

Letter

Crystal structure of the K, Ti analogue of ilímaussite-(Ce), $(\text{Ba,K,Na,Ca})_{11-12}(\text{REE,Fe,Th})_4(\text{Ti,Nb})_6(\text{Si}_6\text{O}_{18})_4(\text{OH})_{12} \cdot 4.5 \text{H}_2\text{O}$: revision of structure model and structural formula

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Abstract. The crystal structure of the K, Ti analogue of ilímaussite-(Ce),

$(\text{Ba,K,Na,Ca})_{11-12}(\text{REE,Fe,Th})_4(\text{Ti,Nb})_6(\text{Si}_6\text{O}_{18})_4(\text{OH})_{12} \cdot 4.5 \text{H}_2\text{O}$, from the Yukspor mountain, Khibiny massif, Kola peninsula, Russia, has been solved by direct methods and refined to $R_1 = 0.077$ on the basis of 1762 reflections with $|F_o| \geq 4\sigma F$. The mineral is rhombohedral, $R\bar{3}2$, $a = 10.708(2)$, $c = 60.073(11)$ Å, $V = 5965.2(17)$ Å³. The structure is based upon a heteropolyhedral framework that consists of layers of corner-linked polyhedra. The SiO_4 tetrahedra share corners to form 6-membered rings which are further interlinked via REEO_6 trigonal prisms and $\text{Ti}\varphi_6$ octahedra ($\varphi = \text{O}, \text{OH}$). The obtained structure model is different from that recently reported by Rastsvetaeva et al. (2003) which is considered incorrect.

Introduction

Recently, porous titano- and niobosilicates have attracted considerable attention due to their applications in catalysis, gas separation, waste management, etc. [1]. Many of the porous titano- and niobosilicates have analogues among the mineral species (e.g. ETS-4 molecular sieve is a synthetic analogue of zorite). Thus, investigations of known mineral species may provide additional information for the design of porous materials in the laboratory. The structure of ilímaussite-(Ce), $\text{Ba}_2\text{Na}_4\text{CeFeNb}_2\text{Si}_8\text{O}_{28} \cdot 5 \text{H}_2\text{O}$, the mineral first described by Semenov et al. [2] from the Ilímaussaq alkaline massif, South Greenland, resisted structure solution for almost 35 years. Ilímaussite-(Ce) has also been described from the Khibiny alkaline complex, Kola peninsula, Russia [3–6]. The structural investigations were difficult because of: (1) large unit-cell dimensions (hexa-

gonal or trigonal, $a \sim 10.7$, $c \sim 60.5$ Å); (2) the pronounced streaking of reflections with $l = 2n$ that was interpreted [3] as a clear evidence of disorder of layers perpendicular to the c axis.

Very recently, Rastsvetaeva et al. [7] reported the crystal structure of the K, Ti analogue of ilímaussite-(Ce) from the Yukspor Mountain, Khibiny alkaline massif. The mineral was reported to be trigonal, space group $R\bar{3}$, $a = 10.713(1)$, $c = 60.67(1)$ Å. The structure was refined to $R = 0.087$ on the basis of 987 reflections with $F > 3\sigma(F)$ with an anisotropic refinement of cations but with isotropic refinement of anions. The structure was reported as consisting of isolated three-membered rings Si_3O_9 and insular SiO_3OH tetrahedra linked into a three-dimensional framework through TiO_6 octahedra, FeO_6 trigonal prisms and CeO_8 polyhedra [7]. Analysis of the structural data for the K, Ti analogue of ilímaussite-(Ce) reported in [7] showed that the structure solution is very probably incorrect. Geometrical parameters of the SiO_4 tetrahedra are out of the limits of possible deviations (O–Si–O angles are in the range of 88–168°; several O–O distances are smaller than 2.2 Å). In this paper, we report results of our independent single-crystal X-ray diffraction study of the K, Ti analogue of ilímaussite-(Ce) from the same locality (collection of the second author).

