

Aqualite, a New Mineral Species of the Eudialyte Group from the Inagli Alkaline Pluton, Sakha-Yakutia, Russia, and the Problem of Oxonium in Hydrated Eudialytes¹

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Abstract—Aqualite, a new eudialyte-group mineral from hydrothermally altered peralkaline pegmatites of the Inagli alkaline pluton (Sakha-Yakutia, Russia) is described in this paper. Natrolite, microcline, eckermanite, aegirine, batisite, innelite, lorezenite, thorite, and galena are associated minerals. Aqualite occurs as isometric crystals up to 3-cm across. The color is pale pink, with a white streak and vitreous luster. The mineral is transparent. The fracture is conchoidal. The mineral is brittle; no cleavage or parting is observed. The Mohs' hardness is 4 to 5. The density is 2.58(2) g/cm³ (measured by the volumetric method) and 2.66 g/cm³ (calculated). Aqualite is optically uniaxial (+), $\alpha = 1.569(1)$ and $\beta = 1.571(1)$. The mineral is pleochroic from colorless to pale pink on X and pink on Y, $\alpha < \beta$. Aqualite is weakly fluorescent with a dull yellow color under ultraviolet light. The mineral is stable in 50% HCl and HNO₃ at room temperature. Weight loss after ignition at 500°C is 9.8%. Aqualite is monoclinic, and the space group is *R*3. The unit-cell dimensions are $a = 14.078(3)$ Å, $c = 31.24(1)$ Å, $V = 5362$ Å³, and $Z = 3$. The strongest reflections in the X-ray powder pattern [d , Å (I)(hkl)] are: 4.39(100)(2005), 2.987(100)(315), 2.850(79)(404), 10.50(44)(003), 6.63(43)(104), 7.06(42)(110), 3.624(41)(027), and 11.43(39)(101). The chemical composition (electron microprobe, H₂O determined with the Penfield method) is as follows (wt %): 2.91 Na₂O, 1.93 K₂O, 11.14 CaO, 1.75 SrO, 2.41 BaO, 0.56 FeO, 0.30 MnO, 0.17 La₂O₃, 0.54 Ce₂O₃, 0.36 Nd₂O₃, 0.34 Al₂O₃, 52.70 SiO₂, 12.33 ZrO₂, 0.78 TiO₂, 0.15 Nb₂O₅; 1.50 Cl, 9.93 H₂O, –O=Cl₂ 0.34; where the total is 99.46. The empirical formula calculated on the basis of Si + Zr + Ti + Al + Nb = 29 apfu is as follows: [(H₃O)_{7.94}Na_{2.74}K_{1.20}Sr_{0.49}Ba_{0.46}Fe_{0.23}Mn_{0.12}]_{Σ13.18}(Ca_{5.79}REE_{0.19})_{Σ5.98}(Zr_{2.92}Ti_{0.08})_{Σ3.0}(Si_{25.57}Ti_{0.21}Al_{0.19}Nb_{0.03})S_{26.0}[O_{66.46}(OH)_{5.54}]_{Σ72.0}[(OH)_{2.77}Cl_{1.23}]_{Σ4.0}. The simplified formula is (H₃O)₈(Na,K,Sr)₅Ca₆Zr₃Si₂₆O₆₆(OH)₉Cl. Aqualite differs from typical eudialyte by the extremely low contents of Na and Fe, with more than 50% Na being replaced with the (H₃O)⁺ group. The presence of oxonium ions is confirmed by IR spectroscopic and X-ray single-crystal diffraction analysis. The mineral is compared with five structurally studied high-oxonium analogues from alkaline plutons of other regions. All of these minerals were formed at a relatively low temperature through the ion-exchange transformation of “proteudialytes”; the successor minerals inherited the principal structural and compositional features of the precursor minerals. The name *aqualite* is derived from the Latin *aqua* in reference to its specific chemical composition. The type material of aqualite is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow.

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INTRODUCTION

The highly hydrated zirconosilicate of the eudialyte group from pegmatites of the Inagli alkaline pluton located in Sakha-Yakutia Republic, Russia, is described in this paper. Significant distinctions of this mineral from other eudialyte-group minerals including previously described hydrated eudialytes from other locations are

established. Taking into account the chemical composition, the new mineral was named *aqualite*.²

The first data on highly hydrated eudialytes (H-eudialytes) were published about 40 years ago, when 3.6 wt % Na₂O (in contrast to 13–15 wt % in typical eudialytes) were detected in combination with unusually high K₂O and H₂O contents (6.38 and 4.09 wt %, respectively) in eudialyte from aegirine–microcline pegmatites at Mount Poachvumchorr, the Khibiny alkaline pluton, Kola Peninsula (Feklichev, 1965). Much lower alkali contents

¹ Mineral and mineral name were approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association, April 3, 2003.

