

Article

On the Isomorphism of Sodium at the M(2) Site in Eudialyte-Group Minerals: The Crystal Structure of Mn-Deficient Manganoeudialyte and the Problem of the Existence of the M(2)Na-Dominant Analogue of Eudialyte

Sergey M. Aksenov ^{1,2,*}, Nikita V. Chukanov ^{3,4}, Igor V. Pekov ⁴, Yulia V. Nelyubina ⁵, Dmitry A. Varlamov ^{3,6} and Lia N. Kogarko ⁷

- ¹ Laboratory of Arctic Mineralogy and Materials Sciences, Russian Academy of Sciences, 14 Fersman Str., 184209 Apatity, Russia
- ² Geological Institute, Kola Science Centre, Russian Academy of Sciences, 14 Fersman Str., 184209 Apatity, Russia
- ³ Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russia; nikchukanov@yandex.ru (N.V.C.); dima@iem.ac.ru (D.A.V.)
- ⁴ Department of Geology, Moscow State University, Vorobievy Gory, 119991 Moscow, Russia; igorpekov@mail.ru
- ⁵ A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russia; unelya@ineos.ac.ru
- Institute of Experimental Mineralogy, Russian Academy of Sciences, 142432 Chernogolovka, Russia
- ⁷ Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin Str., 119991 Moscow, Russia; kogarko@geokhi.ru
 - Correspondence: aks.crys@gmail.com

Abstract: Sodium plays an important role in the crystal structures of eudialyte-group minerals given that it can occupy different crystallographic sites. Predominantly, it distributes between the N(1-5) sites situated in the large cavities of the heteropolyhedral framework. Rarely, Na occupies split sites of the M(2) microregion where it can predominate over other elements (predominantly Mn, Fe²⁺, and Fe³⁺). The crystal structure of the Mn-deficient manganoeudialyte from the Lovozero alkaline complex (Kola Peninsula, Russia) has been refined. The trigonal unit–cell parameters are: a = 14.1848(2) Å, c = 30.4726(3) Å, V = 5309.90(11) Å³. The sample is a rare example of a high-sodium and high-calcium representative of the eudialyte group with Fe + Mn < 2 *apfu*. The idealized formula is Na₁₄Ca₆[(Mn,Fe)₂Na]Zr₃Si₂[Si₂₄O₇₂]O(OH)·2H₂O with bivalent components, Mn²⁺ and Fe²⁺, dominating at the M(2) site. The regularities of isomorphism involving M(2)Na in EGMs and the problem of the existence of the M(2)Na-dominant analogue of eudialyte are discussed. The new data obtained in this work confirm the previous conclusion that the complete isomorphism between Ca-deficient and Ca-rich members of the eudialyte group cannot be realized in frames of a single-space group (*R3m, R-3m* or *R3*). Thus, the existence of the M(2)Na analogue of eudialyte remains questionable.

Keywords: eudialyte-group minerals; blocky isomorphism; solid solution; alkaline rocks; manganeudialyte

1. Introduction

Eudialyte-group minerals (EGMs) are alkali-rich zirconium–calcium silicates that accommodate many different elements in their complex zeolite-like structure [1–4]. The general crystal chemical formula of EGMs is $[N(1)_3N(2)_3N(3)_3N(4)_3N(5)_3]$ { $M(1)_6M(2)_3M(3)M(4)$ $Z_3(Si_9O_{27-3x}(OH)_{3x})_2(Si_3O_9)_2\mathcal{O}_{0-6}$ }X(1)X(2), where $M(1) = ^{VI}Ca$, $^{VI}Mn^{2+}$, ^{VI}REE , ^{VI}Na , $^{VI}Fe^{2+}$; $M(2) = ^{IV,V}Fe^{2+}$, $^{V,VI}Fe^{3+}$, $^{V,VI}Mn^{2+}$, $^{V,VI}Na$, $^{IV,V}Zr$; M(3) and $M(4) = ^{IV}Si$, ^{VI}Nb , ^{VI}Ti , $^{VI}W^{6+}$; $Z = ^{VI}Zr$, ^{VI}Ti ; $\mathcal{O} = O$, OH; N(1-5) are extra-framework cations (Na, H₃O⁺, K, Sr, *Ln*, Y Ba, Mn²⁺, Ca) or H₂O; X(1) and X(2) are extra-framework H₂O molecules, halide (Cl⁻, F⁻) and



Citation: Aksenov, S.M.; Chukanov, N.V.; Pekov, I.V.; Nelyubina, Y.V.; Varlamov, D.A.; Kogarko, L.N. On the Isomorphism of Sodium at the *M*(2) Site in Eudialyte-Group Minerals: The Crystal Structure of Mn-Deficient Manganoeudialyte and the Problem of the Existence of the ^{*M*(2)}Na-Dominant Analogue of Eudialyte. *Minerals* **2022**, *12*, 949. https://doi.org/10.3390/min12080949

Academic Editor: Evgeny Galuskin

Received: 25 June 2022 Accepted: 25 July 2022 Published: 28 July 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).



chalcogenide (S²⁻) anions, and anionic groups (CO₃²⁻, SO₄²⁻); x = 0-1; the coordination numbers of key sites of the framework are indicated with Roman numerals [2,3,5–7]. The basis of crystal structures of EGMs is a heteropolyhedral framework consisting of nineand three-membered rings of SiO₄ tetrahedra sharing common vertices with isolated ZO₆ octahedra and six-membered rings of edge-sharing M(1)O6 octahedra connected with each other via $M(2)O_n$ polyhedra where *n* can vary from 4 for $M(2) = Fe^{2+}$ to 7 for M(2) = Na.

