

# Odigitriaite, $\text{CsNa}_5\text{Ca}_5[\text{Si}_{14}\text{B}_2\text{O}_{38}]\text{F}_2$ , a new caesium borosilicate mineral from the Darai-Pioz alkaline massif, Tajikistan: Description and crystal structure

ATALI A. AGAKHANOV<sup>1,2</sup>, LEONID A. PAUTOV<sup>2</sup>, ELENA SOKOLOVA<sup>3</sup>, FRANK C. HAWTHORNE<sup>3,\*</sup>, VLADIMIR YU. KARPENKO<sup>2</sup>, OLEG I. SIIDRA<sup>1</sup> AND VYACHESLAV A. MUFTAKHOV<sup>4,5</sup>

<sup>1</sup> Department of Crystallography, St. Petersburg State University, University Emb. 7/9, 119034 St Petersburg, Russia

<sup>2</sup> Fersman Mineralogical Museum, Russian Academy of Sciences, Leninskii Pr-t, Bldg. 18, 117071 Moscow, Russia

<sup>3</sup> Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

<sup>4</sup> Institute of Mineralogy, Urals Branch of Russian Academy of Sciences, 456317 Ilmen Nature Reserve, Miass, Russia

<sup>5</sup> Faculty of Geology, National Research South Urals State University, Miass Branch, 8 July Street, Bldg 10, 456304 Miass, Russia

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## ABSTRACT

Odigitriaite, a new  $\text{Cs,Na,Ca}$  borosilicate mineral, was discovered in moraine adjacent to the Darai-Pioz alkaline massif in the upper reaches of the Darai-Pioz river at the intersection of the Turkestansky, Zeravshansky and Alaisky mountain ridges, Tajikistan. It occurs as irregular thin flakes associated with quartz, pectolite, baratovite, fluorite, pekovite, polyolithionite, aegirine, leucosphenite, pyrochlore, neptunite, reedmergnerite, mendeleevite-(Ce), zeravshanite and sokolovaite. It is colourless with a white streak, is translucent and has a vitreous lustre; it does not fluoresce under ultraviolet light. Odigitriaite is brittle with an uneven fracture and a Mohs hardness of 5. The calculated density is  $2.80(2) \text{ g/cm}^3$ . The indices of refraction are  $\alpha = 1.502$ ,  $\beta = 1.564$ ,  $\gamma = 1.576$ ;  $2V_{\text{obs}} = 46(2)^\circ$ , dispersion is weak  $r > v$ , and there is no pleochroism. The chemical composition is as follows (electron microprobe,  $\text{H}_2\text{O}$  calculated from structure):  $\text{SiO}_2$  55.30,  $\text{Al}_2\text{O}_3$  0.09,  $\text{Y}_2\text{O}_3$  0.44,  $\text{MnO}$  0.94,  $\text{FeO}$  0.10,  $\text{PbO}$  0.21,  $\text{K}_2\text{O}$  0.01  $\text{Cs}_2\text{O}$  8.36,  $\text{B}_2\text{O}_3$  4.75,  $\text{H}_2\text{O}$  0.37, F 1.74,  $\text{O} = \text{F}_2$  -0.74, total 99.43 wt.%. The empirical formula of odigitriaite is  $\text{Cs}_{0.90}\text{Na}_{5.12}\text{Ca}_{4.68}\text{Mn}_{0.20}\text{Y}_{0.06}\text{Fe}_{0.02}\text{Pb}_{0.01}[\text{Si}_{13.92}\text{Al}_{0.03}\text{B}_{2.06}\text{O}_{38}]\text{F}_{1.39}(\text{OH})_{0.62}$ . The end-member formula is  $\text{CsNa}_5\text{Ca}_5[\text{Si}_{14}\text{B}_2\text{O}_{38}]\text{F}_2$ . The strong reflections in the powder X-ray diffraction pattern are:  $[(d, \text{\AA}), (I, \%), (hkl)]: 5.45 (25) (1\ 1\ 3), 4.66 (33) (3\ 1\ 1), 4.40 (26) (0\ 2\ 2), 4.10 (36) (\bar{3}\ 1\ 3), 3.95 (25) (3\ 1\ 3), 2.85 (31) (2\ 2\ 2), 2.68 (40) (0\ 0\ 6), 3.62 (45) (0\ 2\ 4), 3.35 (100) (\bar{2}\ 2\ 4), 3.31 (30) (\bar{3}\ 1\ 5), 3.25 (35) (4\ 0\ 4), 3.04 (60) (\bar{4}\ 2\ 2), 2.925 (22) (\bar{4}\ 2\ 3), 1.813 (23) (9\ 1\ 0)$ . Odigitriaite is monoclinic, space group  $C2/c$ ,  $a = 16.652(5)$ ,  $b = 9.598(3)$ ,  $c = 22.120(7) \text{ \AA}$ ,  $\beta = 92.875(14)^\circ$ ,  $V = 3530.9(1.9) \text{ \AA}^3$ ,  $Z = 4$ . The crystal structure of odigitriaite was solved by direct methods and refined to an  $R_1$  value of 2.75% based on single-crystal X-ray data. It is a double-layer sheet-borosilicate mineral; Cs and Na are intercalated within the double-layer sheet, and the double layers are linked by interstitial Ca and Na atoms.

**KEYWORDS:** odigitriaite, new mineral, crystal-structure refinement, electron-microprobe analysis, borosilicate.

## Introduction

ODIGITRIAITE is a new  $\text{Cs,Na,Ca}$  borosilicate found in the Darai-Pioz moraine close to the Darai-Pioz

alkaline massif, Tajikistan. The name odigitriaite is from the Greek word  $\text{Ὀδηγήτρια}$  (She who shows the way; Russian Cyrillic: Оди́гитрия - Указу́ющая Пу́ть). Odigitriaite is so named to emphasize the role of Cs as a major indicator of extreme fractionation. The mineral species and mineral name were approved by the International Mineralogical Association Commission on New

\*E-mail: frank\_hawthorne@umanitoba.ca

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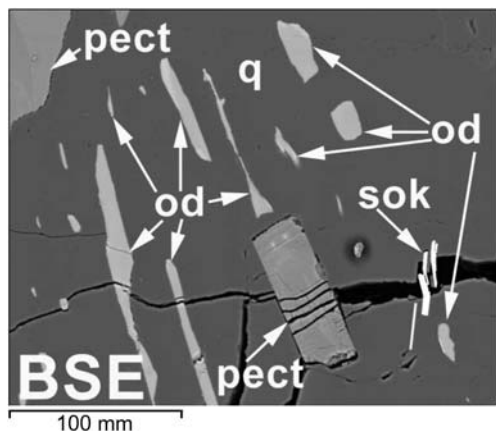


FIG. 1. Back-scattered electron image of odigitriaite and associated minerals in a matrix of quartz; od = odigitriaite, pect = pectolite, sok = sokolovaite, q = quartz.