Experimental

A single brownish crystal of the Ti analogue of ilímaussite-(Ce) ((001) plate) selected for data collection was mounted on a Bruker PLATFORM goniometer equipped with a 1K SMART 1000 CCD detector with a crystal-to-detector distance of 5.4 cm. The data were collected using monochromatic $\text{MoK}\alpha$ X-radiation and frame widths of 0.3° in ω , with 90 s used to acquire each frame. More than a hemisphere of three-dimensional data were collected. Additional information regarding data collection and structure refinement is given in Table 1. The data

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were reduced using the Bruker program SAINT. A semi-empirical absorption-correction based upon the intensities of equivalent reflections was applied (program XPREP), and the data were corrected for Lorentz, polarization, and background effects. The Bruker SHELXTL Version 5.1 system of programs was used for the refinement of the crystal structure. The proper assignment of a space group was a problem. Initially, the non-centrosymmetric group *R3* was chosen. The positions of the heaviest cations (Ba, Ce) were located by direct methods, other cation and anion positions were found from the inspection of the difference Fourier maps. The *R3* model was refined to $R_1 \sim 0.09$. A search for higher symmetry in the *R3* model was done using the program *PLATON* [8] which suggested that the correct space group is *R32*. Consequently, the model was transformed into space group *R32* and the structure was refined to $R_1 \sim 0.085$. The value of the

Flack parameter (0.42(10)) indicated that the crystal under study was either twinned or the structure model corresponded to a different absolute configuration. The merohedral twinning was introduced into the refinement using the matrix [100/010/001] and the ratio of twin components was refined to the approximate value of 1:1. The final refinement included atomic positional and displacement parameters for all atoms. The Ba, K, and Ce sites were refined anisotropically, while all other sites were refined isotropically. The structure refinement demonstrated that the structure exhibits considerable disorder (see discussion below). The refinement resulted in a final agreement index (R_1) of 0.077, calculated for 1762 unique observed reflections ($|F_o| \geq 4\sigma F$) and a goodness-of-fit (*S*) of 1.051 (192 refined parameters). The final atomic parameters are listed in Table 1, selected interatomic distances are in Table 2.

Table 1. Crystallographic data, atomic coordinates and isotropic displacement parameters (\AA^2) for the K, Ti analogue of ilímaussite-(Ce).

<i>a</i> (Å)	10.708(2)			Total Ref.	12362	
<i>c</i> (Å)	60.073(11)			Unique Ref.	3218	
<i>V</i> (Å ³)	5965.2(17)			Unique $ F_o \geq 4\sigma F$	1762	
Space group	<i>R32</i>			<i>R1</i>	0.077	
Crystal size (mm)	0.15 × 0.15 × 0.05			<i>wR2</i>	0.207	
Radiation	MoK α			<i>S</i>	1.051	
Atom	Wyckoff letter	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
K(1)	6c	K _{0.87}	0	0	0.07397(11)	0.025(2)
K(2)	3a	K _{1.00}	0	0	0	0.099(8)
Ba(1)	18f	Ba _{0.50} (H ₂ O) _{0.50}	0.0006(2)	0.3250(2)	0.09959(4)	0.0241(8)
Ba(2)	6c	Ba _{0.90}	1/3	2/3	0.06651(4)	0.0252(8)
Ba(3)	6c	Ba _{0.94}	2/3	1/3	0.06643(3)	0.0234(7)
Na	18f	Na _{0.25} Ca _{0.12}	0.5015(30)	0.5015(30)	0.0281(3)	0.050 ^b
Ce(1)	6c	Ce _{0.62} Fe _{0.20} Th _{0.10}	2/3	1/3	0.00000(2)	0.0232(8)
Ce(2)	9e	Ce _{0.57} Th _{0.05} Fe _{0.05}	1/3	0.0012(2)	1/6	0.0195(9)
Ti	18f	Ti _{0.82} Nb _{0.10}	0.3414(3)	0.3409(3)	0.08387(9)	0.0183(8)
Si(1)	18f	Si _{1.00}	0.3271(5)	0.1664(9)	0.03823(7)	0.0190(11)
Si(2)	18f	Si _{1.00}	0.1602(8)	−0.1674(8)	0.03835(7)	0.0160(11)
Si(3)	18f	Si _{0.67}	0.1699(12)	0.1691(12)	0.13120(13)	0.024(2)
Si(4)	18f	Si _{0.67}	0.3389(9)	0.5024(12)	0.12993(13)	0.027(2)
Si(5)	18f	Si _{0.67}	0.5026(12)	0.3360(10)	0.12962(14)	0.030(2)
O(1)	18f	O _{1.00}	0.3385(12)	0.1866(15)	0.0653(2)	0.028(3)
OH(2)	18f	O _{1.00}	0.4990(30)	0.4991(30)	0.0660(2)	0.049(4)
O(3)	18f	O _{1.00}	0.1493(15)	−0.1885(15)	0.0652(2)	0.021(3)
O(4)	18f	O _{1.00}	0.1820(18)	0.1806(18)	0.1020(2)	0.038(4)
O(5)	18f	O _{1.00}	0.3367(15)	0.4909(19)	0.1013(2)	0.041(4)
O(6)	18f	O _{1.00}	0.4901(18)	0.3361(15)	0.1017(2)	0.035(4)
O(7)	18f	O _{1.00}	0.2215(15)	0.0005(13)	0.0307(2)	0.033(4)
O(8)	18f	O _{1.00}	0.4840(15)	0.2297(17)	0.0268(2)	0.049(4)
O(9)	18f	O _{1.00}	0.2542(18)	−0.2283(18)	0.0264(2)	0.050(4)
O(10)	18f	O _{1.00}	0.2658(14)	0.2654(14)	0.0274(2)	0.026(3)
O(11) ^a	6c	O _{1.00}	2/3	1/3	0.1351(9)	0.100 ^b
O(12)	18f	O _{1.00}	0.3439(24)	0.1962(34)	0.1402(4)	0.100 ^b
O(13)	18f	O _{1.00}	0.4768(32)	0.4690(33)	0.1391(4)	0.100 ^b
O(14)	18f	O _{1.00}	0.2077(30)	0.3422(25)	0.1402(4)	0.100 ^b
O(15) ^a	6c	O _{1.00}	0	0	0.1337(12)	0.150 ^b
O(16) ^a	6c	O _{1.00}	1/3	2/3	0.1354(10)	0.150 ^b
H ₂ O(17)	9d	H ₂ O _{0.50}	0.5092(27)	0.5092(27)	0	0.050 ^b