The members of the eudialyte group are characterized by the wide isomorphous substitutions [8,9] that produce different types of solid solutions within the group [10–12]. Sodium plays an essential role in the crystal structure of EGMs, as it can occupy different crystallographic sites of the crystal structures [3,4]. Predominantly, it distributes among the *N*(1–5) sites situated in large cavities of the heteropolyhedral framework. Because of the topological features of the heteropolyhedral frameworks [7], Na atoms can be partially removed and/or substituted by the other cations or H₂O molecules under low-temperature hydrothermal conditions [13]. Moreover, Na⁺ can also be substituted by H₃O⁺ and other types of hydrated proton complexes [14]. Rarely, Na occupies split sites of the *M*(2) microregion where it can predominate over other elements (predominantly Mn, Fe²⁺, and Fe³⁺), in particular, in the crystal structures of alluaivite [15], dualite [16], labyrinthite [17], raslakite [18], and sergevanite [19]. Based on the chemical composition and structural features of EGMs, the following schemes of the incorporation of Na into the *M*(2) site are most common [4,8,9,18,20]: Fe²⁺ \rightarrow Na⁺_{2/3}Zr⁴⁺_{1/3} and Fe²⁺ \rightarrow Na⁺_{2/3}Fe³⁺_{1/3}. In the latter case, charge balance is achieved by isomorphic substitutions at other key sites.

Such schemes of isomorphic substitutions are mainly induced by the incorporation of Fe²⁺ and Mn²⁺ into the M(1) site, which can result in the division of this site into the M(1a) and M(1b) site alternating in the six-membered ring of octahedra, the ordering of Ca and Fe or Mn in the M(1a) and M(1b) sites, respectively, and the change of symmetry from R3m or R-3m to R3. Among several dozen EGMs with known crystal structures, there are no samples with the symmetry R3m or R-3m in which Na is the dominant component at the M(2) site. In other words, the $^{M(2)}$ Na analogue of eudialyte is unknown, and the predominance of Na at the M(2) site is a specific feature of some EGMs having R3 symmetry, including raslakite [18], sergevanite [19] and the recently approved new mineral selsurite $(H_3O)_{12}$ Na₃(Ca₃Mn₃)(Na₂Fe)Zr₃ \Box Si[Si₂₄O₆₉(OH)₃](OH)Cl·H₂O (IMA 2022-026).

Thus, the existence of the $^{M(2)}$ Na analogue of eudialyte remains questionable. Recently, we described an EGM from Ilimaussaq, Greenland (Figure 1), whose chemical composition could correspond to this mineral. Its empirical formula is $(H_2O, H_3O)_x Na_{10.39}Ca_{4.19}Mn_{0.34}$ Fe_{1.36}*REE*_{1.07}Ti_{0.33}Zr_{2.61}Hf_{0.03}Nb_{0.23}Si_{25.80}S_{0.08}Cl_{0.35}(O,OH)_y. However, the real symmetry of this mineral could not be determined because of a low quality of single-crystal data.



Figure 1. Crystal of a Fe,Mn-deficient EGM from the Ilimaussaq massif. Field of view width: 1 mm. Photographer: Volker Heck.

In this paper, we provide a crystal structure refinement of one more presumed $^{M(2)}$ Na analogue of eudialyte from the Lovozero alkaline complex, Kola Peninsula, Russia. However, the refinement of its crystal structure showed that despite a significant content of Na at the M(2) site, it is a Mn-deficient manganoeudialyte variety. Below, we also discuss general regularities of the isomorphism involving $^{M(2)}$ Na in EGMs.

2. Materials and Methods

2.1. Sample Description

The Mn-deficient manganoeudialyte sample studied in this work was collected from the Severnyi (northern) open pit of the abandoned Umbozero loparite mine in the northwest part of the Lovozero alkaline complex, Kola Peninsula, Russia. Only one tabular, hexagonalin-shape crystal (6 mm across) of this mineral was found. It occurs in massive naujaiterelated peralkaline, agpaitic pegmatite that mainly consists of grey potassic feldspar and greenish-grey nepheline, and contains subordinate amounts of greyish-white sodalite and black aegirine and accessory iron-black loparite-(Ce) and golden-brown murmanite. This pegmatite forms an irregular-in-shape body situated on the contact of naujaite (sodalite syenite) and urtite. The studied mineral is semitransparent, yellow-brown (honey-colored), with vitreous luster.

