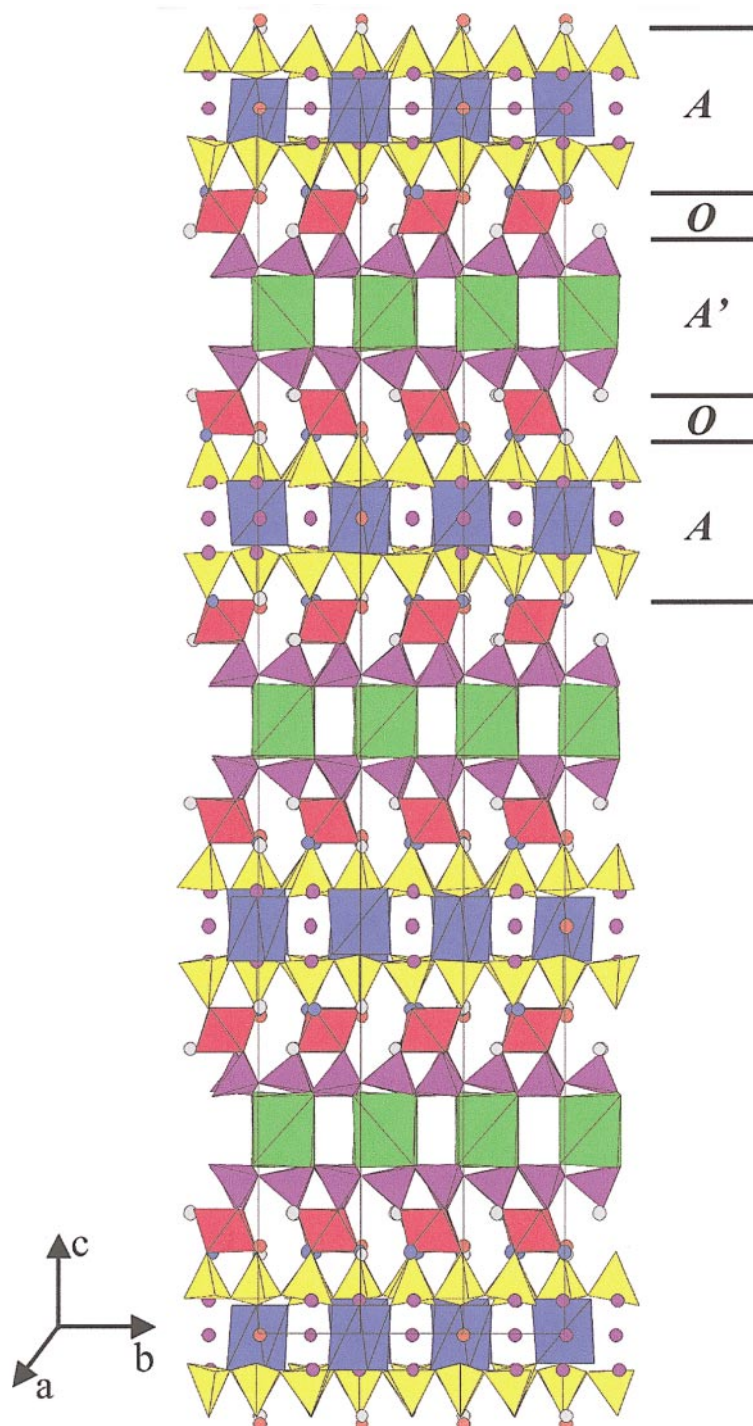


FIG. 1. Structure of ilímaussite-(Ce) projected on the (100) plane. Blue, green, and red polyhedra represent the (Ce1)O<sub>6</sub> and (Ce2)O<sub>6</sub> trigonal prisms, and the NbO<sub>6</sub> octahedra, respectively. In the order, yellow and fuchsia polyhedra represent (Si1, Si2) and (Si3, Si4, Si5) tetrahedra. Grey, orange and fuchsia circles represent Ba, K, and Na cations, respectively; the azure circle represents O<sub>2</sub>, which is the only oxygen atom not linked to Si. The A, O and A' layers described in the text are labeled.

The O layer consists of isolated NbO<sub>6</sub> octahedra that share their corners with SiO<sub>4</sub> tetrahedra belonging to the A (O1, O3) and A' (O4, O5, O6) layers. Ba1, Ba2, Ba3, and K1 occupy the space between the octahedra and show coordination 12, 12, 12, and 9, respectively (Table 5). In KhibK, minor Nb substitutes for Ti.