Minerals, Nomenclature and Classification as IMA 2015-028. The holotype sample has been deposited in the collection of the A.E. Fersman Mineralogical Museum, Russian Academy of Science, Moscow, (reg. N 4706/1).

## Occurrence

The outcrops of the Darai-Pioz massif are difficult to access, and most mineralogical work has been

undertaken on material collected from the associated glacial moraine. The total outcrop is about 18 km<sup>2</sup>, and in plan the massif is oval, slightly elongated to the NW. The central part of the outcrop is comprised of fine- and medium-grained aegirine syenites and fenites. The rim is comprised of medium-grained Late Carboniferous tourmaline granites. In the eastern part of the massif, there is a plug of coarse-grained cancrinite foyaite ~2 km<sup>2</sup> in outcrop (Dusmatov, 1968, 1971). There is extensive rare-metal mineralization associated with alkaline pegmatites, carbonatites and fenites. One important feature of the massif is the wide variety of Cs minerals: Kupletskite-(Cs) (Yefimov *et al.*, 1971), telyushenkoite (Agakhanov *et al.*, 2003; Sokolova *et al.*, 2002), zerafshanite (Pautov *et al.*, 2004; Uvarova *et al.*, 2004), senkevichite (Agakhanov *et al.*, 2005; Uvarova *et al.*, 2006), sokolovaite (Pautov *et al.*, 2006), kirchhoffite (Agakhanov *et al.*, 2012), mendeleeveite-(Ce) (Sokolova *et al.*, 2011; Pautov *et al.*, 2013), mendeleeveite-(Nd) (Agakhanov *et al.*, 2015).

Odigitriaite was found in the most unusual of the rocks from the Darai-Pioz moraine deposits: cobbles and boulders of quartz (and many rare accessory minerals), ranging in size from 5 to 80 cm. Anhedral quartz contains inclusions of slightly deformed 'stacks' of polyolithionite, crystals of pale-green to white microcline, patches of pale-pink reedmergerite,

TABLE 1. Chemical analysis (wt.%) and unit formula for odigitriaite (apfu).

Constituent	Average	Range	Sigma	Unit formula	
SiO <sub>2</sub>	55.30	54.34–56.36	0.53	Si	13.92
Y <sub>2</sub> O <sub>3</sub>	0.44	0.00–1.21	0.41	Y	0.06
Al <sub>2</sub> O <sub>3</sub>	0.09	0.00–1.21	0.10	Al	0.03
B <sub>2</sub> O <sub>3</sub>	4.75	4.33–5.06	0.24	B	2.06
PbO	0.21	0.08–0.42	0.12	Pb	0.01
FeO	0.10	0.00–0.22	0.09	Fe	0.02
MnO	0.94	0.48–1.34	0.23	Mn	0.20
CaO	17.37	16.80–17.92	0.33	Ca	4.68
Cs <sub>2</sub> O	8.36	7.85–9.00	0.33	Cs	0.90
K <sub>2</sub> O	0.01	0.00–0.06	0.02	K	0.00
Na <sub>2</sub> O	10.49	10.07–10.89	0.22	Na	5.12
F	1.74	1.64–1.79	0.04		
H <sub>2</sub> O**	0.37				
–O = F	–0.74				
Total	99.43				

\*Formula calculated on the basis of 40 O apfu, Z = 4.

\*\*H<sub>2</sub>O calculated from structure refinement.

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TABLE 2. Powder X-ray diffraction data for odigitriaite.

I	$d_{\text{obs.}} (\text{\AA})$	$d_{\text{calc.}} (\text{\AA})$	$h k l$	I	$d_{\text{obs.}} (\text{\AA})$	$d_{\text{calc.}} (\text{\AA})$	$h k l$
12	8.31	8.316	2 0 0	16	2.759	2.762	0 0 8
10	7.85	7.846	$\bar{1}$ 1 1	10	2.741	2.742	$\bar{1}$ 3 4
14	5.53	5.523	0 0 4	12	2.676	2.678	5 1 4
25	5.45	5.445	1 1 3	8	2.575	2.572	$\bar{1}$ 3 5
8	4.81	4.799	0 2 0				3 3 3
33	4.66	4.649	3 1 1	13	2.504	2.505	5 1 5
3	4.55	4.55	1 1 4	5	2.437	2.436	4 2 6
26	4.4	4.402	0 2 2	10	2.399	2.401	$\bar{1}$ 3 6
36	4.1	4.104	$\bar{3}$ 1 3			2.4	6 2 0
			$\bar{2}$ 2 1	7	2.378	2.379	1 3 6
25	3.95	3.944	3 1 3	5	2.283	2.282	$\bar{5}$ 1 7
31	3.85	3.858	2 2 2	6	2.214	2.216	1 3 7
		3.83	4 0 2			2.21	0 0 10
40	3.68	3.682	0 0 6	4	2.139	2.138	$\bar{2}$ 4 4
45	3.62	3.623	0 2 4	3	2.101	2.102	5 3 4
100	3.35	3.361	$\bar{2}$ 2 4	4	2.051	2.052	$\bar{6}$ 2 6
30	3.31	3.324	$\bar{3}$ 1 5	3	1.972	1.971	4 2 9
35	3.25	3.245	4 0 4	3	1.932	1.931	2 2 10
10	3.11	3.115	$\bar{1}$ 3 1	8	1.864	1.867	7 3 2
60	3.04	3.053	$\bar{4}$ 2 2			1.865	8 2 2
		3.03	$\bar{1}$ 3 2	23	1.813	1.815	9 1 0
12	2.984	2.986	5 1 2			1.814	6 4 0
		2.975	$\bar{1}$ 1 7			1.814	3 5 0
22	2.925	2.93	$\bar{4}$ 2 3	3	1.752	1.755	3 5 3
		2.926	$\bar{1}$ 3 2	4	1.708	1.708	9 1 5
8	2.901	2.9	$\bar{1}$ 3 3	4	1.697	1.698	$\bar{6}$ 4 5
10	2.838	2.842	5 1 3	6	1.661	1.662	$\bar{6}$ 2 10
		2.828	$\bar{4}$ 0 6	5	1.569	1.571	8 4 0
9	2.789	2.791	$\bar{2}$ 2 6	4	1.545	1.546	10 2 2
		2.789	$\bar{5}$ 1 4				