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² Aqualite was provisionally denoted as *Na,Fe-decationized eudialyte* in a previous publication on the crystal structure of the mineral (Rastsvetaeva and Khomyakov, 2002).

along with a higher water concentration (3.38 wt % $\text{Na}_2\text{O} + \text{K}_2\text{O}$ and 9.46 wt % H_2O) were detected in the altered and partly replaced with secondary eudialyte products from aegirine–eckermanite–microcline pegmatites of the Inagli pluton, South Yakutia (Efimov et al., 1963). The mineral from the Kola Peninsula, provisionally named *aqua–potassium eucolite* (Feklichev, 1965) and later, *potassium–oxonium eudialyte* (Feklichev, 1979), was regarded in the cited publications as a potential new mineral species. The authors who found potassium–oxonium eudialyte at Mount Rasvumchorr, the Khibiny alkaline pluton (Kostyleva-Labuntsova et al., 1978; Rastsvetaeva et al., 1990a; Sokolova et al., 1991) supported this opinion, whereas nobody raised the question about the necessity of considering the hydrated eudialyte from the Inagli pluton as a new mineral species.

We posed this question on the basis of a detailed study of a sample of this mineral from the collection of unusual eudialytes handed over to the first author in 1984 by V.I. Stepanov, the Head of the Mineralogical Museum at the Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements.³ As was established, the mineral from Inagli significantly differs in composition, structure, and properties from the Khibiny potassium–oxonium eudialyte and from a new eudialyte-like mineral ikranite found in the Lovozero pluton (Chukanov et al., 2003).

MODE OF OCCURRENCE, CHEMICAL COMPOSITION, AND PROPERTIES OF AQUALITE

Mode of occurrence. According to published data (Efimov et al., 1963), the Inagli pluton is located in the Aldan Shield 30 km WSW of the town of Aldan. The round, concentrically zoned pluton approximately 20 km² in area cuts through the Archean gneiss sequence, which is locally overlapped with Cambrian limestone. The central dunite body occupies the main volume of this pluton. A marginal zone up to 1-km thick consists of shonkinite, malignite, and leucocratic trachytoid aegirine–eckermanite syenite locally containing nepheline and pseudoleucite. About 50 minerals (including six new species: aqualite, batisite, inaglite, innelite, cuproiridsite, and strontium-apatite) were found in this pluton. Most of them occur in pegmatitic veins that cut through the marginal part of the dunite body. The major minerals of the pegmatites are microcline-perthite, eckermanite, and aegirine with pockets of zeolites (natrolite and thomsonite), sugarlike albite,

and associated rare-metal species. According to Efimov et al. (1963), a mineral that is close in composition and properties to the examined aqualite is a characteristic zirconosilicate from natrolite pockets in pegmatites, where it occurs as euhedral crystals 3-cm across. Microcline, aegirine, batisite, innelite, lorenzeite, thorite, and galena are companion minerals.

We had at our disposal only discrete grains of aqualite 2 to 3 mm in size and approximately 100 mg in weight, which were examined with microprobe, IR spectroscopy, X-ray diffraction imaging, and structural analysis. The most important results are presented in Table 1, where the data obtained are compared with the attributes of ikranite, which is close to aqualite in some important features.

Physical and optical properties. Aqualite is a transparent pale pink mineral with a vitreous luster. The fracture is conchoidal. The streak is white. The mineral is brittle; neither cleavage nor parting is noted. The Mohs' hardness is 4 to 5. The density measured by the volumetric method is 2.58(2) g/cm³; the density calculated from the empirical formula is 2.66 g/cm³. Aqualite is uniaxial positive, $\alpha = 1.569(1)$ and $\beta = 1.571(1)$. The mineral is pleochroic from colorless to pale pink on X and pink on Y, $\alpha < \beta$. Aqualite is not luminescent in the short-wave UV region and reveals a weak and dull yellow luminescence within a long-wave range. In contrast to typical eudialyte easily decomposed in acids at room temperature, aqualite is stable in 50% HCl and HNO₃. The weight loss of a sample ignited at 300°C over 1 h is 8.7%, and an additional 1.1 wt % is lost from 300 to 500°C; thus, the total loss is close to the water content detected by chemical analysis of the mineral (see below).