The A layer contains two equivalent silicate sheets formed by non-interconnected Si<sub>6</sub>O<sub>18</sub> six-membered rings of corner-sharing SiO<sub>4</sub> tetrahedra (Si1 and Si2; Fig. 2a). The two sheets sandwich isolated (Ce1)O<sub>6</sub> trigonal prisms plus Na1, Na2, and K2 cations that show coordination 6, 6, and 12, respectively (Table 5). The

bases of the (Ce1)O<sub>6</sub> trigonal prisms connect the silicate six-membered rings, thus realizing a hexagonal net, as shown in Figure 2a. Owing to the short Na1–Na2 distance 1.70(2) Å, Na statistically occupies only 50% of the Na1 and Na2 sites. In KhibK, H<sub>2</sub>O molecules instead of Na have been assigned to the Na1 site. In ilímaussite-(Ce), the assignment of Na to this site is justified both by the electron content of the site (Table 4) and by the larger availability of non-tetrahedrally coordinated cations (see below).

The A' layer contains two equivalent silicate sheets composed of (Si3)O<sub>4</sub>, (Si4)O<sub>4</sub>, (Si5)O<sub>4</sub> tetrahedra; the sheets sandwich (Ce2)O<sub>6</sub> trigonal prisms only. The three independent Si sites are 50% occupied only. The reason for this statistical distribution can be understood by considering the configuration of the basal atoms of oxygen (O11, O12, O13, O14, O15, O16). As shown in Figure 2b, ideally the basal atoms of oxygen are arranged according to a two-dimensional close-packing array, and each oxygen atom is shared either by three equivalent Si atoms (O11, O15, O16) or by two equivalent Si and one Ce atom (O12, O13, O14). Both situations are

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR ILÍMAUSSITE-(Ce) FROM ILÍMAUSSAQ, SOUTH GREENLAND

1		2		3		hkl
I <sub>obs</sub> *	d <sub>obs</sub> (Å)	I <sub>obs</sub>	d <sub>obs</sub> (Å)	I <sub>calc</sub>	d <sub>calc</sub> (Å)	
				41	20.35	003
				100	10.17	006
				15	9.22	111
10	5.20			41	5.21	120
10	4.66			13, 9	4.650, 4.61	021, 222
10	3.50			8	3.53	1016
60	3.25	35	3.20	83	3.25	1215
50	3.12			89	3.11	030
40	2.98	25	2.95	30	2.97	336
100	2.67	100	2.65	26, 28, 78	2.69, 2.67, 2.65	240, 243, 3312
20	2.50	10	2.48	12	2.50	249
30	2.24	30	2.24	33	2.25	3415
20b	2.022	20b	2.01	17	2.035	0030
20b	1.816	15b	1.81	20, 15	1.820, 1.795	4515, 360
10b	1.694			7	1.693	3612
20	1.562	25	1.56	27	1.555	060
10	1.408			8	1.402	5715

Samples: 1: Holotype (Semenov *et al.* 1968), 2: present sample, 3: Values calculated using the structural data; the three strong low-angle intensities cannot be seen with the X-ray powder-diffraction camera used. \*: Ten times the values published for the holotype. b: broad line.

TABLE 3. EXPERIMENTAL AND REFINEMENT DATA FOR ILÍMAUSSITE-(Ce)

Radiation and wavelength, Å	MoKα; 0.71069
μ, mm <sup>-1</sup>	5.74
Diffractometer; monochrom.	Nonius Kappa CCD; graphite
Space group; Z	R32; 3
Unit-cell dimensions, Å	a 10.770(3), c 61.05(2)
Unit-cell volume, Å <sup>3</sup>	6132.6
D(calc.), D(meas.), g/cm <sup>3</sup>	3.595, 3.6
Crystal size, mm	0.14 × 0.11 × 0.08
Index ranges	-14 ≤ h ≤ 14, -11 ≤ k ≤ 11, -78 ≤ l ≤ 80
Exposure time (s) per frame	100
CCD frames measured	541
Collected reflections	6542
Unique reflections	3353
Independent Reflections with  F <sub>o</sub>   > 4σ( F <sub>o</sub>  )	1663; R <sub>m</sub> = 0.085
Number of refined parameters	116
Refinement method	full-matrix least-squares on F <sup>2</sup>
Weights	1/[σ <sup>2</sup> (F <sub>o</sub> ) + (0.2P) <sup>2</sup> + 0.0P], P = [max(F <sub>o</sub> ) <sup>2</sup> + 2(F <sub>c</sub> ) <sup>2</sup> ]/3
R(F), wR( F ), Goof	0.11; 0.41; 1.33