2.2. Electron Probe Microanalysis

Electron probe microanalyses and including imaging of the objects in the secondary and back-scattered electron modes were performed on an analytical suite including a digital scanning electron microscope Tescan VEGA-II XMU equipped with an energydispersive spectrometer (EDS) INCA Energy 450 with semiconducting Si (Li) detector Link INCA Energy and wave-dispersive spectrometer (WDS) Oxford INCA Wave 700 (produced by Tescan Orsay Hld., Brno, Czech Republic). Additionally, the electron microscope is equipped by detectors of secondary and back-scattered electrons on YAG basis (Y-Al garnets). Calculations of results of the X-ray spectral microanalysis were carried out by means of a software package of INCA Microanalysis Suite 4.15 (version 18d + SP4) with an option of the accounting of possible matrix effects for WDS analysis. The errors of the EDS measurements are below 0.3 wt.% for Na (in the absence of significant contents of F, Mg, and Zn) and below 0.2 wt.% for other elements.

In order to check the correctness of the EDS analyses of some problematic elements, including Na, Sr, Zr, and Hf, their contents were determined using WDS mode analysis. Both methods have shown a good compatibility. Based on our long-time experience in the analyses of microporous Na-rich silicate minerals published in more than 300 articles (including several dozen papers on eudialyte-group minerals), we concluded that EDS mode analyses with low currents (about 100 pA) and electron beam defocused on areas of 10×10 to $30 \times 30 \ \mu\text{m}^2$ are more correct than WDS analyses with currents up to 40 nA in the standard mode.

Ten analyses of the Mn-deficient manganoeudialyte were performed at an accelerating voltage of 20 kV. Current of the absorbed electrons was 120 pA on a reference sample of cobalt and in the range of 90–100 pA on the studied polished sample. The size of an electronic "spot" on the sample surface was in the range of 110–120 nm, and the diameter of the excitation zone was about 3 μ m. The spectra acquisition time was equal to 100 s. The sample-to-detector distance was 25 mm. To control the "losses" of Na during the analysis, measurements were made with a beam defocused of areas of 20 × 20 μ m. The following standards and analytical lines were used: CaF₂ (FK), albite (NaK), sanidine (KK), wollastonite (CaK), synthetic Al₂O₃ (AlK), BaSO₄ (SK), SiO₂ (SiK), pure Fe (FeK), pure Mn (MnK), pure Ti (TiK), pure Zr (ZrL), pure Hf (HfL), pure Nb (NbL), *REE*(PO₄) (*REEL*) for rare-earth elements, and synthetic NaCl (ClK).

The H₂O content was determined by means of the Penfield method.

2.3. Infrared Spectroscopy

In order to obtain infrared (IR) absorption spectrum, powdered sample was mixed with dried KBr, pelletized and analyzed using an ALPHA FTIR spectrometer (Bruker Optics, Ettlingen, Germany) in the range $360-4000 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} and 16 scans. An IR spectrum of an analogous pellet prepared from pure KBr was used as a reference.

2.4. Single Crystal X-ray Diffraction Analysis

Single-crystal X-ray diffraction studies of Mn-deficient manganoeudialyte were carried out at room temperature with a Bruker SMART APEX II diffractometer with graphite monochromatized MoK_{α} radiation ($\lambda = 0.71073$ Å) and a CCD detector using the ω - θ -scanning mode. Raw data were integrated by using the program SAINT [21] and then scaled, merged, and corrected for Lorentz polarization effects using the SADABS package [22].

3. Results

3.1. Chemical Composition

Chemical data of the studied sample are given in Table 1. The empirical formula calculated on the basis of 26 Si + Al + Nb atoms per formula unit is $H_{7.17}Na_{13.40}K_{0.03}Sr_{0.61}Ln_{0.69}$ Ca_{5.22}Mn_{1.36}Fe_{0.38}Zr_{2.88}Ti_{0.25}Hf_{0.04}Nb_{0.27}Al_{0.07}Si_{25.66}(SO₄)_{0.50}Cl_{0.21}O_{76.94}.

Table 1. Chemical composition of the studied sample.

Constituents —	Contents (wt.%)	
	Mean	Ranges
Na ₂ O	13.50	11.54–14.55
K ₂ O	0.05	<i>bdl</i> -0.16
CaO	9.52	9.10-10.08
MnO	3.14	2.89-3.54
FeO	0.88	0.56–1.19
SrO	2.04	<i>bdl</i> -4.68
Al ₂ O ₃	0.12	bdl-0.27
La ₂ O ₃	0.90	0.23–1.40
Ce ₂ O ₃	1.69	1.08-2.29
Pr ₂ O ₃	0.14	<i>bdl</i> -0.52
Nd ₂ O ₃	0.86	0.29–1.30
SiO ₂	50.11	47.85–51.79
TiO ₂	0.66	0.26-1.09
ZrO ₂	11.53	10.40–12.25
HfO ₂	0.28	<i>bdl</i> -1.14
Nb ₂ O ₅	1.18	0.61–1.71
SO ₃	1.29	0.97–1.66
Cl	0.24	0.12–0.37
H ₂ O	2.10	
O = Cl	-0.05	
Total	100.31	

Note: bdl, below detection limit.