Infrared spectroscopy. The IR spectrum of aqualite (Fig. 1) is characterized by well-resolved absorption bands (cm⁻¹; sh is shoulder; s, m, and w are strong, moderate, and weak bands, respectively): 450s, 475s, 520sh, 640m, 735m, 780w, 920sh, 1025s, 1070s, 1630m, 1750m, and 3350m. Along with bands of typical eudialyte, specific bands 1630, 1750 and 3350 cm⁻¹ in the IR spectrum of the new mineral confirm the presence of oxonium ions (H_3O^+), (OH^-) groups, and molecules of water in aqualite.

The **chemical composition** of aqualite (Table 2) was determined by G.N. Nechelyustov on a Superprobe-733 electron microprobe and was filled up by water determination using the Penfield method (analyst S.P. Purusova). The compositions of five grains have been analyzed (not less than 3–5 points in each grain). The following standards were used: chkalovite (Na), $\text{K}_2\text{ZrSi}_2\text{O}_7$ (K, Zr), diopside (Ca, Si), SrTiO_3 (Sr, Ti), barite (Ba), almandine (Fe), rhodonite (Mn), LaPO_4 (La), CePO_4 (Ce), NdPO_4 (Nd), AlPO_4 (Al), LiNbO_3 (Nb), and chlorapatite (Cl). Iron presenting in the mineral as an impurity is conditionally accepted to be bivalent.

Taking into account the results of the crystal structure determination (see below), the average composi-

³ Unfortunately, we could not to perform the follow-up examination of the original samples of hydrated eudialyte from Inagli described by Efimov et al. (1963), because these samples have been lost by the time of our study. However, we obtained new data (reported in this paper) for the fragments of the original potassium–oxonium eudialyte from pegmatites at Mount Poachvumchorr in the Khibiny pluton kindly placed at our disposal by V.G. Feklichev.

Table 1. Comparative characteristics of aqualite and ikranite

Parameter	Aqualite (1)	Ikranite (2)
Formula	$(\text{H}_3\text{O})_8(\text{Na}, \text{K}, \text{Sr})_5\text{Ca}_6\text{Zr}_3\text{Si}_{26}\text{O}_{66} \cdot (\text{OH})_9\text{Cl}$	$(\text{Na}, \text{H}_3\text{O})_{15}(\text{Ca}, \text{Mn}, \text{REE})_6\text{Fe}_2^{3+}\text{Zr}_3(\square, \text{Zr}) \cdot (\square, \text{Si})\text{Si}_{24}$
Symmetry	Trigonal	Trigonal
Space group	$R\bar{3}$	$R\bar{3}m$
a , (Å)	14.078(3)	14.167(2)
c , (Å)	31.24(1)	30.081(2)
V (Å ³)	5362	5228.5
Z	3	3
D , g/cm ³	2.58	2.82
Strong reflections in the X-ray powder pattern, d , Å ($I(hkl)$)	4.39(100)(205) 2.987(100)(315) 2.850(79)(404) 10.50(44)(003) 6.63(43)(104) 7.06(42)(110) 3.624(41)(027) 11.43(39)(101)	2.841(100)(404) 2.963(92)(315) 4.30(91)(205) 3.521(57)(027) 3.205(44)(208) 6.41(41)(104) 2.588(37)(039) 4.09(36)(116)
Optical character	+	+
α	1.569	1.612
β	1.571	1.615
Color	Pale pink	Brownish yellow

Note: Sources: (1) this study, (2) Chukanov et al. (2003).

tion of aqualite calculated on the basis of Si + Zr + Ti + Al + Nb = 29 apfu ($Z = 3$) in the empirical formula is as follows: $[(\text{H}_3\text{O})_{7.94}\text{Na}_{2.74}\text{K}_{1.20}\text{Sr}_{0.49}\text{Ba}_{0.46}\text{Fe}_{0.23}\text{Mn}_{0.12}]_{\Sigma 13.18}(\text{Ca}_{5.79}\text{REE}_{0.19})_{\Sigma 5.98}(\text{Zr}_{2.92}\text{Ti}_{0.08})_{\Sigma 3.0}(\text{Si}_{25.57}\text{Ti}_{0.21}\text{Al}_{0.19}\text{Nb}_{0.03})_{\Sigma 26.0}[\text{O}_{66.46}(\text{OH})_{5.54}]_{\Sigma 72.0}[(\text{OH})_{2.77}\text{Cl}_{1.23}]_{\Sigma 4.0}$. The simplified formula is $(\text{H}_3\text{O})_8(\text{Na}, \text{K}, \text{Sr})_5\text{Ca}_6\text{Zr}_3\text{Si}_{26}\text{O}_{66}(\text{OH})_9\text{Cl}$. According to the results of XRD analysis, the mineral contains (in addition to the components given in Table 2) sulfate group $[\text{SO}_4]$ in an amount equal to ~0.5 SO_3 wt % equiv. According to the microprobe results, the sulfur concentration in aqualite is below the detection limit (~0.1 wt %). Aqualite differs from typical eudialyte by extremely low contents of Na and Fe replaced mainly with oxonium ions (see below).

