THE CRYSTAL STRUCTURE OF ILÍMAUSSITE-(Ce), (Ba,Na)10K3Na4\textsubscript{5}Ce\textsubscript{5}(Nb,Ti)\textsubscript{6}[Si\textsubscript{12}O\textsubscript{36}][Si\textsubscript{9}O\textsubscript{18}(O,OH)\textsubscript{24}]O\textsubscript{6}, AND THE “ILÍMAUSSITE” PROBLEM

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ABSTRACT

The crystal structure of ilímaussite-(Ce), (Ba,Na)\textsubscript{10}K\textsubscript{3}Na\textsubscript{4.5}Ce\textsubscript{5}(Nb,Ti)\textsubscript{6}[Si\textsubscript{12}O\textsubscript{36}][Si\textsubscript{9}O\textsubscript{18}(O,OH)\textsubscript{24}]O\textsubscript{6}, 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 \( R\textsubscript{32}, Z = 3; \) MoK\( \alpha \) radiation; Nonius Kappa CCD X-ray diffractometer. The structure consists of three pairs of (001) silicate sheets. These sheets sandwich: CeO\textsubscript{6} trigonal prisms and Na cations (A layer), NbO\textsubscript{6} octahedra, Ba, and K (O layer), and CeO\textsubscript{6} trigonal prisms (A’ layer). The layers are stacked according to the sequence AO<A’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)\textsubscript{10}K\textsubscript{3}Na\textsubscript{4.5}Ce\textsubscript{5}(Nb,Ti)\textsubscript{6}[Si\textsubscript{12}O\textsubscript{36}][Si\textsubscript{9}O\textsubscript{18}(O,OH)\textsubscript{24}]O\textsubscript{6}, provenant de la localité-type, le complexe alcalin d’Ilímaussaq, dans le sud du Groënland, et nous l’avons affiné jusqu’à un résidu \( R = 0.11 \) pour 1663 réflexions observées, prélévées sur un cristal de bien piètre qualité \([a] 10.770(3), c 61.05(2) \) Å; groupe spatial \( R\textsubscript{32}, Z = 3; \) rayonnement MoK\( \alpha \); diffractomètre Nonius Kappa CCD]. La structure est faite de trois paires de feuillet silicatés. Ces feuillets (001) intercalent: les prismes trigonaux CeO\textsubscript{6} et les cations Na (feuillet A), les octaèdres NbO\textsubscript{6}, Ba, et K (feuillet O), et les prismes trigonaux CeO\textsubscript{6} (feuillet A’). Les feuillets sont empilés selon la séquence AO<A’O. Les sites tétraédriques du feuillet 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 Ti-dominant analogue de l’ilímaussite-(Ce), à comparer avec diversilite-(Ce), les mêmes sites ont été décris 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 feuillet A’.

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

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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 × 10 × 3 mm cluster consisting of brownish yellow lamellae with a resinous luster and associated with chkalovite and epistolite. The simplified formula of ilímaussite-(Ce), Na$_2$Ba$_2$CeFeNb$_3$Si$_8$O$_{28}$·5H$_2$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 $P6_3/mmc$, $P6_3/cm$ or $P6_22$.

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 $a$ 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 $R3$) for KhibR is substantially wrong. In particular, mixed-tetrahedron complexes formed by three-membered rings Si$_6$O$_{18}$ and isolated SiO$_4$ tetrahedra described for the $R3$ model are replaced by six-membered Si$_6$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, CuKα 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 Fe$^{3+}$. The deficiency of the sum from 100% compares with the weight loss reported by the same authors and is assigned to H$_2$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 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 MoKα radiation. All tested fragments showed broad, streaked and commonly split diffraction maxima. In particular, only hk0 and 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 20 = 55° (1.5° of 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 $R32$ and 1663 observed ones with $|F_o| > 4σ(F_o)$. Details of collection of the single-crystal X-ray data and the structure refinement of ilímaussite-(Ce) are given in Table 3.
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) for KhibK, 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 |Fo| > 4σ(|Fo|). 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 F0 andFc is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

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

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<thead>
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<th>4</th>
<th>5</th>
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<tr>
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<td>3.30</td>
<td>1.93</td>
<td>1.92</td>
<td>3.61</td>
<td>5.68</td>
<td>8.00</td>
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<td>1.56</td>
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<td>0.60</td>
<td>0.55</td>
<td>1.56</td>
<td>1.57</td>
<td>0.18</td>
</tr>
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<td>3.10</td>
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<td>0.60</td>
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<td>0.18</td>
</tr>
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<td>0.60</td>
<td>0.55</td>
<td>1.56</td>
<td>1.57</td>
<td>0.18</td>
</tr>
<tr>
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<td>3.10</td>
<td>0.60</td>
<td>0.60</td>
<td>0.55</td>
<td>1.56</td>
<td>1.57</td>
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<td>1.57</td>
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<td>1.56</td>
<td>1.57</td>
<td>0.18</td>
</tr>
</tbody>
</table>

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 |F0| > 4σ(|F0|). 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 F0 andFc 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 AOO’.
FIG. 1. Structure of ilimaussite-(Ce) projected on the (100) plane. Blue, green, and red polyhedra represent the (Ce1)O$_6$ and (Ce2)O$_6$ trigonal prisms, and the NbO$_6$ 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 O2, 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$_6$ octahedra that share their corners with SiO$_4$ 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$_{18}$O$_{62}$ six-membered rings of corner-sharing SiO$_4$ tetrahedra (Si1 and Si2; Fig. 2a). The two sheets sandwich isolated (Ce1)O$_6$ trigonal prisms plus Na1, Na2, and K2 cations that show coordination 6, 6, and 12, respectively (Table 5). The bases of the (Ce1)O$_6$ 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$_2$O molecules instead of Na have been assigned to the Na1 site.