3.2. Infrared Spectrum

The infrared spectrum of the studied sample is given in Figure 2. The bands in the ranges of 3000–3700 and 1630–1650 cm⁻¹ are due to O–H stretching vibrations and bending vibrations of H₂O molecules, respectively. The ranges of 900–1100, 650–740 and 440–480 cm⁻¹ correspond to stretching, mixed and bending modes of the rings of tetrahedra. The peaks at 372 and 523 cm⁻¹ and the shoulder at 1130 cm⁻¹ are due to Ca–O, (Mn,Fe)–O and S–O stretching vibrations, respectively. Relatively low intensities of the bands at 523 and 931 cm⁻¹ reflect lowered contents of Fe and Mn at the *M*(2) site and Si at the *M*(4) site, as compared to eudialyte [4]. The assignment of IR bands was made based on the analysis of IR spectra of several tens of structurally investigated eudialyte-group minerals, in accordance with [4].



Figure 2. Infrared spectrum of the studied EGM sample.

3.3. Crystal Structure

A total of 26,619 reflections within the sphere limited by $\theta = 30.52^{\circ}$ were measured. Based on the single-crystal X-ray analysis, the following unit–cell parameters have been obtained by the least-squares refinement of all reflections: a = 14.1848(2) Å, c = 30.4726(3) Å, V = 5309.90(11) Å³. The analysis of systematic absences of reflections shows *R*-centering, common for eudialyte-group minerals. The space group *R3m* was chosen. The experimental details are given in Table 2.

The crystal structure determination and refinement of Mn-deficient manganoeudialyte were carried out based on 3330 independent reflections with $I > 2\sigma(I)$ using the program JANA2006 [23]. Extra-framework sites including split and partially occupied ones have been localized from a series of difference electron-density map calculations. Because of the complex chemical composition, the cation distribution on the structural sites was proposed taking into account site-scattering factors, interatomic distances and ionic radii of the cations: at the first step, the number of electrons associated with the atoms at the site (e_{calc}) [24] was determined, and at the second step, for each value of e_{calc} , the most suitable ratio between the atoms with the closest final refined amount of electrons (e_{ref}) was selected, and the atom coordinates and ADPs were refined. Atomic scattering factors for neutral atoms together with anomalous dispersion corrections were taken from *International Tables for Crystallography* [25]. Illustrations were produced with the JANA2006 program package in combination with the program DIAMOND [26].

Crystal Data			
Simplified formula	$Na_{14}Ca_6(Na_2Mn)Zr_3Si_2[Si_{24}O_{72}](OH)_2 \cdot 2H_2O$		
Formula weight, M_r (g)	2985.87		
Crystal system, space group	Trigonal, R3m (#143)		
Temperature (K)	293		
<i>a, c</i> (Å)	14.1848(2), 30.4726(3)		
V (Å ³)	5309.90(11)		
Z	3		
Radiation type; λ	ΜοΚα; 0.71073		
Absorption coefficient, μ (mm ⁻¹)	2.653		
Crystal size (mm)	0.05 imes 0.08 imes 0.12		
Data Collection			
Diffractometer	Bruker SMART APEX II		
Absorption correction	Multi scan		
No. of measured, independent and observed $(I > 2\sigma(I))$ reflections	26,619, 3838, 3330		
R _{int}	3.63		
Data range θ (°); h, k, l	$\begin{array}{l} 1.79-30.52;\\ -19 < h < 20,\\ -18 < k < 20,\\ -43 < l < 43 \end{array}$		
Refinement			
Refinement on	Full-matrix least squares on F^2		
$R(I > 2\sigma(I)), wR(I), S$	3.43, 4.34, 1.36		
Weight scheme	$1/(\sigma^2 F + 0.0004F)$		
Δho_{max} , Δho_{min} (e Å ⁻³)	-0.81/0.96		

Table 2. Crystal data, data collection information and structure refinement details for Mn-deficient manganoeudialyte.

CDS 2193026 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, accessed on 20 June 2022, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033.