a: average of three disordered O sites

b: fixed during refinement.

Table 2. Selected bond lengths (Å) for the K, Ti analogue of ilimaussite-(Ce).

K(1)–O(4)	2.57(2) 3	Ti–O(5)	1.94(2)
K(1)–O(3)	3.18(2) 3×	Ti–O(6)	1.94(2)
K(1)–O(1)	3.19(2) 3×	Ti–O(3)	1.97(1)
⟨K(1)–O⟩	2.98	Ti–O(1)	1.98(1)
		Ti–OH(2)	2.00(3)
K(2)–O(7)	3.00(1) 6×	Ti–O(4)	2.03(2)
K(2)–O(10)	3.29(1) 6×	⟨Ti– φ^a ⟩	1.98
⟨K(2)–O⟩	3.15		
		Si(1)–O(8)	1.62(2)
Ba(1)–OH(2)	2.76(2)	Si(1)–O(7)	1.62(2)
Ba(1)–O(1)	2.83(1)	Si(1)–O(10)	1.64(1)
Ba(1)–O(3)	2.84(1)	Si(1)–O(1)	1.64(1)
Ba(1)–O(4)	3.01(1)	⟨Si(1)–O⟩	1.63
Ba(1)–O(4)	3.03(1)		
Ba(1)–O(5)	3.12(1)	Si(2)–O(9)	1.62(2)
Ba(1)–O(6)	3.13(1)	Si(2)–O(3)	1.62(1)
Ba(1)–O(5)	3.14(1)	Si(2)–O(10)	1.64(1)
Ba(1)–O(6)	3.16(1)	Si(2)–O(7)	1.64(1)
Ba(1)–O(12)	3.16(3)	⟨Si(2)–O⟩	1.63
Ba(1)–O(13)	3.22(3)		
Ba(1)–O(14)	3.24(3)	Si(3)–O(4)	1.76(2)
⟨Ba(1)– φ^a ⟩	3.05	Si(3)–O(14)	1.77(3)
		Si(3)–O(12)	1.82(3)
Ba(2)–O(5)	2.83(2) 3×	Si(3)–O(15)	1.82(1)
Ba(2)–O(9)	2.96(1) 3×	⟨Si(3)–O⟩	1.79
Ba(2)–O(3)	3.06(1) 3×		
Ba(2)–OH(2)	3.09(1) 3×	Si(4)–O(14)	1.70(3)
⟨Ba(2)– φ^a ⟩	2.99	Si(4)–O(5)	1.72(2)
		Si(4)–O(13)	1.77(3)
Ba(3)–O(6)	2.85(2) 3×	Si(4)–O(16)	1.82(2)
Ba(3)–O(8)	2.92(1) 3×	⟨Si(4)–O⟩	1.75
Ba(3)–O(1)	3.05(1) 3×		
Ba(3)–OH(2)	3.09(1) 3×	Si(5)–O(13)	1.68(3)
⟨Ba(3)– φ^a ⟩	2.98	Si(5)–O(6)	1.68(2)
		Si(5)–O(12)	1.73(3)
Ce(1)–O(9)	2.34(1) 3×	Si(5)–O(11)	1.80(2)
Ce(1)–O(8)	2.34(1) 3×	⟨Si(5)–O⟩	1.72
⟨Ce(1)–O⟩	2.34		
Ce(2)–O(12)	2.58(3) 2×		
Ce(2)–O(13)	2.66(3) 2×		
Ce(2)–O(14)	2.70(3) 2×		
⟨Ce(2)–O⟩	2.65		