randomly distributed black idiomorphic crystals of aegirine, rare red-brown translucent lenticular crystals of stillwellite-(Ce), grass-green translucent to transparent crystals of leucosphenite, violet-pink plates of sogdianite, and dark-green crystals of turkestanite. Brown patches (up to 30 cm) of pectolite, quartz, Sr-rich fluorite, aegirine, polyolithionite and a wide range of rare minerals are also common. Odigitriaite occurs in these brown patches associated with pectolite aggregate, pekovite, mendeleevite-(Ce), orlovite, kirchhoffite, neptunite, zeravshanite, senkevichite, nordite-(Ce), alamosite, hyalotekite and khvorovite (Fig. 1).

## Physical properties

Odigitriaite occurs as irregular elongated grains up to 100  $\mu\text{m}$  long. It is colourless with a white streak, is translucent and has a vitreous lustre; it does not

fluoresce under ultraviolet light. The cleavage is perfect on {001} and no parting or twinning was observed. The Mohs hardness is 5, microhardness VHN, measured with PMT-3, calibrated with NaCl, is 606  $\text{kg/mm}^2$  (average of 10 measurements ranging from 560 to 655  $\text{kg/mm}^2$ , loading is 50 g); odigitriaite is brittle with an uneven fracture, and tends to be rather fragile. The observed density, measured by flotation in a mixture of dimethylformamide and bromoform, is 2.80(2)  $\text{g/cm}^3$  and the calculated density is 2.830  $\text{g/cm}^3$ . Optical properties were measured for the wavelength 590 nm. The indices of refraction are  $\alpha(\text{calc}) = 1.502$ ,  $\beta = 1.564$ ,  $\gamma = 1.576$ , all  $\pm 0.002$ ;  $2V_{\text{meas.}} = 46(2)^\circ$  (measured with a Fedorov stage); we could not measure the  $\alpha$  refractive index because the flakes are only a couple of micrometres thick, and  $\alpha$  was calculated from  $\beta$ ,  $\gamma$  and  $2V_{\text{meas.}}$ . The dispersion is  $r > v$ , weak. No pleochroism was observed.

TABLE 3. Miscellaneous information on data collection and structure refinement.

<i>a</i> (Å)	16.652 (5)
<i>b</i>	9.598 (3)
<i>c</i>	22.120 (7)
β (°)	92.875 (14)
<i>V</i> (Å <sup>3</sup> )	3530.9 (19)
Space group	<i>C2/c</i>
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	2.830
Crystal size (μm)	30 × 60 × 80
Radiation	MoKα
No. of reflections	20,765
No. unique reflections	5219
No. with ( <i>F</i> <sub>o</sub> > 4σ <i>F</i> )	4886
<i>R</i> <sub>1</sub> %	2.75
<i>wR</i> <sub>2</sub> %	7.28

$$R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_c|$$

$$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$$

$$w = 1 / [\sigma^2(F_o^2) + (0.0328 P)^2 + 16.69 P] \text{ where } P = (\max(F_o^2, 0) + 2F_c^2) / 3.$$

### Chemical composition

Electron-microprobe analyses of odigitriaite were carried out with a JEOL JCXA-733 instrument operating in energy-dispersive mode for all elements (except B and F) with an accelerating voltage of 50 kV, a beam current of 2 nA and a beam diameter of 1 μm. Boron and F were analysed in wavelength-dispersive mode with an accelerating voltage of 10 kV, a beam current of 20 nA and a beam diameter of 5 μm. The standards used are as follows: microcline USNM 143966 (Si, Al, K), anorthite USNM 137041 (Ca), ilmenite USMN 96189 (Fe), Mn (Mn), YPO<sub>4</sub> (Y), omphacite USNM 110607 (Na), MgF<sub>2</sub> (F), danburite (B). The grains are homogenous and free of included minerals. Data were reduced using the correction procedure of Pouchou and Pichoir (1985). The chemical composition (mean of 10 determinations) is given in Table 1. The empirical formula was calculated on the basis of 40 anions with (F + OH) = 2 apfu (atoms per formula unit) and is as follows: Cs<sub>0.90</sub>Na<sub>5.12</sub>Ca<sub>4.68</sub>Mn<sub>0.20</sub>Y<sub>0.06</sub>Fe<sub>0.02</sub>Pb<sub>0.01</sub>[Si<sub>13.92</sub>Al<sub>0.03</sub>B<sub>2.06</sub>O<sub>38</sub>]F<sub>1.39</sub>(OH)<sub>0.62</sub>, the simplified formula is (Cs,Na)Na<sub>5</sub>(Ca,Mn,Fe,Y,Pb)<sub>5</sub>[Si<sub>14</sub>B<sub>2</sub>O<sub>38</sub>]F<sub>2</sub>, and the end-member formula is CsNa<sub>5</sub>Ca<sub>5</sub>[Si<sub>14</sub>B<sub>2</sub>O<sub>38</sub>]F<sub>2</sub>.

### Powder X-ray diffraction

We did not collect powder X-ray diffraction data because of the paucity of material. We provide

two-dimensional data by collapsing the three-dimensional diffraction data into two dimensions (Table 2); in this way, we can guarantee that the data are representative of the chemical composition and crystal structure also presented here.