The studied mineral is isostructural with other 12-layered members of the eudyalite group with the space group *R3m*, which is most common for eudialyte-group minerals. Based on the refined site-scattering factors, the crystal chemical formula of can be written as follows (*Z* = 3): {^{*N*(1)}Na₃ ^{*N*(2)}Na₃ ^{*N*(3)}[Na_{2.36}Sr_{0.61}K_{0.03}] ^{*N*(4)}[Na_{2.2}(H₂O,H₃O)_{0.8}] ^{*N*(5)}[Na_{1.5}(H₂O,H₃O)_{1.5}] {^{*Z*}[Zr_{2.88}Ti_{0.09}Hf_{0.03}] ^{*M*(1)}[Ca_{5.22}Ln_{0.69}Mn_{0.09}] ^{*M*(2)}[Na_{1.36}Mn_{1.26}Fe²⁺_{0.38}] ^{*M*(3)}[Si(OH)] ^{*M*(4a)}[Si_{0.56}(OH)_{0.56}] ^{*M*(4b)}[(Nb_{0.27}Ti_{0.15})O_{1.26}] [Si₃O₉]₂ [Si₉O₂₇][Si₉O_{25.74}(OH)_{1.26}] ^{*X*(1)}[(SO₄)_{0.5}(H₂O)_{0.5}] ^{*X*(2)}[(H₂O)_{0.79}Cl_{0.21}] where braces and brackets enclose contents of the key sites. The idealized formula is Na₁₄Ca₆(Na₂Mn)*Z*r₃Si₂[Si₂₄O₇₂](OH)₂·2H₂O. In accordance with the modern scheme of EGMs [6], the studied mineral can be considered as a Na-enriched Mn-deficient analogue of manganoeudialyte [27].

The crystal structure of the Mn-deficient analogue of manganoeudialyte is based on the heteropolyhedral framework, which is characterized by the predominance of the tetrahedral cations in the "additional" M(3) and M(4) sites in the centers of nine-membered tetrahedral [Si₉O₂₇]-rings, with the full occupancy of the M(2) site located between adjacent six-membered octahedral rings [7]. In the crystal structure of the Mn-deficient analogue of manganoeudialyte, the octahedral M(1) site with the mean distance M(1)–O = 2.354 Å is predominantly occupied by calcium (5.22 atoms per formula unit; apfu) with the small impurities of rare-earth elements (0.69 apfu) and manganese (0.09 apfu). The single M(2)site in the crystal structure of the studied sample is split into two sites (M(2a)-M(2b))distance of 0.696 Å) with the statistical predominance of Na (1.36 *apfu*) at the M(2b) site. Manganese (1.26 *apfu*) and Fe²⁺ (0.38 *apfu*) both occupy the $M(2a)O_5$ -square pyramid with the mean distance $\langle M(2a) - O \rangle = 2.175$ Å (Figure 3). In accordance with the dominant valence rule [28], the number of bivalent cations should be summed, and therefore, the content of Na is less than the Mn + Fe sum, and the sample cannot be considered as M(2)Na-dominant at the M(2) site. Both the M(3) and M(4) microregions, located at the centers of the nine-membered $[Si_9O_{27}]$ rings, are predominantly occupied by silicon. The single M(3) site is fully occupied by silicon, whereas in the M(4) microregion, there are two partially occupied M(4a) and M(4b) sites (with the M(4a)-M(4b) distances of 1.276 Å) in a tetrahedral and octahedral coordination environment, respectively. The tetrahedral M(4a)site with the mean $\langle M(4a)-\varphi\rangle$ distance of 1.590 Å is occupied by silicon (0.56 *apfu*), while the octahedral M(4b) site is occupied by niobium (0.27 *apfu*) and titanium (0.15 *apfu*) with a mean $\langle M(4a)-\phi \rangle$ distance of 1.854 Å. The $M(4b)\phi_6$ octahedron links to the $M(2)\phi_6$ square pyramid via a common OH^{M(4b)}-vertex of the coordination polyhedra.



Figure 3. The arrangement of the cations over M(2), M(3), and M(4) sites in the crystal structure of the Mn-deficient analogue of manganoeudialyte.

The distribution of large cations over the extra-framework N(1-5) sites in the crystal structure of the Mn-deficient analogue of manganoeudialyte is generally similar to that observed for manganoeudialute [27] and is characterized by the predominance of Na at the N(1-5) sites. The N(1) and N(2) sites are both fully occupied by sodium. The N(3) site is characterized by the mixed composition and is predominantly occupied by potassium (2.36 *apfu*) with admixture of strontium (0.61 *apfu*) and potassium (0.03 *apfu*). The N(4) and N(5) sites are both characterized by the presence of H₂O molecules and, probably, H₃O⁺ groups (by the analogy with the hydrated eudialytes [14]).

The anionic X(1) microregion is occupied by sulfate $(SO_4)^{2-}$ -groups (0.5 apfu) and H₂O molecules (0.5 apfu), while in the X(2) microregion, H₂O molecules (0.79 apfu) predominate over chlorine (0.21 apfu).

4. Discussion

All $^{M(2)}$ Na-dominant EGMs structurally studied earlier are characterized by the space group R3 [19], which is caused by the incorporation of Fe²⁺ and/or Mn²⁺ in the ring of M(2)

octahedra and ordering of the Ca- and (Mn^{2+}, Fe^{2+}) -dominant sites there. The dominance of vacancy in the M(2) microregion in some Na-deficient H-rich members of the eudialyte group (aqualite [29] and related minerals [4]) also leads to the space group R3. Space group R3m is typical for EGMs, which are Fe²⁺-, Mn^{2+} - or Fe³⁺-dominant at the M(2) site. Based on this regularity, one can suppose that the presence of univalent or zero-valence components at M(2) is a significant factor affecting the symmetry of EGMs. Until recently, high-calcium (with Ca > 5 *apfu*) (Fe,Mn)-deficient minerals were known only among H₃O⁺-dominant representatives of the eudialyte group [14,30].