TABLE 4. ATOM COORDINATES, EQUIVALENT (U<sub>eq</sub>) ANISOTROPIC (U<sub>11</sub>) DISPLACEMENT-PARAMETERS (Å<sup>2</sup>), COMPOSITION (C<sub>site</sub>) AT THE SITES WITH MIXED-CATION OCCUPANCY, TOGETHER WITH THE CORRESPONDING CALCULATED (e<sub>calc</sub>) AND REFINED (e<sub>ref</sub>) NUMBER OF ELECTRONS FOR ILÍMAUSSITE-(Ce)

Atom	C <sub>site</sub>	e <sub>calc</sub>	e <sub>ref</sub> <sup>b</sup>	x	y	z	U <sub>eq</sub> /U <sub>iso</sub>
Ce1 <sup>c</sup>	Ce <sub>1.7</sub> Fe <sub>0.3</sub>	53	57	2/3	1/3	-0.00005(4)	0.027(2) <sup>e</sup>
Ce2 <sup>b</sup>	Ce <sub>2.0</sub> Fe <sub>1.0</sub>	47	44	1/3	0.0005(4)	1/6	0.048(3) <sup>f</sup>
Ba1	Ba <sub>4.0</sub> Na <sub>1.3</sub> K <sub>0.7</sub>	42	44	0.0005(3)	0.3263(3)	0.1001(1)	0.044(2) <sup>e</sup>
Ba2 <sup>c</sup>	Ba <sub>1.7</sub> Tb <sub>0.3</sub>	61	62	1/3	2/3	0.0657(1)	0.043(2) <sup>e</sup>
Ba3 <sup>c</sup>	Ba <sub>1.0</sub> K <sub>0.3</sub>	55	61	2/3	1/3	0.06561(7)	0.037(1) <sup>e</sup>
Nb	Nb <sub>3.7</sub> Ti <sub>2.0</sub> Fe <sub>0.3</sub>	34	35	0.3439(4)	0.3427(5)	0.0844(2)	0.038(1) <sup>f</sup>
Na1	Na <sub>3</sub> <sup>f</sup>			0.489(2)	0.485(2)	0.0277(3)	0.015(5)
Na2 <sup>b</sup>	Na <sub>1.5</sub> <sup>f</sup>			0.505(2)	0.505(2)	0	0.05 <sup>e</sup>
K1 <sup>c</sup>	K <sub>1.8</sub> Ba <sub>0.2</sub>	23	24	0	0	0.0728(2)	0.029(3) <sup>f</sup>
K2 <sup>d</sup>	K <sub>0.8</sub> Sr <sub>0.1</sub> Ba <sub>0.1</sub>	25	27	0	0	0	0.042(6) <sup>e</sup>
Si1		0.3254(8)	0.168(1)	0.0386(1)			0.026(2)
Si2		0.1562(9)	0.8297(9)	0.0387(2)			0.021(2) <sup>e</sup>
Si3 <sup>f</sup>		0.168(1)	0.167(1)	0.1302(3)			0.016(4)
Si4 <sup>f</sup>		0.333(1)	0.502(2)	0.1292(3)			0.017(4)
Si5 <sup>f</sup>		0.505(1)	0.331(1)	0.1292(3)			0.018(4)
O1		0.332(2)	0.175(3)	0.0670(4)			0.030(6)
O2		0.486(3)	0.489(3)	0.0678(4)			0.041(7)
O3		0.157(3)	0.822(3)	0.0673(4)			0.033(6)
O4		0.175(3)	0.183(3)	0.1032(4)			0.037(7)
O5		0.328(3)	0.473(3)	0.1022(3)			0.045(8)
O6		0.486(4)	0.333(2)	0.1023(3)			0.040(8)
O7		0.216(3)	-0.000(2)	0.0300(4)			0.039(6)
O8		0.478(2)	0.220(2)	0.0267(3)			0.034(5)
O9		0.264(2)	0.783(2)	0.0270(3)			0.03(5)
O10		0.270(2)	0.273(2)	0.0281(3)			0.029(5)
O11(OH) <sup>e</sup>		2/3	1/3	0.1290 <sup>a</sup>			0.10 <sup>a</sup>
O12(OH)		0.3439 <sup>a</sup>	0.1962 <sup>a</sup>	0.1390 <sup>a</sup>			0.10 <sup>a</sup>
O13(OH)		0.4768 <sup>a</sup>	0.4690 <sup>a</sup>	0.1360 <sup>a</sup>			0.10 <sup>a</sup>
O14(OH)		0.2077 <sup>a</sup>	0.3422 <sup>a</sup>	0.1380 <sup>a</sup>			0.10 <sup>a</sup>
O15(OH) <sup>e</sup>		0	0	0.1290 <sup>a</sup>			0.15 <sup>a</sup>
O16(OH) <sup>e</sup>		1/6	1/3	0.1290 <sup>a</sup>			0.15 <sup>a</sup>