X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

The X-ray diffraction pattern of aqualite (Table 3) is characteristic and differs from the X-ray patterns of eudialyte and ikranite, in particular, by the high d values of most reflections. The strongest reflections [d , Å ($I(hkl)$)] are: 4.39(100)(205), 2.987(100)(315), 2.850(79)(404), 10.50(44)(003), 6.63(43)(104), 7.06(42)(110), 3.624(41)(027), and 11.43(39)(101). The unit-cell parameters (hexagonal symmetry) calcu-

lated from the X-ray pattern are $a = 14.128(2)$, $c = 31.514(8)$ Å appreciably differ from the dimensions obtained on the basis of a single-crystal XRD examination: $a = 14.078(3)$ and $c = 31.24(1)$ Å. The discrepancy is probably caused by the heterogeneity of the mineral grains.

To provide insight into the structural features of aqualite, let us dwell on the current concept of crystal chemistry and the nomenclature of the eudialyte-group minerals (Johnsen and Grice, 1999; Johnsen et al., 2003; Khomyakov, 2002a, 2005; Rastsvetaeva and Khomyakov, 2003; Khomyakov et al., 2006).

According to the cited publications, the eudialyte group combines phyllo- and cyclo- zircono- and titano-silicates with a general formula $N(1)_3N(2)_3N(3)_3N(4)_3N(5)_3M(1)_6M(2)_{3-6}M(3)M(4)Z_3[\text{Si}_{24}\text{O}_{72}]O'_{4-6}X_2$ or its variety $A(1)_3A(2)_3A(3)_3A(4)_3A(5)_3B_{3-6}CD\{M_6Z_3[T_{24}O_{72}]\}(\text{O}, \text{OH})_{2-6}X_2$, where the fragments to the right and to the left of the square brackets correspond to cations and anions, respectively, which are not incorporated into the rings of the silicate portion of the structure. As a rule, sites $N(1)$ – $N(5)$ are dominated by Na; $M(1) = \text{Ca}, \text{Mn}, \text{Sr}, \text{REE}, \text{Y}, \text{Na}$; $M(2) = \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mn}, \text{Zr}, \text{Na}, \text{K}$; $M(3) = \text{Nb}, \text{W}, \text{Ti}, \text{Mn}, \text{Si}$; $M(4) = \text{Si}, \text{Nb}$; $Z = \text{Zr}, \text{Ti}$; $\text{O}' = \text{O}, \text{OH}, \text{H}_2\text{O}$; and $X = \text{Cl}, \text{F}, \text{H}_2\text{O}, \text{OH}$,

Table 2. Chemical composition of aqualite, wt %

Component	Content in five grains	
	range	average
Na ₂ O	1.81–3.07	2.91
K ₂ O	1.57–2.00	1.93
CaO	10.84–11.21	11.14
SrO	1.65–1.80	1.75
BaO	2.09–2.53	2.41
FeO	0.46–0.64	0.56
MnO	0.28–0.35	0.30
La ₂ O ₃	0.13–0.19	0.17
Ce ₂ O ₃	0.39–0.60	0.54
Nd ₂ O ₃	0.28–0.39	0.36
Al ₂ O ₃	0.30–0.36	0.34
SiO ₂	52.37–53.28	52.70
ZrO ₂	12.20–12.41	12.33
TiO ₂	0.68–0.82	0.78
Nb ₂ O ₅	0.09–0.20	0.15
Cl	1.42–1.63	1.50
H ₂ O		9.93
–O=Cl		0.34
Total		99.46