All IMA-approved EGMs having R3 symmetry, except for aqualite, in which a major part of Na is substituted with H_3O^+ and H_2O , are Ca deficient with < 4 Ca *apfu*. The lack of Ca promotes the ordering of large (Ca^{2+} , Na^+ , REE^+) and smaller (Fe^{2+} , Mn^{2+}) cations in the sixmembered ring of octahedra. These minerals can be divided into two types. In minerals of the first type, namely, voronkovite, ideally Na₁₅[(Na,Ca)₃Mn₃]Fe²⁺₃Zr₃Si₂(Si₂₄O₇₂)(OH,O)₄Cl·H₂O, and oneillite, Na₁₅[Ca₃Mn₃]Fe²⁺₃Zr₃[SiNb](Si₂₄O₇₂)(O,OH,H₂O)₄Cl₂, as well as some other EGMs that are structurally investigated but are not approved by the IMA CNMNC [4]. The M(2) site is predominantly occupied by Fe²⁺. In EGMs belonging to the second type, namely, raslakite, Na₁₅[Ca₃Fe₃](Na₂Zr)Zr₃[(Si,Nb)Si](Si₂₄O₇₂)(OH,H₂O,O)₄Cl, sergevanite, Na₁₅(Ca₃Mn₃)(Na₂Fe²⁺)Zr₃[Si₂][Si₂₄O₇₂](OH,H₂O,SO₄), and selsurtite, (H₃O)₁₂Na₃(Ca₃Mn₃) $(Na_2Fe)Zr_3\Box Si[Si_{24}O_{69}(OH)_3](OH)Cl \cdot H_2O$, the M(2) site is predominantly occupied by Na with subordinate amounts of Fe^{2+} or Zr. The total amounts of Fe + Mn in all these minerals are rather high (\geq 4 apfu). A part of this amount substitutes Ca at the *M*(1b) site, and the remaining part of Fe + Mn occurs at the M(2) site and can be a dominant or a subordinate bivalent component depending on the total amount of Fe + Mn. However, it is unclear whether similar regularities can take place in Ca-rich EGMs and the possibility of the occurrence of high amounts of Fe and/or Mn in the six-membered ring of octahedra with disordered distribution of cations seems problematic.

These observations and considerations call into question the existence of a wide isomorphism between $^{M(2)}$ Na- and $^{M(2)}$ (Fe,Mn)-dominant high-sodium EGMs belonging to the space groups R3m or R-3m and the existence of the $^{M(2)}$ Na-dominant analogue of eudialyte as an individual mineral species [31,32]. New data obtained in this work confirm this conclusion. The deficit of Ca is important to the formation of the R3 space group, which results in concentrations of a significant part of Fe and Mn in the six-membered ring of octahedra rather than at the M(2) site, which may become Na dominant. However, this scheme does not work in Ca-rich EGMs.

The studied Mn-deficient manganoeudialyte is a rare example of a high-sodium and high-calcium representative of the eudialyte group with Fe + Mn < 2 *apfu*. It could have been considered as a $M^{(2)}$ Na-dominant analogue of eudialyte provided that most deficit of Ca at M(2) is filled by Fe²⁺ and/or Mn²⁺, as it takes place in EGMs with the symmetry of *R*3. However, the crystal structure refinement has shown that most Mn and Fe occurs at the M(2) site, whereas the M(1) site is mainly occupied with Ca and subordinate *REE*. As a result, the occupancy of the M(2) microregion is Na_{0.46}Mn²⁺_{0.42}Fe²⁺_{0.13}, and bivalent cations prevail there over Na in total. According to the current rules of the IMA Commission on New Minerals, Nomenclature and Classification [28], this mineral should be considered as a Mn-deficient variety of manganoeudialyte.

Author Contributions: Conceptualization, S.M.A. and N.V.C.; methodology, S.M.A., N.V.C. and D.A.V.; mineral collecting, I.V.P.; investigation, S.M.A., N.V.C., Y.V.N. and D.A.V.; data curation, S.M.A., N.V.C. and D.A.V.; writing—original draft preparation, S.M.A.; writing—review and editing, S.M.A., N.V.C., D.A.V. and I.V.P.; supervision, L.N.K. All authors have read and agreed to the published version of the manuscript.

Funding: The research was carried out with the financial support of the project of the Russian Federation represented by the Ministry of Science and Higher Education of the Russian Federation No. 13.1902.21.0018 (agreement 075-15-2020-802).