The general position has multiplicity 18. <sup>a</sup> Fixed values. <sup>b</sup> Atoms in special position with site multiplicity 9. <sup>c</sup> Atoms in special position with site multiplicity 6. <sup>d</sup> Atoms in special position with site multiplicity 3. <sup>e</sup> Anisotropic refinement. <sup>f</sup> 50% occupied sites. <sup>g</sup> The estimated standard deviation is 1 electron. Numbers in parentheses are the estimated standard deviations.

crystallochemically impossible if full occupancy of the  $\text{SiO}_4$  tetrahedra occurs; in fact, the bond valence of an oxygen atom would already be saturated by two Si–O bonds. If the  $\text{SiO}_4$  tetrahedra are 50% occupied only, ideally each oxygen atom would instead receive 1.5 bond-valence units. Actually, the bond-valence discussion reported below shows that all the basal atoms of oxygen of the A' layer partially represent OH groups, in agreement with the  $\text{H}_2\text{O}$  content indicated by the chemical analysis (Table 1). The 50% statistical occupancy of the Si sites means that locally the  $\text{SiO}_4$  tetrahedra cannot be connected to form rings, as shown in Figure 2b. Locally, a “six-membered ring” must be interrupted because, on average, it contains only three filled tetrahedra (see below for further discussion). The partial occupancy of the Si sites causes disorder in the position of the basal atoms of oxygen, which show no vacancy but, locally, are shifted toward the occupied Si positions. For this reason, the positions of the basal atoms of oxygen cannot be properly refined and have been constrained to values that allow, at the same time, the formation of tetrahedra and their connectivity as shown in Figure 2b. Consequently, the average structure represented by the coordinates given in Table 4 shows quite “expanded” tetrahedra in the A' layer (Table 5). In KhibK, the occupancy of the Si3, Si4 and Si5 sites has been found to be  $\frac{2}{3}$ , as further discussed below.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF ILÍMAUSSITE-(Ce)

Ce1 – O9	2.41(1) × 3	Nb – O5	1.85(2)	Si1 – O8	1.62(2)
	2.41(2) × 3	O2	1.85(2)	O10	1.66(2)
Ave.	2.41	O6	1.92(3)	O7	1.68(2)
		O3	2.03(3)	O1	1.74(2)
Ce2 – O12	2.659(3) × 2	O1	2.04(2)	Ave.	1.67
	2.806(2) × 2	O4	2.11(3)		
O13	2.806(2) × 2	Ave.	1.97	Si2 – O10	1.58(2)
O14	2.806(2) × 2			O9	1.638(9)
Ave.	2.757			O7	1.69(2)
				O3	1.75(3)
Ba1 – O3	2.73(3)	Na1 – O10	2.33(3)	Ave.	1.66
O1	2.74(4)	O2	2.45(3)		
O2	2.81(3)	O9	2.55(3)	Si3 – O4	1.66(3)
O4	2.98(2)	O8	2.56(3)	O14	1.78(1)
O5	3.06(2)	O8	2.80(3)	O15	1.81(1)
O13	3.083(6)	O9	2.91(3)	O12	1.83(1)
O6	3.12(2)	Ave.	2.60	Ave.	1.77
O12	3.124(6)				
O4	3.12(2)				
O14	3.160(6)	Na2 – O9	2.93(2) × 2	Si4 – O14	1.66(1)
O6	3.19(2)	O8	2.96(2) × 2	O5	1.67(2)
O5	3.24(2)	O10	3.05(3) × 2	O16	1.77(1)
Ave.	3.03	Ave.	2.98	O13	1.81(1)
				Ave.	1.73
Ba2 – O9	2.94(2) × 3	K1 – O4	2.67(3) × 3	Si5 – O6	1.66(1)
O5	3.03(2) × 3	O1	3.12(2) × 3	O13	1.70(1)
O2	3.09(2) × 3	O3	3.15(2) × 3	O12	1.72(1)
O3	3.10(2) × 3	Ave.	2.98	O11	1.73(1)
Ave.	3.04			Ave.	1.70
		K2 – O7	2.96(2) × 6		
Ba3 – O8	2.96(2) × 3	O10	3.39(2) × 6		
O6	2.97(2) × 3	Ave.	3.17		
O1	3.12(2) × 3				
O2	3.14(2) × 3				
Ave.	3.05				