In ilímaussite-(Ce), the assignment of Na1 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$_6$ (Si4)O$_6$ (Si5)O$_6$ tetrahedra; the sheets sandwich (Ce2)O$_6$ 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
crystallographically impossible if full occupancy of the SiO₄ tetrahedra occurs; in fact, the bond valence of an oxygen atom would already be saturated by two Si–O bonds. If the SiO₄ tetrahedra are 50% occupied only, ideally each oxygen atom would instead receive 1.5 bond-valence units. Actually, the bond-valence discussion below shows that all the basal atoms of oxygen of the A' layer partially represent OH groups, in agreement with the H₂O content indicated by the chemical analysis (Table 1). The 50% statistical occupancy of the Si sites means that locally the SiO₄ 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 KhbK, the occupancy of the Si3, Si4 and Si5 sites has been found to be ½, as further discussed below.

**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).

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

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<tr>
<th></th>
<th>Ce1 – O9</th>
<th>O8 – O9</th>
<th>O2 – O8</th>
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<th>Si1 – O9</th>
<th>Si1 – O10</th>
<th>Si1 – O16</th>
<th>Si2 – O10</th>
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<th>Si4 – O10</th>
<th>Si4 – O16</th>
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<td>2.41(2)</td>
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**TABLE 6. ANION–CATION BOND CONNECTIONS IN THE STRUCTURE OF ILÍMAUSSITE-(Ce)**

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* The Si3, Si4 and Si5 sites are 50% occupied. Each * indicates one bond.
• 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$_2$O 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 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 H2O. 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: (Ba0.84K3.58Na8.02Sr7.03)Σ12.74(REE)3.32Th0.19Fe3+1.01Mn0.18Si2.43(Nb1.42Ti1.87)Σ2.52Si3.07Al0.34O6.25(ΟΗ)1.17Σ2.11[Ο62.24(ΟΗ)20.29F1.17]Σ24.10, where REE = Ce2.04La0.81Nd0.31Pr0.13Sm0.03.

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: (Ba7)2K1.4Na5.8Th0.3Sr0.1)Σ11–12(ΚhibK)Ce3.7Fe3+1.3O6.73(Nb)Σ11–12(ΚhibK)Fe3+1.3O6.25(ΟΗ)1.17Σ2.11[Ο62.24(ΟΗ)20.29F1.17]Σ24.10, where REE = Ce2.04La0.81Nd0.31Pr0.13Sm0.03.

The values of density of ilímaussite-(Ce), calculated for the empirical (3.40 g/cm³) and the structural formula (3.595 g/cm³), are close to the measured value of 3.6 g/cm³ 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 Fe3+ (r = 0.65 Å) is not commonly reported in the literature; presumably, part of Fe could correspond to the larger Fe2+ (r = 0.78 Å). Krivovich 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 (BaNa)10K1.4Na5.8Ce3.7Fe3+1.3O6.73(Nb)Σ11–12(ΟΗ)1.17Σ2.11[Ο62.24(ΟΗ)20.29F1.17]Σ24.10. 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, Krivovich et al. (2003) obtained the structural formula (Ba,K,Na,Ca)1.12(REE,Fe,Th)(Ti,Nb)2(Σi2O36)Σ24.5H2O 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 Rastveteva 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 H2O molecules as follows.

1. The Si sites in the A′ layer are ⅔ instead of ½ 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 (Si6O18) rings in the cyclosilicate KhibK and (Si6O18) (A′ layers) rings plus the complex [Si6O18(O,OH)2] 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 (Ce2)O6 octahedron (2 instead of 3 Ce2 apfu).

3. Whereas molecular H2O is absent in ilímaussite-(Ce), it occupies the Na2 site and 50% of the Ba1 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 ≤ Ce ≤ 24 apfu and 5 ≤ Ce ≤ 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 Krivovich 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 to (other cations). The crystal structure of ilímaussite-(Ce), according to the following empirical formula: (Ba,K,Na,Ca)1.12(REE,Fe,Th)(Ti,Nb)2(Σi2O36)Σ24.5H2O 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 Rastveteva et al. (2003). Further chemical data obtained by us (Table 1, columns 8 and 9) for diversilite-(Ce) confirm ratios of about 0.9.

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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 ≤ Ce ≤ 24 apfu and 5 ≤ Ce ≤ 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 Krivovich 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 = 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 ≈ 60 Å has been found by us for ilímaussite-(Ce). There can be several reasons for the appearance of c = 20 Å. First, as mentioned above, the diffraction maxima with l = 3n are by far stronger than those with l ≠ 3n (indexing with c ≈ 60 Å), as can be seen also from the powder-diffrac-
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 ≤ Si ≤ 24 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 ≈ 20 Å 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.

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 ≤ Si ≤ 24 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 ≈ 20 Å 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.

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References


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