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Johnsen, O.; Grice, J.D. The crystal chemistry of eudialyte group. Can. Mineral. 1999, 37, 865–891.
- 2. Johnsen, O.; Ferraris, G.; Gault, R.A.; Grice, J.D.; Kampf, A.R.; Pekov, I.V. The nomenclature of eudialyte-group minerals. *Can. Mineral.* 2003, *41*, 785–794. [CrossRef]
- 3. Rastsvetaeva, R.K.; Chukanov, N.V. Classification of eudialyte-group minerals. Geol. Ore Depos. 2012, 54, 487–497. [CrossRef]
- Rastsvetaeva, R.K.; Chukanov, N.V.; Aksenov, S.M. Minerals of Eudialyte Group: Crystal Chemistry, Properties, Genesis; University of Nizhni Novgorod: Nizhniy Novgorod, Russia, 2012; ISBN 978-5-91326-207-3.
- 5. Rastsvetaeva, R.K. Structural mineralogy of the eudialyte group: A review. Crystallogr. Rep. 2007, 52, 47–64. [CrossRef]
- 6. Mikhailova, J.A.; Stepenshchikov, D.G.; Kalashnikov, A.O.; Aksenov, S.M. Who Is Who in the Eudialyte Group: A New Algorithm for the Express Allocation of a Mineral Name Based on the Chemical Composition. *Minerals* **2022**, *12*, 224. [CrossRef]
- Aksenov, S.M.; Kabanova, N.A.; Chukanov, N.V.; Panikorovskii, T.L.; Blatov, V.A.; Krivovichev, S.V. The role of local heteropolyhedral substitutions in the stoichiometry, topological characteristics and ion-migration paths in the eudialyte-related structures: A quantitative analysis. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* 2022, *78*, 80–90. [CrossRef]
- 8. Rastsvetaeva, R.K.; Chukanov, N.V. New Data on the Isomorphism in Eudialyte-Group Minerals. 2. Crystal-Chemical Mechanisms of Blocky Isomorphism at the Key Sites. *Minerals* 2020, *10*, 720. [CrossRef]
- Rastsvetaeva, R.K.; Chukanov, N.V.; Pekov, I.V.; Schäfer, C.; Van, K.V. New Data on the Isomorphism in Eudialyte-Group Minerals.
 Crystal Chemistry of Eudialyte-Group Members with Na Incorporated into the Framework as a Marker of Hyperagpaitic Conditions. *Minerals* 2020, 10, 587. [CrossRef]
- 10. Rastsvetaeva, R.K.; Chukanov, N.V. New Data on the Isomorphism in Eudialyte-Group Minerals. X: Crystal Structure of the Intermediate Member of the Raslakite–Sergevanite Series. *Crystallogr. Rep.* **2021**, *66*, 120–125. [CrossRef]
- Rastsvetaeva, R.K.; Chukanov, N.V.; Möckel, S.; Dudka, A.P.; Aksenov, S.M. New Data on the Isomorphism in Eudialyte-Group Minerals. V: Crystal Structure of an Intermediate Member of the Manganoeudialyte–Ilyukhinite Isomorphous Series. *Crystallogr. Rep.* 2020, 65, 27–32. [CrossRef]
- 12. Rastsvetaeva, R.K.; Chukanov, N.V.; Van, K.V. New Data on the Isomorphism in Eudialyte-Group Minerals. VII: Crystal Structure of the Eudialyte–Sergevanite Series Mineral from the Lovozero Alkaline Massif. *Crystallogr. Rep.* 2020, *65*, 554–559. [CrossRef]
- 13. Rastsvetaeva, R.K.; Aksenov, S.M.; Rozenberg, K.A. Crystal structure and genesis of the hydrated analog of rastsvetaevite. *Crystallogr. Rep.* **2015**, *60*, 831–840. [CrossRef]
- 14. Chukanov, N.V.; Vigasina, M.F.; Rastsvetaeva, R.K.; Aksenov, S.M.; Mikhailova, J.A.; Pekov, I.V. The evidence of hydrated proton in eudialyte-group minerals based on Raman spectroscopy data. *J. Raman Spectrosc.* **2022**, *53*, 1188–1203. [CrossRef]
- 15. Khomyakov, A.P.; Netschelyustov, G.N.; Rastsvetaeva, R.K. Alluaivite Na₁₉(Ca,Mn)₆(Ti,Nb)₃Si₂₆O₇₄Cl·2H₂O—A new titanosilicate of of eudialyte–like structure. *Proc. Russ. Mineral. Soc.* **1990**, *119*, 117–120.
- Khomyakov, A.P.; Nechelyustov, G.N.; Rastsvetaeva, R.K. Dualite, Na₃₀(Ca,Na,Ce,Sr)₁₂(Na,Mn,Fe,Ti)₆Zr₃Ti₃MnSi₅₁O₁₄₄(OH,H₂O,Cl)₉, a new zircono-titanosilicate with a modular eudialyte-like structure from the Lovozero alkaline Pluton, Kola Peninsula, Russia. *Geol. Ore Depos.* 2008, 50, 574–582. [CrossRef]
- Khomyakov, A.P.; Nechelyustov, G.N.; Rastvetaeva, R.K. Labyrinthite (Na,K,Sr)₃₅Ca₁₂Fe₃Zr₆TiSi₅₁O₁₄₄(O,OH,H₂O)₉Cl₃, a new mineral with the modular eudialyte-like structure from Khibiny alkaline massif, Kola Peninsula. *Proc. Russ. Mineral. Soc.* 2006, 135, 38–48.
- 18. Chukanov, N.V.; Pekov, I.V.; Zadov, A.E.; Korovushkin, V.V.; Ekimenkova, I.A.; Rastsvetaeva, R.K. Ikranite, (Na,H₃O)₁₅(Ca,Mn,REE)₆ Fe³⁺₂Zr₃(□,Zr)(□,Si)Si₂₄O₆₆(O,OH)₆Cl·*n*H₂O and raslakite Na₁₅Ca₃Fe₃(Na,Zr)₃Zr₃(Si,Nb)(Si₂₅O₇₃)(OH,H₂O)₃(Cl,OH)—The new eudialyte-group minerals from Lovozero massif, Kola peninsula. *Proc. Russ. Mineral. Soc.* **2003**, *132*, 22–33.
- Chukanov, N.V.; Aksenov, S.M.; Pekov, I.V.; Belakovskiy, D.I.; Vozchikova, S.A.; Britvin, S.N. Sergevanite, Na₁₅(Ca₃Mn₃)(Na₂Fe)Zr₃ Si₂₆O₇₂(OH)₃·H₂O, a new eudialyte-group mineral from the Lovozero alkaline massif, Kola Peninsula. *Can. Mineral.* 2020, *58*, 421–436. [CrossRef]
- Rastsvetaeva, R.K.; Chukanov, N.V.; Pekov, I.V.; Varlamov, D.A.; Kazheva, O.N. New Data on the Isomorphism in Eudialyte-Group Minerals. XI: Crystal Structure of a Potentially New Mineral—A Case of Complete Substitution of Fe2+ with Na⁺_{2/3}Zr⁴⁺_{1/3} in the E.eudialyte-type structures. *Crystallogr. Rep.* 2022, *67*, 166–171. [CrossRef]
- 21. Bruker. SAINT; Bruker AXS Inc.: Madison, WI, USA, 2012.
- 22. Bruker. SADABS; Bruker AXS Inc.: Madison, WI, USA, 2001.
- 23. Petricek, V.; Dusek, M.; Palatinus, L. Crystallographic Computing System JANA2006: General features. Z. Für Krist. 2014, 229, 345–352.
- 24. Hawthorne, F.C.; Ungaretti, L.; Oberti, R. Site populations in minerals; terminology and presentation of results of crystal-structure refinement. *Can. Mineral.* **1995**, *33*, 907–911.
- 25. Prince, E. (Ed.) Volume C: Mathematical, Physical and Chemical Tables. In *International Tables for Crystallography*, 3rd ed.; IUCr Editorial Office: Chester, UK, 2004; ISBN 978-0-470-71029-6.
- 26. Brandenburg, K.; Putz, H. DIAMOND, version 3; Crystal Impact GbR: Bonn, Germany, 2005.
- 27. Nomura, S.F.; Atencio, D.; Chukanov, N.V.; Rastsvetaeva, R.K.; Cutinho, J.M.V.; Karipidis, T.K. Manganoeudialyte, a new mineral from Poços de Caldas, Minas Gerais, Brazil. *Proc. Russ. Mineral. Soc.* **2010**, 139, 35–47.
- 28. Bosi, F.; Hatert, F.; Hålenius, U.; Pasero, M.; Miyawaki, R.; Mills, S.J. On the application of the IMA–CNMNC dominant-valency rule to complex mineral compositions. *Mineral. Mag.* **2019**, *83*, 627–632. [CrossRef]