The occurrence of isolated  $\text{Si}_6\text{O}_{18}$  six-membered rings and, in general, of  $T_6\text{O}_{18}$  six-membered rings [cf. Kahlenberg (2001) for  $\text{Sr}_3\text{Ga}_2\text{O}_6$  and related compounds], is quite rare (Liebau 1999). Clearly, this type of ring occurs in the A layer of both KhibK and ilímaussite-(Ce). On the other hand, the presence of the same ring in the A' layer of both minerals is questionable because of the partial occupancy of the tetrahedra. In principle, the  $\frac{2}{3}$  occupancy reported for KhibK leaves open the possibility of having six-membered  $\text{Si}_6\text{O}_{18}$  rings in the A' layer. However, the  $\frac{1}{2}$  occupancy observed for the tetrahedra of the A' layer in ilímaussite-(Ce) excludes the possibility of having only  $\text{Si}_6\text{O}_{18}$  six-membered rings in this layer. Presumably, in the A' layer of ilímaussite-(Ce), the silicate tetrahedra are grouped in fragments not larger than a “horseshoe-like” trimer (*i.e.*, half a six-membered ring). Thus, this mineral would belong to the rare (Kahlenberg & Hösch 2002) group of mixed anion compounds containing triple and (possibly) single or double tetrahedra, besides the sextuple tetrahedra of the A layer. A similar situation cannot be firmly excluded also for KhibK, even if this mineral does more likely correspond to a six-membered cyclosilicate.

#### BOND VALENCES AND CRYSTAL-CHEMICAL FORMULA

Because of the structural disorder mentioned above, a realistic bond-valence calculation is not feasible. However, keeping in mind the partially occupied sites (Si3, Si4, Si5, Na1, and Na2), an inspection of the site multiplicities and occupancies (Table 4), bond lengths (Table 5), and cation–anion bond connectivities (Table 6) allows us to draw the following conclusions on the crystal chemistry of ilímaussite-(Ce).

TABLE 6. ANION–CATION BOND CONNECTIONS IN THE STRUCTURE OF ILÍMAUSSITE-(Ce)

	Si1, Si2	*Si3, Si4, Si5	Ce	Ba	Nb	Na	K
O1	×			×	×		×
O2				×	×	×	
O3	×			×	×		×
O4		×		×	×		×
O5		×		×	×		×
O6		×		×	×		×
O7	×						×
O8	×		×			×	×
O9	×		×			×	×
O10	×					×	×
O11(OH)		×					
O12(OH)		×	×	×			
O13(OH)		×	×	×			
O14(OH)		×	×	×			
O15(OH)		×					
O16(OH)		×					

\* The Si3, Si4 and Si5 sites are 50% occupied. Each × indicates one bond.