a: $\varphi = \text{O, OH}$

The chemical analyses were performed using CAMECA MS-46 electron microprobe operated at 20 kV and 20–40 nA. The following standards were used: lorenzenite (Na and Ti), diopside (Ca, Si), wadeite (K), MnCO_3 syn. (Mn), hematite (Fe), celestine (Sr), Nb metal (Nb), LaCeS_3 (La, Ce), $\text{LiNd}(\text{MoO}_4)_2$ (Nd), ThO_2 (Th), and BaSO_4 syn. (Ba). The chemical composition (wt%): Na_2O 1.32, SiO_2 39.78, K_2O 3.33, CaO 1.01, TiO_2

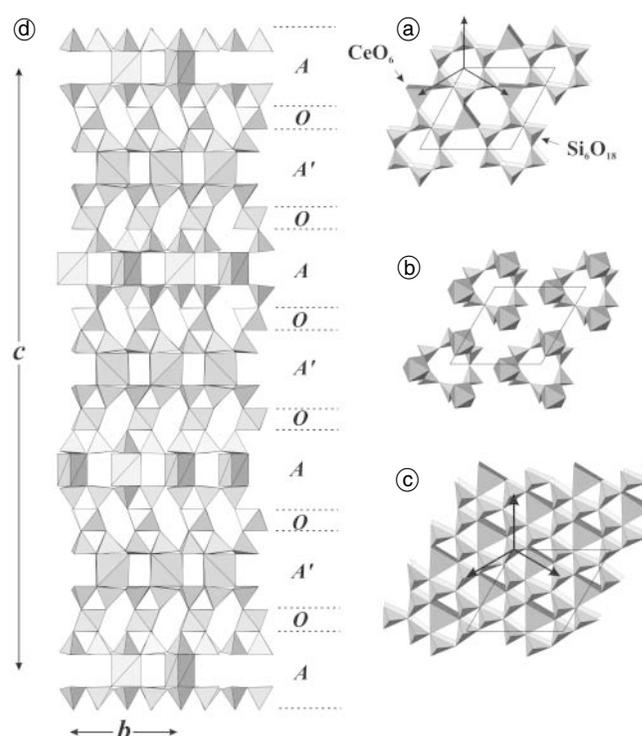


Fig. 1. The crystal structure of Ti analogue of ilimaussite-(Ce) projected along [201] (a); the A layer (b); the Ti octahedra from the O layer linked to the silicate rings of the A layer (c); the average structure of the A' layer (d). The arrows in (b) and (d) indicate the $\pm 1/3$ (a + 2b) shifts of the layer A (b) that produce the average arrangement of (d).