- 29. Khomyakov, A.P.; Nechelyustov, G.N.; Rastsvetaeva, R.K. Aqualite, (H₃O)₈(Na,K,Sr)₅Ca₆Zr₃Si₂₆O₆₆(OH)₉Cl, a new eudialytegroup mineral from Inagli alkaline massif (Sakha-Yakutia,Russia),and the problem of oxonium in hydrated eudialytes. *Proc. Russ. Mineral. Soc.* **2007**, *136*, 39–55.
- Rozenberg, K.A.; Rastsvetaeva, R.K.; Khomyakov, A.P. Decationized and hydrated eudialytes. Oxonium problem. *Eur. J. Mineral.* 2006, 17, 875–882. [CrossRef]
- Rastsvetaeva, R.K.; Chukanov, N.V.; Lisitsin, D.V.; Van, K.V.; Viktorova, K.A. First find of a potentially new mineral, Na-dominant at M 2-site eudialyte analogue: Crystal structure and significance as a marker of ultraagpaitic environment. *Vestn. Geosci.* 2021, 14–20. [CrossRef]
- 32. Rastsvetaeva, R.K.; Chukanov, N.V.; Schäfer, C. Na-dominant (at the M2 site) eudialyte analogue: Crystal structure and indicatory significance. *Vestn. Geosci.* 2020, *9*, 19–25. [CrossRef]