CO₃. The zeolite-like structure of the eudialyte-group mineral is based on the heteropolyhedral framework formed by (001) layers alternating along the *c* axis in the running order *MTZT* [...], where the *M*-layers are six-membered rings consisting of Ca- and more complicated octahedrons, the *T*-layers present isolated rings [Si₉O₂₇] and [Si₃O₉], and the *Z*-layers are discrete Zr- and/or Ti-octahedrons. Cations with a valence from 1+ to 6+, additional anions, and molecules of water occupy the cages of the framework. All eudialytes pertain to the rhombohedral system and the space groups $R\bar{3}m$, $R3m$, or $R3$. Most eudialytes have a 12-layered structural motif and unit-cell dimensions $a \sim 14.2$ and $c \sim 30$ Å. However, 24-layered eudialytes with a doubled-period *c* are also identified. According to the crystallochemical nomenclature (Khomyakov, 2004; Khomyakov, 2005; Khomyakov et al., 2006), the eudialyte group is divided into six major subgroups (eudialyte, kentbrooksite, oneillite, alluaivite, rastsvetaevite, and labyrinthite groups) discriminated by a combination of the two above-mentioned structural motifs with each of three space groups established among the eudialyte-group minerals. Aqualite pertains to the oneillite subgroup that combines 12-layered eudialytes with the space group $R3$. In addition to aqualite and oneillite Na₁₅Ca₃Mn₃Fe₃Zr₃Nb(Si₂₅O₇₃)(O,OH,H₂O)₃(OH,Cl) (Johnsen et al., 1999), this subgroup includes raslakite

Table 3. X-ray powder data for aqualite

<i>I</i>	<i>d</i> _{meas} , Å	<i>d</i> _{calc} , Å	<i>hkl</i>	<i>I</i>	<i>d</i> _{meas} , Å	<i>d</i> _{calc} , Å	<i>hkl</i>
39	11.43	11.41	101	20	3.347	3.348	223
44	10.50	10.50	003	30	3.312	3.312	208
42	7.06	7.06	110	25	3.224	3.226	217
43	6.63	6.62	104	13	3.141	3.137	119
30	6.01	6.01	021	100	2.987	2.988	315
18	5.70	5.70	202	24	2.932	2.931	226
22	5.60	5.60	015	79	2.850	2.851	404
7	5.25	5.25	006	21	2.800	2.801	0.2.10
8	4.58	4.57	211	20	2.707	2.710	137
11	4.43	4.44	122	30	2.645	2.644	324
100	4.39	4.39	205	14	2.302	2.306	241
31	4.22	4.22	107			2.298	333
10	4.08	4.08	300	25	2.192	2.194	4.0.10
22	3.986	3.988	214			2.189	3.1.11
28	3.804	3.802	033	17	2.098	2.107	2.2.12
25	3.730	3.729	125			2.096	3.2.10
41	3.624	3.626	027	13	2.000	2.002	063
16	3.531	3.532	220	14	1.901	1.901	606
22	3.375	3.374	131			1.901	066

Note: Diffractometer, CuK_{α1} irradiation; Ni filter. Indices were corrected for the results of X-ray single-crystal examination. The *d*_{calc} values correspond to the unit-cell dimensions refined from the X-ray powder diffraction pattern: $a = 14.128(2)$ and $c = 31.514(8)$ Å.

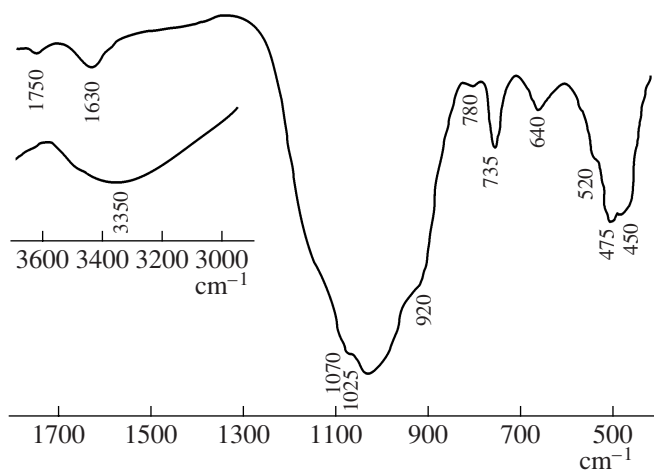


Fig. 1. Infrared spectrum of aqualite.