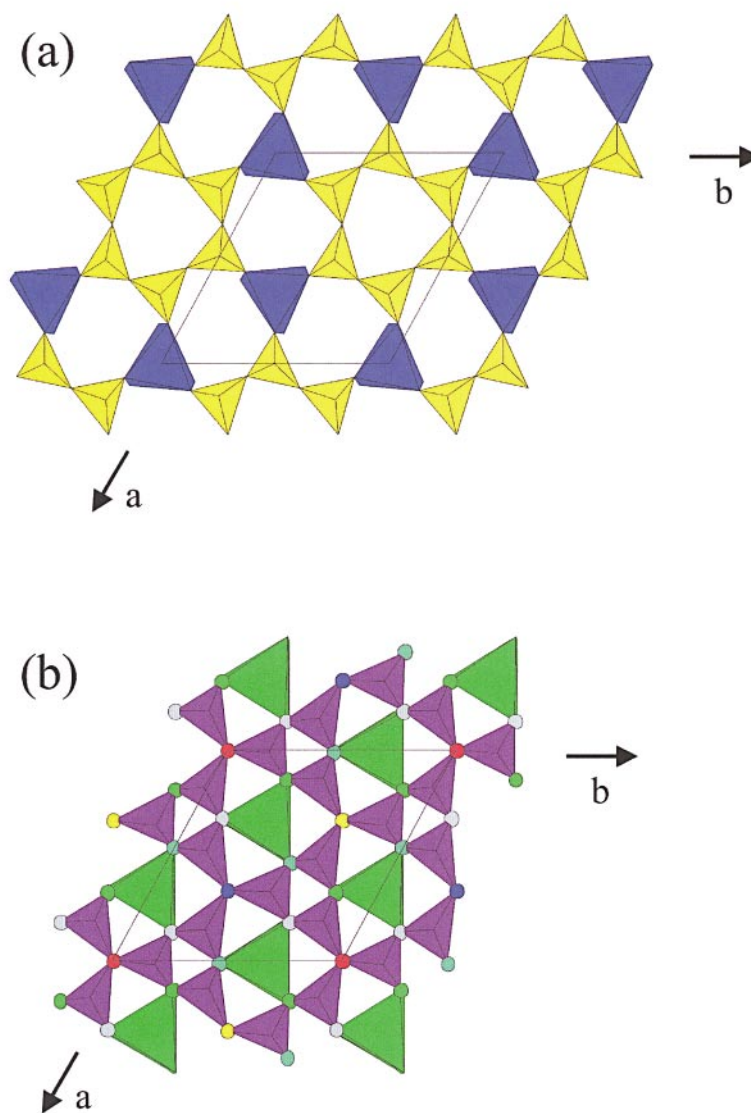


Fig. 2. A (001) projection of the A (a) and A' (b) layers in the structure of ilímaussite-(Ce). In the A' layer, the tetrahedra are 50% statistically occupied. Ba, K and Na cations are not indicated. The basal oxygen atoms shown in b) as circles correspond to O11 (red), O12 (grey), O13 (green), O14 (azure), O15 (blue), and O16 (yellow). Colors of polyhedra are as in Figure 1.

- Anion O2, the only oxygen atom not linked to Si, must account for the small quantity of F found by chemical analysis, but mainly corresponds to  $O^{2-}$ . Anion O2 is represented by azure circles in Figure 1 and is reported at the end of the ideal formula in the title.
- Anions O11, O12, O13, O14, O15, and O16 are undersaturated and must (mainly) represent OH groups.
- All other O positions must represent  $O^{2-}$  anions.

- The presence of molecular  $H_2O$  represented by oxygen atoms other than those mentioned above is excluded, as shown by the attribution of the electron density given in Table 4. Thus, the broad absorption centered on  $3400\text{ cm}^{-1}$  must be due to the presence of OH only.

The difference of the analytical total from 100% in the electron-microprobe data is quite close to the weight

loss determined by Semenov *et al.* (1968) (Table 1); therefore, we assume it to be H<sub>2</sub>O. The chemical analysis done on the very small crystal used to collect the X-ray-diffraction data (Table 1, column 4) is close to that obtained from more suitable grains. Thus, the average WDS data collected on these grains (Table 1, column 3) were normalized to (Si + Al) = 21 atoms per formula unit (*apfu*) and used to represent our sample of ilímaussite-(Ce), according to the following empirical formula: (Ba<sub>6.83</sub>K<sub>3.54</sub>Na<sub>7.02</sub>Sr<sub>0.03</sub>) $\Sigma$ <sub>17.42</sub>(REE<sub>3.32</sub>Th<sub>0.19</sub>Fe<sup>3+</sup><sub>1.04</sub>Mn<sub>0.18</sub>) $\Sigma$ <sub>4.73</sub>(Nb<sub>3.42</sub>Ti<sub>1.87</sub>) $\Sigma$ <sub>5.29</sub>(Si<sub>20.68</sub>Al<sub>0.32</sub>) $\Sigma$ <sub>21</sub>[O<sub>62.64</sub>(OH)<sub>20.29</sub>F<sub>1.17</sub>] $\Sigma$ <sub>84.10</sub>, where REE = Ce<sub>2.04</sub>La<sub>0.81</sub>Nd<sub>0.31</sub>Pr<sub>0.13</sub>Sm<sub>0.03</sub>.

On the basis of the cation occupancies assigned to the sites, which take into account the corresponding refined electron-density (Table 4), our discussion on the silicate content of the A and A' layers, the bonding involving the oxygen atoms, and the chemical data obtained on our sample (Table 1), the following crystal-chemical structural formula is obtained: (Ba<sub>7.9</sub>K<sub>3.4</sub>Na<sub>5.8</sub>Th<sub>0.3</sub>Sr<sub>0.1</sub>) $\Sigma$ <sub>17.5</sub>(Ce<sub>3.7</sub>F<sup>3+</sup><sub>1.3</sub>) $\Sigma$ <sub>5</sub>(Nb<sub>3.7</sub>Ti<sub>2.0</sub>Fe<sup>3+</sup><sub>0.3</sub>) $\Sigma$ <sub>6</sub>[Si<sub>12</sub>O<sub>36</sub>][Si<sub>9</sub>O<sub>26.8</sub>(OH)<sub>15.2</sub>]<sub>6</sub>O<sub>6</sub>.