### Single-crystal X-ray diffraction

A single crystal was attached to a tapered glass fibre and mounted on a Bruker APEX II ULTRA three-circle diffractometer equipped with a rotating-anode generator (MoKα), multilayer optics and an APEX II 4 K CCD detector. A total of 69,088 intensities was collected to 60°2θ using 30 s per 0.2° frame with a crystal-to-detector distance of 5 cm. Empirical absorption corrections (*SADABS*, Sheldrick, 2008) were applied, Lorentz, polarization and background corrections were carried out, and equivalent reflections were merged, resulting in 5219 unique reflections. The unit-cell dimensions (Table 3) were obtained by least-squares refinement of the positions of 4059 reflections with *I* > 10σ*I*.

### Crystal-structure solution and refinement

The structure of odigitriaite was solved by direct methods in the space group *C2/c* using *F*<sup>2</sup> in the *SHELXTL PLUS* (PC version) software package. Eight sites, labelled *T*, are tetrahedrally coordinated and the formula indicates that they are occupied by Si and B. Preliminary refinement and examination of refined site-scattering values (Hawthorne *et al.*, 1995) and <*T*–O> distances showed that *T*(1–6) are occupied by Si and the site occupancies were set to unity. The *T*(7–8) sites showed site-scattering values less than 14 eps (electrons per site) and <*T*–O> distances significantly less than 1.60 Å; thus the *T*(7–8) sites were assigned as occupied by both Si and B and their site-scattering values were refined. Similarly, preliminary refinement of the [6]- and [7]-coordinated *Ca*(1–3) sites showed *Ca*(2) and *Ca*(3) to have site-scattering values consonant with complete occupancy by Ca, and these sites were fixed as such in the refinement. The *Ca*(1) site showed a site-scattering slightly larger than that of Ca. As the formula shows an additional five cations (probably) occupying this site, the occupancy of Ca at *Ca*(1) was set as variable in the refinement. There were three sites with coordinations of [5] and 2 × [6] and with scattering values and mean distances that indicated occupancy dominantly by Na; these sites were labelled *Na* (1–3). In preliminary refinement, the site-scattering

TABLE 4. Atom coordinates and displacement parameters ( $\text{\AA}^2$ ) for odigitriaite.

Site	x	y	z	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$	$U_{\text{eq}}$
Cs	0	0.22942(3)	$\frac{1}{4}$	0.0716(3)	0.02393(15)	0.04100(18)	0	0.03639(16)	0	0.04438(13)
Na(1)	0	-0.23884(17)	$\frac{1}{4}$	0.0154(6)	0.0367(8)	0.0230(7)	0	-0.0013(5)	0	0.0251(3)
Na(2)	-0.23858(13)	0.96181(19)	0.24945(10)	0.0886(13)	0.0502(9)	0.0920(13)	-0.0387(9)	-0.0578(11)	0.0522(10)	0.0790(7)
Na(3)	0.28573(4)	0.42751(8)	-0.00566(3)	0.0191(4)	0.0159(4)	0.0213(4)	-0.0068(3)	-0.0042(3)	0.0059(3)	0.0189(3)
Na(4)	0.0206(11)	0.219(2)	0.3398(10)	0.036(10)	0.036(10)	0.067(14)	-0.010(9)	0.011(8)	-0.001(7)	0.046(7)
Ca(1)	0.14318(2)	0.71156(4)	0.02193(2)	0.00887(17)	0.00886(17)	0.01083(18)	0.00005(12)	0.00122(12)	-0.00077(11)	0.00950(11)
Ca(2)	-0.06985(2)	0.64883(4)	0.00514(2)	0.01113(17)	0.01174(17)	0.01369(18)	0.00164(13)	-0.00039(13)	-0.00069(13)	0.01222(8)