$\text{Na}_{15}(\text{Ca}_3\text{Fe}_3)(\text{Na,Zr})_3(\text{Si,Nb})(\text{Si}_{25}\text{O}_{73})(\text{OH,H}_2\text{O})_3(\text{Cl, OH})_2$ (Chukanov et al., 2003) and a number of structurally examined H-eudialytes (see below). The most important crystallochemical feature of the oneillite subgroup is the division of the octahedral site $M(1)$ with a multiplicity of 18 into two independent octahedral sites $M(1a)$ and $M(1b)$ with a multiplicity of 9. As a result, the general formula of the eudialyte-group minerals may be modified as follows: $[N(1)N(2)N(3)N(4)N(5)]_3[M(1a)M(1b)]_3M(2)_3M(3)M(4)Z_3[\text{Si}_{24}\text{O}_{72}]O_4X_2$.

The **crystal structure of aqualite** is shown in Fig. 2. The structure is determined on the basis of the experimental dataset collected with an Enraf-Nonius 4-circle diffractometer and is refined for 1734 independent reflections [$F_o > 4\sigma(F)$] to R index of 5.50% (Rastsvetaeva and Khomykov, 2002). The space group is $R\bar{3}$,

$a = 14.078(3) \text{ \AA}$, $c = 31.24(1) \text{ \AA}$, $V = 5362(2) \text{ \AA}^3$, and $Z = 3$. The following distribution of atoms by key cation sites (without splitting into subsites, $Z = 3$) was established: $N(1) = (\text{H}_3\text{O})_{3.0}$, $N(2) = [\text{Na}_{1.57}(\text{H}_3\text{O})_{0.83}\text{Ba}_{0.53}\text{Ce}_{0.07}]_{3.0}$, $M(1b) = (\text{Ca}_{2.88}\text{Ce}_{0.12})_{3.0}$, $M(2) = [(\text{H}_3\text{O}_{1.27}\text{Na}_{0.73}(\text{Fe,Mw})_{0.33}(\text{OH})_{0.67})_{3.0}]$, $M(3) = \text{Si}_{1.0}$, and $M(4) = (\text{Si}_{0.5}\text{Ti}_{0.25}\text{Al}_{0.22}\text{Nb}_{0.03})_{1.0}$; and $Z = \text{Zr}_{3.0}$. According to the results obtained, the crystallochemical formula of aqualite may be presented at $Z = 1$ as follows: $[(\text{H}_3\text{O})_{22.7}\text{Na}_{6.5}\text{K}_{3.6}\text{Ba}_{1.6}\text{Sr}_{1.3}\text{Ce}_{0.2}]^{\text{VII-IX}}[\text{Ca}_9(\text{Ca}_{8.64}\text{Ce}_{0.36})]^{\text{VI}}[(\text{H}_3\text{O})_{3.8}\text{Na}_{2.2}^{\text{IV}}(\text{Fe,Mn})_{1.0}^{\text{VI}}][\text{Zr}_9^{\text{VI}}][\text{Si}_3^{\text{IV}}][\text{Si}_{1.5}^{\text{IV}}\text{Ti}_{0.75}^{\text{VI}}(\text{Al}_{0.65}\text{Nb}_{0.1})^{\text{VI}}][\text{Si}_{72}\text{O}_{200.3}(\text{OH})_{15.7}](\text{OH})_{9.6}\text{Cl}_{3.9}(\text{H}_2\text{O})_{2.2}(\text{SO}_4)_{0.6}$, where the compositions of the key structural fragments are placed into square brackets, the coordination numbers are marked with Roman numerals, and the charge-balance constraints are used to estimate the number of the OH groups within a framework fragment $[\text{Si}_{72}\text{O}_{200.3}(\text{OH})_{15.7}]$.

An unusually low total content of Na and Fe atoms that equals 2.2 in the described mineral 7.5 in contrast to 54 atoms in the unit cell of the ideal eudialyte $\text{Na}_{45}\text{Ca}_{18}\text{Fe}_9\text{Zr}_9\text{Si}_{78}(\text{O,OH})_6\text{Cl}_6$ and a high content of proton–oxygen clusters, foremost oxonium (H_3O^+), in the out-of-framework N sites are the main crystallochemical features of aqualite. In comparison with previously described H-eudialytes, the studied mineral contains a maximum amount of H_3O groups. Sites $N(1)$, $N(3)$, and $N(4)$, where oxonium groups had been already identified in potassium–oxonium eudialyte (Rastsvetaeva et al., 1990a) and ikranite (Ekimenkova et al., 2000), are supplemented in aqualite by the H_3O -containing site $N(2)$ and two high-coordination (c.n. = 9) subsites of the $M(2)$ site corresponding to the $N(6)$ and $N(7)$ sites in high-alkaline 24-layered eudia-