The values of density of ilímaussite-(Ce), calculated for the empirical (3.40 g/cm<sup>3</sup>) and the structural formula (3.595 g/cm<sup>3</sup>), are close to the measured value of 3.6 g/cm<sup>3</sup> published for the holotype specimen by Semenov *et al.* (1968). In the crystal-chemical formula, the small quantity of Mn has been included with Fe that, following Semenov *et al.* (1968), is considered trivalent. A replacement of REE (Ce) (ionic radius  $r = 1.01$  Å) by Fe<sup>3+</sup> ( $r = 0.65$  Å) is not commonly reported in the literature; presumably, part of Fe could correspond to the larger Fe<sup>2+</sup> ( $r = 0.78$  Å). Krivovichev *et al.* (2003) also assigned Ce and Fe to the same site; on the other hand, this solution is suggested by the constraint posed by a reasonable matching between the chemical data and the refined electron-density (Table 4).

The deficit in the proportion of hydroxyl shown by the structural formula (compared to the empirical formula) is due to the higher use of high-charge heavy atoms to match the refined electron-density; on the other hand, the composition of ilímaussite-(Ce) is clearly variable, as shown by the chemical data (Table 1). In conclusion, taking into account the (partial) order shown by the cations (Table 4), an ideal chemical formula for ilímaussite-(Ce) is (Ba,Na)<sub>10</sub>K<sub>3</sub>Na<sub>4.5</sub>Ce<sub>5</sub>(Nb,Ti)<sub>6</sub>[Si<sub>12</sub>O<sub>36</sub>][Si<sub>9</sub>O<sub>18</sub>(O,OH)<sub>24</sub>]<sub>6</sub>O<sub>6</sub>. The O2 oxygen atom not linked to Si is shown at the end of the formula.

#### COMPARISON WITH RELATED MINERALS

From the chemical data (Table 1, column 7) and a structural analysis of their sample, Krivovichev *et al.* (2003) obtained the structural formula (Ba,K,Na,Ca)<sub>11-12</sub>(REE,Fe,Th)<sub>4</sub>(Ti,Nb)<sub>6</sub>(Si<sub>6</sub>O<sub>18</sub>)<sub>4</sub>(OH)<sub>12</sub>•4.5H<sub>2</sub>O for a Ti-dominant analogue (KhibK) of ilímaussite-(Ce). In addition to a dominance of Ti over Nb, the ratio (Si + Al) to (other cations) = 1.26 (1.12 according to the structure

refinement) represents the major difference compared to our ilímaussite-(Ce) which, instead, shows (Si+Al)/(other cations) = 0.76 (Table 1, column 3; 0.74 for the structure refinement). The same value, 0.76, is obtained from the data of Semenov *et al.* (1968) for the holotype ilímaussite-(Ce) (Table 1, column 1). Ratios close to those of ilímaussite-(Ce) are shown by the structural (0.86) and chemical (0.83; Table 1, column 6) data published for their Ti-dominant samples (KhibR), *i.e.*, diversilite-(Ce), by Khomyakov *et al.* (2003) and Rastsvetaeva *et al.* (2003). Further chemical data obtained by us (Table 1, columns 8 and 9) for diversilite-(Ce) confirm ratios of about 0.9.

The crystal structure published for KhibK shows the same number of oxygen atoms as ilímaussite-(Ce) (84 *apfu*), but differs in the contents of cations and H<sub>2</sub>O molecules as follows.

1. The Si sites in the A' layer are  $\frac{2}{3}$  instead of  $\frac{1}{2}$  occupied; thus, (Si + Al) amounts to 24 *apfu* in KhibK and 21 in ilímaussite-(Ce). That difference justifies the different structural formulae written above for the silicate part of the two minerals: only (Si<sub>6</sub>O<sub>18</sub>) rings in the cyclosilicate KhibK and (Si<sub>6</sub>O<sub>18</sub>) (A layer) rings plus the complex [Si<sub>9</sub>O<sub>18</sub>(O,OH)<sub>24</sub>] anion (A' layer) for the mixed anion silicate ilímaussite-(Ce).

2. As a result of the higher Si occupancy in the A' layer of KhibK, there is a minor occupancy of the (Ce<sub>2</sub>)O<sub>6</sub> octahedron (2 instead of 3 Ce<sub>2</sub> *apfu*).