Ca(3)	0	0	0	0.0160(3)	0.0129(3)	0.0164(3)	0.0007(2)	-0.0015(2)	0.0013(2)	0.01520(11)
T(1)	0.04129(3)	0.52038(6)	0.12996(2)	0.0081(2)	0.0082(2)	0.0095(2)	0.00010(17)	0.00040(17)	0.00032(17)	0.00862(10)
T(2)	0.20603(3)	0.15894(5)	0.38613(2)	0.0090(2)	0.0076(2)	0.0097(2)	-0.00055(17)	-0.00017(17)	0.00057(17)	0.00877(10)
T(3)	0.14023(3)	0.45648(6)	0.38147(2)	0.0090(2)	0.0091(2)	0.0099(2)	0.00052(17)	0.00080(17)	0.00141(17)	0.00932(10)
T(4)	0.09505(3)	-0.03464(6)	0.13559(2)	0.0098(2)	0.0085(2)	0.0113(2)	-0.00117(18)	-0.00051(17)	-0.00038(17)	0.00991(10)
T(5)	0.08953(3)	-0.08956(6)	0.37070(2)	0.0097(2)	0.0104(2)	0.0103(2)	0.00027(18)	-0.00051(17)	-0.00107(18)	0.01017(10)
T(6)	0.15885(3)	0.26902(6)	0.12826(3)	0.0107(2)	0.0090(2)	0.0122(2)	-0.00088(18)	-0.00190(18)	0.00079(18)	0.01070(11)
T(7)	-0.18767(4)	0.70221(7)	0.19060(3)	0.0073(3)	0.0073(3)	0.0096(3)	-0.0001(2)	0.0001(2)	0.0000(2)	0.0081(2)
T(8)	-0.15271(8)	0.70804(14)	0.31480(6)	0.0084(6)	0.0092(7)	0.0155(7)	0.0007(5)	0.0024(5)	-0.0002(4)	0.0110(4)
O(1)	0.04528(9)	0.55534(16)	0.05966(7)	0.0124(6)	0.0166(7)	0.0109(6)	0.0023(5)	0.0001(5)	-0.0018(5)	0.0133(3)
O(2)	0.09367(9)	0.38313(16)	0.14931(7)	0.0143(7)	0.0119(7)	0.0204(7)	0.0018(6)	0.0013(6)	0.0043(5)	0.0155(3)
O(3)	0.06935(8)	0.64704(16)	0.17513(7)	0.0098(6)	0.0130(7)	0.0173(7)	-0.0056(5)	0.0016(5)	-0.0023(5)	0.0133(3)
O(4)	0.05003(8)	0.48320(16)	0.35214(7)	0.0083(6)	0.0163(7)	0.0161(7)	0.0006(5)	0.0013(5)	0.0021(5)	0.0135(3)
O(5)	0.21301(8)	0.14800(15)	0.45762(6)	0.0120(6)	0.0127(6)	0.0096(6)	-0.0003(5)	0.0012(5)	0.0000(5)	0.0114(3)
O(6)	0.29940(8)	0.15726(16)	0.36703(7)	0.0103(6)	0.0156(7)	0.0119(6)	0.0026(5)	0.0033(5)	0.0018(5)	0.0125(3)
O(7)	0.16432(9)	0.30124(16)	0.35897(7)	0.0185(7)	0.0103(6)	0.0153(7)	-0.0009(5)	-0.0014(5)	0.0057(5)	0.0148(3)
O(8)	0.15243(9)	0.03430(16)	0.35340(7)	0.0143(6)	0.0113(6)	0.0146(7)	-0.0018(5)	-0.0004(5)	-0.0037(5)	0.0134(3)
O(9)	0.15087(9)	0.47989(16)	0.45236(6)	0.0170(7)	0.0139(7)	0.0096(6)	-0.0005(5)	0.0006(5)	0.0019(5)	0.0135(3)
O(10)	-0.19864(9)	0.56221(17)	0.15374(7)	0.0113(6)	0.0150(7)	0.0218(7)	-0.0077(6)	0.0022(5)	0.0006(5)	0.0160(3)
O(11)	0.10692(10)	-0.07276(17)	0.06711(7)	0.0253(8)	0.0157(7)	0.0117(6)	-0.0028(6)	-0.0009(6)	0.0049(6)	0.0176(3)
O(12)	0.12434(9)	0.12204(16)	0.15404(8)	0.0158(7)	0.0092(6)	0.0245(8)	-0.0028(6)	0.0013(6)	-0.0030(5)	0.0165(3)
O(13)	0.14356(9)	-0.13588(16)	0.18441(7)	0.0143(6)	0.0116(6)	0.0146(7)	0.0005(5)	-0.0026(5)	0.0005(5)	0.0136(3)
O(14)	0.00004(9)	-0.03692(17)	0.34642(8)	0.0095(6)	0.0174(7)	0.0258(8)	0.0014(6)	-0.0004(6)	0.0014(5)	0.0176(3)
O(15)	0.09324(10)	-0.13452(17)	0.43962(7)	0.0223(8)	0.0192(7)	0.0115(7)	0.0009(6)	0.0003(6)	-0.0023(6)	0.0177(3)
O(16)	-0.10818(9)	0.78374(15)	0.17699(7)	0.0113(6)	0.0115(6)	0.0150(7)	0.0032(5)	0.0005(5)	0.0006(5)	0.0126(3)
O(17)	0.17500(10)	0.27294(18)	0.05854(7)	0.0237(8)	0.0217(8)	0.0132(7)	-0.0023(6)	-0.0024(6)	0.0073(6)	0.0197(3)
O(18)	-0.26116(9)	0.80151(16)	0.17221(7)	0.0114(6)	0.0108(6)	0.0201(7)	-0.0004(5)	-0.0004(5)	0.0002(5)	0.0143(3)
O(19)	-0.19195(10)	0.66343(18)	0.25854(8)	0.0211(8)	0.0198(8)	0.0200(8)	-0.0001(6)	0.0014(6)	-0.0096(6)	0.0203(3)
O(20)	0.02583(8)	0.78222(15)	-0.03563(7)	0.0090(6)	0.0102(6)	0.0133(6)	-0.0008(5)	0.0012(5)	-0.0010(5)	0.0109(3)