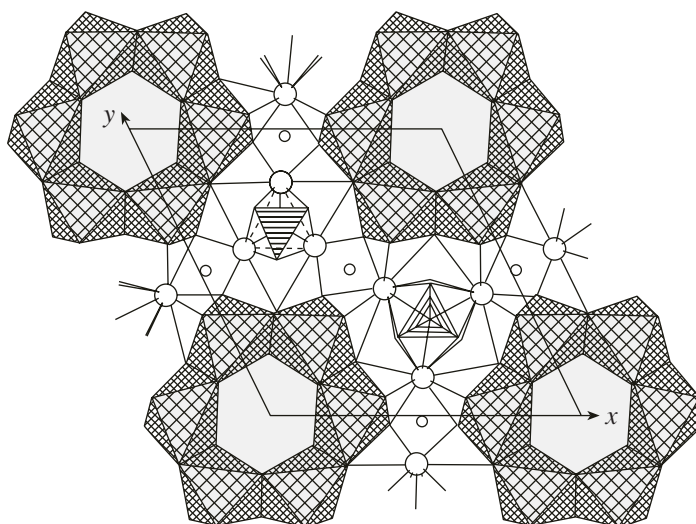


Fig. 2. M layer of the aqualite structure projected on (001). Large circles indicate oxonium ions in sites $N(6)$ and $N(7)$, small circles are Na atoms in site $M(2)$; Si-tetrahedrons and (Ti,Al,Nb) octahedrons in sites $M(3)$ and $M(4)$ are hatched.

lytes. The distance between the sites $N(6)$ and $N(7)$ is correlated with the dimensions of the cations that occupy these sites and increases in the series $\text{Na-K-H}_2\text{O}$ from a minimum of 2.8 Å in alluaivite (Rastsvetaeva et al., 1990b) through intermediate 3.2 Å in rastsvetaevite (Rastsvetaeva and Khomyakov, 2001; Khomyakov et al., 2006) to the maximum that equals 3.8 Å in aqualite.

The Ti-octahedron of site $M(4)$ oriented inward from the cavity flattened out along the c axis and limited by the $[\text{Si}_9\text{O}_{27}]$ rings from above and below is a remarkable feature of the considered structure. Such an orientation of the axial octahedrons reported only for hydrated eudialyte is controlled by the absence of Na atoms in this site; Na atoms occupy the site $N(5)$ in typical eudialytes. Similar to structures of H-eudialytes (Rastsvetaeva et al., 1990a; Ekimenkova et al., 2000), the interring cage is filled with hydroxy groups, which frame the tetrahedral and octahedral cations on the 3-fold axis.

An anomalous elongation along the 3-fold axis and the right-angle compression of the structure is a spectacular feature of aqualite; the unit-cell parameters $c = 31.24$ and $a = 14.08$ Å are significantly distinct from those of typical eudialytes ranging from 29.9 to 30.3 and from 14.18 to 14.30 Å, respectively (Johnsen and Grice, 1999). This geometrical anomaly most probably results from the presence of oxonium and the absence of Fe atoms in the Ca-layer of the structure. This suggestion is confirmed by the deformed oxygen "square" of the planar group $[M(2)\text{O}_4]$: pairs of vertical and horizontal edges of this square in the studied structure range within 3.32–3.42 and 3.13–3.58 Å, respectively, whereas in other eudialytes with known structure lengths of these edges range from 2.79 to 3.24 and from 2.91 to 3.25 Å, respectively.

The important feature of the aqualite structure is that it belongs to the space group $R\bar{3}$, which is unusual for eudialytes. Degradation of the symmetry relative to the common $R\bar{3}m$ pointed out for a number of eudialyte structures, particularly for oneillite, is frequently caused by the ordered distribution of Ca and some substituting elements in sites $M(1a)$ and $M(1b)$ of six-membered rings $[\text{Ca}_6\text{O}_{24}]$. Ca and (Ca, Ce) are ordered in the aqualite structure. However, the main reason for the lowering of the symmetry is likely related to the destabilization of the structure due to the replacement of 3/4 Na with more loose and mobile H_2O groups, which is expressed in the overstated thermal parameters of atoms and their displacement from vertical plane m .