3. Whereas molecular H<sub>2</sub>O is absent in ilímaussite-(Ce), it occupies the Na<sub>2</sub> site and 50% of the Ba<sub>1</sub> site in KhibK.

The above features justify the different ratio of (Si + Al) to (other cations) observed in KhibK and in ilímaussite-(Ce). In principle, the possibility of a series of ilímaussite-type structures with  $21 \leq \text{Si} \leq 24$  *apfu* and  $5 \leq \text{Ce} \leq 6$  *apfu* (plus further substitutions to balance the crystal-chemical formula) can be entertained. However, it must be noted that (Si + Al)/(other cations) = 1.26 shown by KhibK is by far higher than those obtained in the other samples (Table 1) of "Ti-dominant ilímaussite", which are in the range 0.83–0.91.

As discussed by Krivovichev *et al.* (2003), the structural disorder observed in KhibK, and confirmed in ilímaussite-(Ce), represents an average structure corresponding to a real structure where Si (and Ce) is ordered in the A' layer. A periodically ordered stacking of Si-ordered A' layers would produce different polytypes, as supported by the report of samples of "ilímaussite" samples with  $c \approx 20$  Å by Semenov *et al.* (1968) and Sokolova *et al.* (1968). The same value of the  $c$  parameter has been found during our unsuccessful search for a crystal of Ti-dominant "ilímaussite" suitable for a single-crystal X-ray study; instead, only  $c \approx 60$  Å has been found by us for ilímaussite-(Ce). There can be several reasons for the appearance of  $c \approx 20$  Å. First, as mentioned above, the diffraction maxima with  $l = 3n$  are by far stronger than those with  $l \neq 3n$  (indexing with  $c \approx 60$  Å), as can be seen also from the powder-diffrac-



tion pattern (Table 2); thus,  $c \approx 20 \text{ \AA}$  can be obtained if the weak reflections are missed. This is a realistic possibility, particularly if small and poor crystals are used together with classical data-collection methods (e.g., point-counter diffractometers, as we did in our preliminary search for crystals). Note that our structure determination and those of Rastsvetaeva *et al.* (2003) and Krivovichev *et al.* (2003) are based on CCD data. A second reason is that the  $c \approx 20 \text{ \AA}$  "ilímaussite" may represent an ordered one-layer polytype, (cf. the diffuse diffraction-maxima with  $l \neq 3n$  mentioned above), the common  $c \approx 60 \text{ \AA}$  "ilímaussite" being a disordered three-layer polytype. Presumably, polytypism and chemical composition are correlated if only the one-layer polytype occurs (or is more common) in the Ti-rich samples.

#### CONCLUSIONS

The crystal structure of ilímaussite-(Ce) from the Ilímaussaq type locality has been determined, and the chemical formula of Semenov *et al.* (1968) has been confirmed and re-arranged on a crystal-chemical basis. According to the structural study of Krivovichev *et al.* (2003), their Ti-dominant "ilímaussite", to be compared with diversilite-(Ce) defined by Khomyakov *et al.* (2003), differs from ilímaussite-(Ce) by a higher Si content. Presumably, a series of "ilímaussite" samples with  $21 \leq \text{Si} \leq 24 \text{ apfu}$  can exist, as well as different polytypes correlated with the chemical composition. Polytypism is favored by the close packing arrangement of the basal atoms of oxygen in the A' layer. A better assessment of the crystal chemistry in this group of minerals requires more reliable structure-refinements, so as to carefully determine the site occupancies. The supposed one-layer polytype with  $c \approx 20 \text{ \AA}$  should in principle show an ordered structure, but so far no suitable single crystals with this structure have been found, presumably because it occurs only as domains within other polytypes.

#### ACKNOWLEDGEMENTS

We are grateful to I.M. Kulikova and N.V. Chukanov for their assistance in obtaining electron-microprobe and IR data. The constructive comments of referees F. Liebau and P. Piilonen, Associate Editor E. Sokolova, and R.F. Martin helped to improve the content and form of the original text. The work was in part supported by the Russian Scientific Foundation (Grants 03–05–64054) and the Russian Universities Programme. G.F. and A.G. acknowledge the financial support by MIUR (PRIN and FIRB grants) and CNR (instrument facilities at Università di Modena e Reggio Emilia and Università di Torino). A stay in Italy by D.Yu.P. was made possible by a grant from MAE (Rome) in the framework of an Italian–Russian scientific and technological agreement. We are grateful to G. Giester for his kind assistance in collecting and processing the X-ray-

diffraction data at the Institute of Mineralogy of University of Vienna.

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Received November 20, 2003, revised manuscript accepted April 9, 2004.