TABLE 5. Selected interatomic distances (Å) and angles (°) in odigitriaite.

<i>T</i> (1)–O(1)	1.596(2)	<i>T</i> (2)–O(5)	1.583(2)	<i>T</i> (3)–O(4)	1.626(2)
<i>T</i> (1)–O(2)	1.625(2)	<i>T</i> (2)–O(6)	1.632(2)	<i>T</i> (3)–O(7)	1.628(2)
<i>T</i> (1)–O(3)	1.627(2)	<i>T</i> (2)–O(7)	1.633(2)	<i>T</i> (3)–O(9)	1.585(2)
<i>T</i> (1)–O(4)a	<u>1.630(2)</u>	<i>T</i> (2)–O(8)	<u>1.639(2)</u>	<i>T</i> (3)–O(10)a	<u>1.630(2)</u>
< <i>T</i> (1)–O>	1.620	< <i>T</i> (2)–O>	1.622	< <i>T</i> (3)–O>	1.617
<i>T</i> (4)–O(11)	1.580(2)	<i>T</i> (5)–O(8)	1.642(2)	<i>T</i> (6)–O(2)	1.626(2)
<i>T</i> (4)–O(12)	1.627(2)	<i>T</i> (5)–O(14)	1.638(2)	<i>T</i> (6)–O(12)	1.637(2)
<i>T</i> (4)–O(13)	1.636(2)	<i>T</i> (5)–O(15)	1.583(2)	<i>T</i> (6)–O(17)	1.579(2)
<i>T</i> (4)–O(14)a	<u>1.652(2)</u>	<i>T</i> (5)–O(16)b	<u>1.650(2)</u>	<i>T</i> (6)–O(18)c	<u>1.639(2)</u>
< <i>T</i> (4)–O>	1.624	< <i>T</i> (5)–O>	1.628	< <i>T</i> (6)–O>	1.620
<i>T</i> (7)–O(10)	1.578(2)	<i>T</i> (8)–O(3)a	1.513(2)	<i>Ca</i> (3)–O(11)f	2.366(2) ×2
<i>T</i> (7)–O(16)	1.580(2)	<i>T</i> (8)–O(6)d	1.517(2)	<i>Ca</i> (3)–O(15)e	2.464(2) ×2
<i>T</i> (7)–O(18)	1.588(2)	<i>T</i> (8)–O(13)e	1.506(2)	<i>Ca</i> (3)–O(20)	2.282(2) ×2
<i>T</i> (7)–O(19)	<u>1.553(2)</u>	<i>T</i> (8)–O(19)	<u>1.441(2)</u>	< <i>Ca</i> (3)–O>	2.371
< <i>T</i> (7)–O>	1.575	< <i>T</i> (8)–O>	1.494		
<i>Ca</i> (1)–O(1)	2.396(2)	<i>Ca</i> (2)–O(1)	2.388(2)	<i>Na</i> (3)–O(5)h	2.368(2)
<i>Ca</i> (1)–O(5)g	2.315(2)	<i>Ca</i> (2)–O(1)i	2.474(2)	<i>Na</i> (3)–O(9)g	2.547(2)
<i>Ca</i> (1)–O(5)h	2.404(2)	<i>Ca</i> (2)–O(9)a	2.337(2)	<i>Na</i> (3)–O(11)k	2.689(2)
<i>Ca</i> (1)–O(6)h	2.643(2)	<i>Ca</i> (2)–O(15)e	2.453(2)	<i>Na</i> (3)–O(15)h	2.501(2)
<i>Ca</i> (1)–O(9)g	2.491(2)	<i>Ca</i> (2)–O(17)i	2.317(2)	<i>Na</i> (3)–O(17)k	2.361(2)
<i>Ca</i> (1)–O(11)f	2.390(2)	<i>Ca</i> (2)–O(20)	<u>2.266(2)</u>	<i>Na</i> (3)–O(17)	<u>2.807(2)</u>
<i>Ca</i> (1)–O(20)	<u>2.377(2)</u>	< <i>Ca</i> (2)–O>	2.373	< <i>Na</i> (3)–O>	2.546
< <i>Ca</i> (1)–O>	2.431				
<i>Na</i> (1)–O(3)b	2.338(2) ×2	<i>Na</i> (2)–O(8)e	2.837(2)	<i>Cs</i> –O(2)	3.149(2) ×2
<i>Na</i> (1)–O(14)	2.882(2) ×2	<i>Na</i> (2)–O(10)j	2.614(2)	<i>Cs</i> –O(4)	3.398(2) ×2
<i>Na</i> (1)–O(16)b	2.368(2) ×2	<i>Na</i> (2)–O(13)e	2.300(2)	<i>Cs</i> –O(12)	3.209(2) ×2
< <i>Na</i> (1)–O>	2.529	<i>Na</i> (2)–O(18)	2.316(2)	<i>Cs</i> –O(14)	<u>3.329(2)</u> ×2
		<i>Na</i> (2)–O(19)j	<u>2.257(2)</u>	< <i>Cs</i> –O>	3.271
<i>Na</i> (4)–O(2)a	2.49(2)	< <i>Na</i> (2)–O>	2.465		
<i>Na</i> (4)–O(4)	2.59(2)				
<i>Na</i> (4)–O(7)	2.53(2)				
<i>Na</i> (4)–O(8)	2.83(2)	<i>Na</i> (4)– <i>Cs</i>	2.00(2)		
<i>Na</i> (4)–O(12)a	2.60(2)				
<i>Na</i> (4)–O(14)	2.49(2)	<i>Cs</i> – <i>Na</i> (4)a	2.00(2) ×2		
<i>Na</i> (4)–O(20)l	<u>2.75(2)</u>				
< <i>Na</i> (4)–O>	2.61				

a: –x, y, –z + 1/2; b: –x, y–1, –z + 1/2; c: x + 1/2, y–1/2, z; d: x–1/2, y + 1/2, z; e: –x, y + 1, –z + 1/2; f: x, y + 1, z; g: x, –y + 1, z–1/2; h: –x + 1/2, y + 1/2, –z + 1/2; i: –x, –y + 1, –z; j: –x–1/2, y + 1/2, –z + 1/2; k: –x + 1/2, –y + 1/2, –z; l: x, –y + 1, z + 1/2.

values of *Na*(1) and *Na*(2) were consistent with complete occupancy by Na, and these sites were fixed as such in the refinement, whereas the occupancy of Na and Ca at the *Na*(3) site was refined. Another [6]-coordinated site showed a very low site-scattering; the formula suggested that this site contains minor Na, it was labelled *Na*(4) and the occupancy of Na was refined. There was one [10]-coordinated site with an extremely high

scattering that was consonant with occupancy by Cs, in accord with the formula (Table 1); this site was labelled *Cs* and the occupancy of *Cs* was considered as variable in the refinement. An extinction correction was introduced in the final stages of refinement, and the structure converged to an *R*<sub>1</sub> index of 2.75%. Final atom coordinates and anisotropic-displacement parameters are given in Table 4, selected interatomic distances are given in

TABLE 6. Refined site-scattering values and assigned site-populations for odigitriaite.

Site	Refined site-scattering (epfu)		Assigned site-population (apfu)	Calculated site-scattering (epfu)	$\langle X-\varphi \rangle_{\text{obs.}}$ (Å)	Ideal composition (apfu)
<i>T</i> (1–6)	168	12 Si		168.0	1.622	
<i>T</i> (7)	23.0(1)	1.44 Si + 0.56 B		22.96	1.575	
<i>T</i> (8)	13.6(1)	1.60 B + 0.40 Si		13.60	1.494	
$\Sigma T$ (1–8)	204.6	13.84 Si + 2.16 B		203.98		Si <sub>14</sub> B <sub>2</sub>
<sup>16</sup> <i>Na</i> (1)	11	1.00 Na		11.0	2.529	Na
<sup>15</sup> <i>Na</i> (2)	22	2.00 Na		22.0	2.465	Na <sub>2</sub>
<sup>16</sup> <i>Na</i> (3)	26.9(2)	1.46 Na + 0.54 Ca		26.9	2.546	Na <sub>2</sub>
<sup>17</sup> <i>Na</i> (4)	1.7(1)	0.15 Na + 1.85 □		1.7	2.612	□ <sub>2</sub>
$\Sigma Na$ (1–4)	61.6	4.61 Na + 0.54 Ca		61.6		Na <sub>5</sub>
<sup>17</sup> <i>Ca</i> (1)	41.9(1)	1.60 Ca + 0.11 Na + 0.20 Mn + 0.06 Y + 0.02 Fe + 0.01 Pb		41.9	2.431	Ca <sub>2</sub>
<sup>16</sup> <i>Ca</i> (2)	40	2.00 Ca		40.0	2.94	Ca <sub>2</sub>
<sup>16</sup> <i>Ca</i> (3)	20	1.00 Ca		20.0	2.86	Ca
$\Sigma Ca$ (1–3)	101.9	4.60 Ca + 0.11 Na + 0.20 Mn + 0.06 Y + 0.02 Fe + 0.01 Pb		101.9		Ca <sub>5</sub>
<sup>110</sup> <i>Cs</i>	49.9(1)	0.91 Cs + 0.10 □		50.0	2.371	Cs
O(20)	16	1.40 F + 0.60 OH				F <sub>2</sub>