10.82, MnO 0.05, Fe_2O_3 1.63, SrO 0.64, Nb_2O_5 2.52, BaO 22.17, La_2O_3 2.89, CeO_2 6.59, Nd_2O_3 0.84, Sm_2O_3 0.12, ThO_2 2.00, total 95.71. The empirical chemical formula, calculated on the basis of $\text{Si} = 24$, is $(\text{Na}_{1.55}\text{K}_{2.56}\text{Ba}_{5.24}\text{Ca}_{0.65}\text{Sr}_{0.22})_{\Sigma=10.22}(\text{Ce}_{1.39}\text{Fe}_{0.74}\text{La}_{0.64}\text{Th}_{0.27}\text{Nd}_{0.18}\text{Mn}_{0.03}\text{Sm}_{0.02})_{\Sigma=3.28}(\text{Ti}_{4.91}\text{Nb}_{0.69})_{\Sigma=5.60}\text{Si}_{24}\text{O}_{73.44}$.

Results

There are two Ce sites in the structure and they are coordinated by six O atoms to form CeO_6 trigonal prisms. The threefold rotation axes of the prisms are parallel to the c axis. One symmetrically independent Ti position is octahedrally coordinated by six anions. There are five symmetrically independent Si sites in the structure and all of them are tetrahedrally coordinated by four O atoms. The Si(1) and Si(2) sites are fully occupied whereas the Si(3),

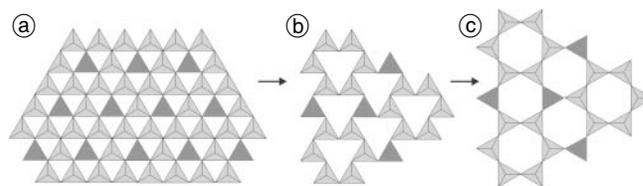


Fig. 2. The average structure of the A' layer (a) is a superposition of three A-type layers which are intermediate between (b) and (c). The cation positions within this layer are well-defined, whereas almost all anion positions are highly disordered. See text for further discussion.

Si(4) and Si(5) sites have refined site-occupancy factors of $2/3$. Because the O ligands of these three Si sites are disordered, the respective Si–O bonds are anomalously long (Table 2), an explanation is given in the Discussion. There are two symmetrically independent K positions, K(1) and K(2), coordinated by nine and twelve anions, respectively. The three symmetrically independent Ba atoms are coordinated by twelve anions each. One of the Ba sites is assumed to be occupied also by H_2O , with a occupancy ratio Ba: H_2O of 1:1. The one Na position is disordered (s.o.f. <0.5 ; s.o.f. = site-occupancy factor) and has approximately sevenfold coordination with Na–O bond lengths in the range of 2.27–2.83 Å.

The structure of the Ti analogue of ilímaussite-(Ce) is shown in Fig. 1a. It represents a heteropolyhedral framework that can be described as consisting of different types of layers of corner-linked polyhedra. Within the layer *A* (Fig. 1b), the Si(1)O₄ and Si(2)O₄ tetrahedra share corners to form Si₆O₁₈ six-membered rings that are parallel to (001). The SiO₄ tetrahedra of the Si₆O₁₈ rings share corners with Ce(1)O₆ trigonal prisms to form double layers parallel to (001). The layer *O* (Fig. 1c) consists of TiO₅(OH) octahedra that share two corners each with two silicate tetrahedra of the six-membered rings. The layer *A'* (Fig. 1d) consists of three Si sites, Si(3), Si(4) and Si(5), and the Ce(2) site. These latter cation sites are only $2/3$ occupied. The apical oxygen atoms of the SiO₄ tetrahedra are well-defined and correspond to O positions of the Tiφ₆ octahedra (φ = O, OH) within the *O* layer. These are the O(4), O(5) and O(6) sites that are bonded to the Si(3), Si(4) and Si(5) atoms, respectively. As the s.o.f.s of the Si positions are $2/3$, the occupancies of the O(4), O(5) and O(6) sites are defined as O_{2/3}(OH)_{1/3}. In contrast to the apical vertices of the SiO₄ tetrahedra, their triangular bases parallel to (001) are poorly defined. The anions corresponding to these vertices are located in the plane at $z = 0.13–0.14$. During the structure determination, it was observed that the anions within this plane are highly disordered. In order to get a physically reasonable atomic arrangement, the O(11), O(15), and O(16) atoms were placed on threefold symmetry axes, though their real positions were in fact disordered over three sites each related by these axes. The O(12), O(13), and O(14) positions were restrained to be at reasonable distances from the two Si sites each. The resulting average structure of the *A'* layer is shown in Fig. 1d. This structure is crystal-chemically impossible if all Si positions are fully occupied as the O(11), O(15), and O(16) atoms would be shared between three SiO₄ tetrahedra each. However, taking into account the $2/3$ occupancies of the Si(3), Si(4), Si(5), and Ce(2) sites, we suggest that the observed *A'* layer is the result of superposition of three ordered arrangements shifted by $\pm 1/3(\mathbf{a} + 2\mathbf{b})$ with respect to each other. This is schematically shown in Fig. 2. The arrangement shown in Fig. 2a represents the idealized structure of the refined average *A'* layer (compare with Fig. 1d). Removal of $1/3$ of SiO₄ tetrahedra and CeO₆ trigonal prisms results in the sheet shown in Fig. 2b. This sheet consists of Si₆O₁₈ rings interlinked by CeO₆ trigonal prisms, i.e. it is topologically identical to the *A* layer (Fig. 1b). Local adjustments of the Si–O bonds within the SiO₄ tetrahedra would result in the