X = cation,  $\varphi$  = O, F.

Coordination numbers are given for non-[4]-coordinated cations.

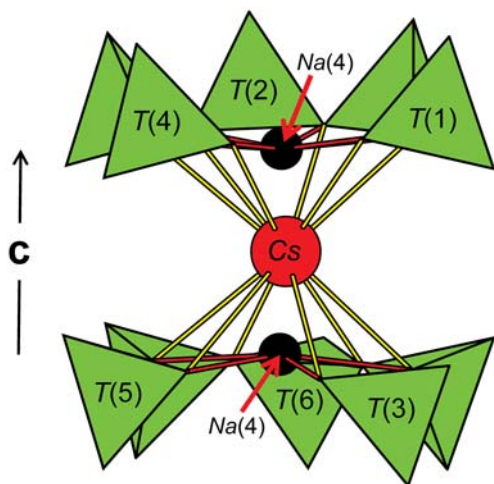


FIG. 2. The Cs and Na(4) sites within the double-layer sheet of odigitriaite; Cs: large red circle; Na(4): small black circle;  $(\text{SiO}_4)^{4-}$  tetrahedra: green; Cs–O bonds are indicated by yellow lines. Cs–Na(4) = 2.00 Å, Na(4)–Na(4) = 4.00 Å; hence locally adjacent Cs–Na(4) sites cannot both be occupied, whereas locally adjacent Na(4)–Na(4) sites can both be occupied.

Table 5, and refined site-scattering values and site-populations are given in Table 6.

### Cation coordination

There are eight *T* sites that are each coordinated by four O atoms in a tetrahedral arrangement, and the unit formula (Table 1) indicates that these sites contain 13.92 Si + 2.06 B + 0.03 Al (~16 apfu). For the *T*(1–6) sites, the  $\langle T\text{--O} \rangle$  distances are in the range 1.617–1.628 Å and the observed scattering at these sites is in accord with their occupancy by Si only; thus the B in the formula (Table 1) must occupy the *T*(7) and *T*(8) sites. Site-scattering refinement (Hawthorne *et al.*, 1995) indicates that B dominates the *T*(8) site and is a minor constituent at the *T*(7) site in accord with the observed distances of  $\langle T(8)\text{--O} \rangle = 1.494$  and  $\langle T(7)\text{--O} \rangle = 1.575$  Å.

There are three *Ca* sites occupied predominantly by Ca with minor (Mn + Na + Y + Fe + Pb). When all *Ca* sites were assigned as Ca, the *Ca*(2) and *Ca*(3) sites had equivalent isotropic-displacement parameters of  $\sim 0.013$  Å<sup>2</sup> whereas the equivalent isotropic-displacement parameter of the *Ca*(3) site was significantly smaller, indicating that *Ca*(3) has more scattering than could be provided by Ca. Thus the minor components associated with Ca in the formula (Table 1) were assigned to *Ca*(1) as they are dominantly of higher atomic number than Ca. The resultant site-populations are given in Table 6. *Ca*(1) is coordinated by seven  $\text{O}^{2-}$  anions with a

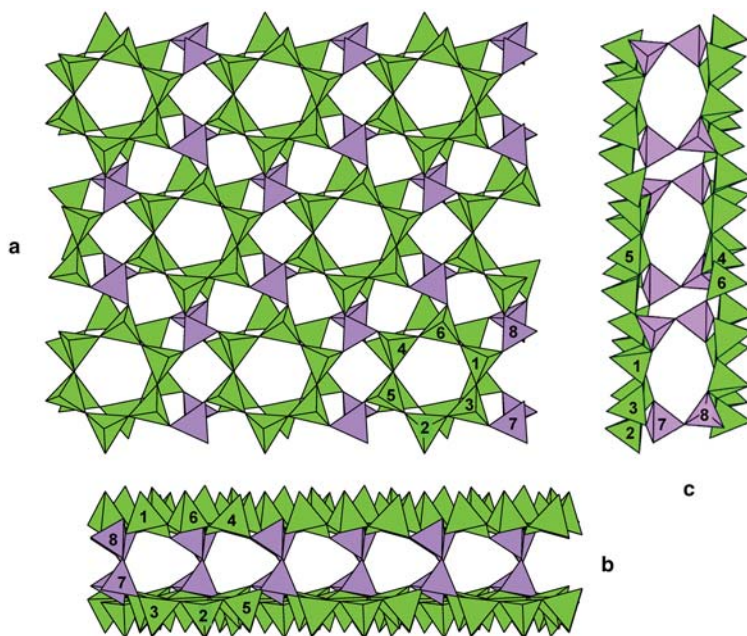


FIG. 3. The double-layer borosilicate sheet in odigitriaite; (a) plan view (viewed in the *c* direction); (b,c) cross sections. *T*(1–6) (= Si) tetrahedra: green; *T*(7–8) (Si,B) tetrahedra: violet. The numbers indicate the different *T* tetrahedra.