idealized sheet shown in Fig. 2c. However, it is most likely that the correct arrangement is intermediate between the sheets shown in Figs. 2b and 2c. The proposed model of the average structure of the *A'* layer as a superposition of three ordered arrangements shifted relative to each other by $\pm 1/3(\mathbf{a} + 2\mathbf{b})$ helps to explain: (1) site-occupancies of $2/3$ for the Si(3), Si(4), Si(5), and Ce(2) sites; (2) strong disorder of anions within the atomic plane at $z = 0.13–0.14$; (3) the anomalously long Si–O distances. Moreover, from the viewpoint of structural complexity, it is also reasonable that the *A'* layer, in its ordered version, is topologically identical to the *A* layer separated from it by the *O* sheet of the TiO₆ octahedra.

The crystal-chemical formula of Ti analogue of ilímaussite-(Ce) determined on the basis of this structure analysis is

$(Ba_{6.68}K_{2.74}Na_{1.50}Ca_{0.72})_{\Sigma=11.64}(Ce_{2.95}Fe_{0.55}Th_{0.35})_{\Sigma=3.85} \cdot (Ti_{4.92}Nb_{0.60})_{\Sigma=5.52}[Si_6O_{18}]_4(OH,O)_{12} \cdot 4.5 H_2O$. This formula is in general agreement with the empirical formula given above. The simplified formula is $(Ba,K,Na,Ca)_{11-12}(REE,Fe,Th)_4M_6[Si_6O_{18}]_4(OH,O)_{12} \cdot n H_2O$ where *REE* = Ce for ilímaussite-(Ce), *M* = Ti or Nb for the Khibiny and Ilímaussaq samples, respectively.

Discussion

The structure of ilímaussite-(Ce) consists of alternating topologically identical ordered and disordered layers. The presence of two-dimensional structural disorder within the *A'* layer is in complete agreement with the conclusions derived by Sokolova et al. [3] from analysis of the partially diffuse character of the single-crystal diffraction pattern of ilímaussite-(Ce). The disorder observed in the structure of the Ti analogue of ilímaussite-(Ce) is usual for layered silicate structures such as micas [9] or chlorites [10].

Taking into account the existence of “ilímaussites” with $c \sim 20$ Å [2, 3, 7], it is possible that the structure reported in this paper represents a disordered three-layer polytype of ilímaussite, whereas the 20 Å structure would be a one-layer polytype. Further investigations of “ilímaussites” are necessary in order to study possible existence of other polytypes in this mineral group.

The structural model determined for the K, Ti analogue of ilímaussite-(Ce) in this work is remarkably different from that reported by Rastsvetaeva et al. [7]. The major difference is that the structure is based upon Si₆O₁₈ six-membered rings of silicate tetrahedra, instead of three-membered Si₃O₉ rings and insular SiO₃OH tetrahedra as reported in [7]. The correct space group is the non-centrosymmetric group *R*32 instead of the centrosymmetric group *R* $\bar{3}$ proposed by Rastsvetaeva et al. [7]. As a result of the wrong space group assignment, the structural model reported by Rastsvetaeva et al. [7] is incorrect.

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