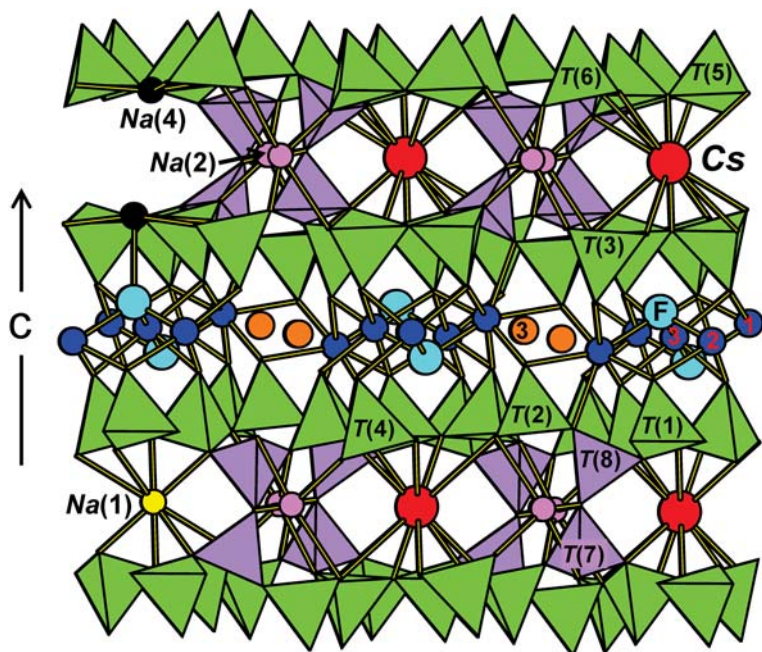


FIG. 4. The positions of the interlayer sites in odigitriaite viewed in the **b** direction; Cs: red circle; Na(1): yellow; Na(2): pink; Na(3): orange (indicated also by the number 3); Na(4): black; Ca(1–3): dark blue; (F,OH): pale blue. Polyhedra and interlayer sites are labelled; those sites labelled with just numbers are the Ca and Na(3) sites.

$\langle \text{Ca}(1)\text{--O} \rangle$  distance of 2.431 Å, whereas Ca(2) and Ca(3) are each coordinated by six  $\text{O}^{2-}$  anions with  $\langle \text{Ca--O} \rangle$  distances of 2.377 and 2.371 Å, respectively.

There are four Na sites. The observed scattering at Na(1) and Na(2) indicate that these sites are occupied completely by Na. Na(1) is coordinated by six  $\text{O}^{2-}$  anions with a  $\langle \text{Na}(1)\text{--O} \rangle$  distance of 2.529 Å, and Na(2) is coordinated by five  $\text{O}^{2-}$  anions with a  $\langle \text{Na}(2)\text{--O} \rangle$  distance of 2.465 Å. The refined scattering at the Na(3) site, 26.9 epfu (electrons per formula unit, Table 6), is somewhat in excess of that required for complete occupancy by Na (22 epfu) in accord with Ca in excess of that required to fill the Ca sites, and this Ca was assigned to the Na(3) site. The Na(4) site was not discovered until later in the refinement of the structure, and has very low site-scattering: 1.7(1) epfu, and hence the Na(4) site is dominated by □ (vacancy) (Table 6).

There is one Cs site occupied predominantly by Cs with minor □, in accord with both the refined site-scattering and the formula calculated from the chemical composition (Table 1). The Cs site is surrounded by eight  $\text{O}^{2-}$  anions with a  $\langle \text{Cs--O} \rangle$  distance of 3.271 Å.

### Short-range disorder

Inspection of Table 5 shows that there are short cation-cation distances listed: Cs–Na(4) = 2.00 Å. Obviously the Cs and Na(4) sites cannot both be locally occupied, i.e. there must be two local arrangements involving  $\text{Cs--Na}(4)\square$  and  $\text{Cs}\square\text{--Na}(4)\text{Na}$ . Such disorder can occur only if there are vacancies at the Cs and Na(4) sites, and inspection of Table 6 shows this to be the case. Note that although both Cs and Na(4) sites cannot be locally occupied, one or both of the locally associated Na(4) sites can be occupied where the locally associated Cs site is vacant (Fig. 2) as the Na(4)–Na(4) distance is 4.00 Å. As a result of this, the sum of the occupancies at the Cs and Na(4) sites are not constrained to be 1.0. The possible short-range arrangements involving Ca and Na at these sites are as follows:  $\text{Na}(4)\square\text{--Cs--Na}(4)\square$ ,  $\text{Na--Cs}\square\text{--Na}(4)\square$  and  $\text{Na--Cs}\square\text{--Na}$ . We know that  $\text{Na}(4)\square\text{--Cs--Na}(4)\square = 0.91$  as this is dictated by the occupancy of the Cs site. If  $x$  is the fraction of the arrangement  $\text{Na--Cs}\square\text{--Na}$ , then the total Na content of Na(4) is  $2x + (1.0 - 0.91)x = 0.09 + x = 0.15$  Na (Table 6);  $x = 0.06$ . Thus the short-range arrangements have the following abundance:  $\text{Na}(4)\square\text{--Cs--Na}(4)\square = 0.91$ ,  $\text{Na--Cs}\square\text{--Na}(4)\square = 0.03$  and  $\text{Na--Cs}\square\text{--Na} = 0.06$ .

## Bond topology

Odigitriaite is a double-layer sheet-borosilicate mineral (nomenclature of Liebau, 1985). The parent single-layer (nomenclature of Hawthorne, 2015) (Fig. 3) consists of a  $6^3$  sheet of tetrahedra with six-membered rings of  $\text{SiO}_4$  tetrahedra (green in Fig. 2) that all point one way (upwards in Fig. 3), and six-membered rings of  $\text{SiO}_4$  and  $(\text{B},\text{Si})\text{O}_4$  tetrahedra (violet in Fig. 3) in which the  $(\text{B},\text{Si})\text{O}_4$  tetrahedra point downwards. In the double-layer sheet, the upper and lower layers link by corner-sharing of the  $(\text{B},\text{Si})\text{O}_4$  tetrahedra (Fig. 4). The  $\text{Cs}$ ,  $\text{Na}(1)$  and  $\text{Na}(2)$  sites are intercalated within the double-layer sheet (Fig. 4), and the  $\text{Ca}(1-4)$  sites link adjacent double-layer sheets in the  $c$  direction.

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