One more consequence of the replacement of Na^+ with larger H_3O^+ ions is an increase in the interatomic distances in the respective polyhedrons that is traced upon comparing aqualite with oneillite, since its structural counterpart did not undergo decationization (Johnsen et al., 1999). The average interatomic Na–O and $\text{O}(\text{H}_3\text{O})$ –O distances range from 2.59 to 2.71 and

from 2.59 to 2.85 Å, respectively, in polyhedrons $N(1)$ – $N(4)$ occupied mainly by Na ions in the oneillite structure and by oxonium ions in the aqualite structure. In addition, the coordination numbers of these polyhedrons increase from 6 to 9 in the oneillite structure and from 7 to 9 in the aqualite structure.⁴

OXONIUM PROBLEM IN HYDRATED EUDIALYTES

Different compensation schemes of the alkaline cation deficiency such as $\text{A}^+ = (\text{H}_3\text{O})^+$, $\text{A}^+ = \text{H}^+$, $\text{A}^+ = (\text{H}_2\text{O})^0 + \text{H}^+$, and $\text{A}^+ + \text{O}^{2-} = \square + (\text{OH})^-$ have been discussed in the literature concerning the charge balance of hydrated eudialyte formulas (Kostyleva, 1937; Feklichev, 1965, 1979; Rastsvetaeva et al., 1990a; Rastsvetaeva and Khomyakov, 2002; Rozenberg et al., 2005). From the four aforementioned scheme, the second was criticized on the basis that "the H ion is dimensionless and only the (H_3O) ion close in radius to the alkalis can replace them in silicates" (Feklichev, 1965). The third and fourth schemes suggesting the replacement of the framework O with a proton in parallel with the replacement of the alkali sites with neutral water molecules or vacancies are dubious in terms of the requirement of the local balance of valence (see below). Only the first scheme based on a general crystallochemical concept and suggested several decades ago (Feklichev, 1965, 1979) turned out to be quite valid. This scheme was confirmed later with physical methods (Sokolova et al., 1991) and used fruitfully in further resolving the problem of oxonium incorporation into H-eudialytes. The determination of the crystal structures of potassium-oxonium eudialyte (Rastsvetaeva et al., 1990a), ikranite (Ekimenkova et al., 2000), aqualite (Rastsvetaeva and Khomyakov, 2002), and some thus far poorly studied hydrated eudialytes made a great contribution to resolving this problem.

Recently, this problem was comprehensively considered again taking into account new factual data (Rozenberg et al., 2005) and the results of the XRD examination of the representative collection of H-eudialyte samples taken by the first author in various regions and preliminarily studied with optical methods, IR spectroscopy, X-ray imaging, and electron microprobe. Six new samples including aqualite from the Inagli and Konder (South Yakutia), Baruun Makhan (NW Mongolia), and Khibiny (Kola Peninsula) were examined.

The main results of the XRD analysis and the data on the distribution of low-charge cations, including oxonium, by key sites of the respective structures are listed in Table 4. Empirical and crystallochemical formulas providing the outlines of the bulk chemical com-

⁴ Interatomic distances and coordination numbers of aqualite were taken from (Rastsvetaeva and Khomyakov, 2002); for oneillite, they were calculated from published atomic coordinates (Johnsen and Grice, 1999).

Table 4. Distribution of large cations and H₂O groups by *N* sites of hydrated eudialites

Sample number	Mineral and pluton	<i>a</i> , Å <i>c</i> , Å Space group	<i>N</i> (1)	<i>N</i> (2)	<i>N</i> (3)	<i>N</i> (4)	<i>N</i> (5)	<i>N</i> (6) + <i>N</i> (7)
1	Aqualite, Inagli	14.078 31.24 <i>R</i> 3	(H ₃ O) _{3,0}	Na _{1,57} (H ₃ O) _{0,83} Ba _{0,53} Ce _{0,07}	(H ₃ O) _{1,63} K _{1,2} Sr _{0,17}	(H ₃ O) _{2,1} Na _{0,6} Sr _{0,27}	–	(H ₃ O) _{1,27} (OH) _{0,67}
2	Eudialyte-3397, Inagli	14.156 30.998 <i>R</i> 3 <i>m</i>	Na _{2,64} Ba _{0,36}	(H ₃ O) _{3,0}	Na _{2,32} K _{0,53} Sr _{0,15}	(H ₃ O) _{2,1} Na _{0,9}	(H ₃ O) _{1,5}	(H ₃ O) _{2,72} (H ₂ O) _{0,1}
3	Eudialyte-3398, Konder	14.104 31.074 <i>R</i> 3	Na _{2,79} Ba _{0,15} K _{0,06}	(H ₃ O) _{1,73} Na _{0,72} Sr _{0,55}	(H ₃ O) _{2,7} Y _{0,3}	(H ₃ O) _{1,98} Ce _{0,45} (OH) _{0,57}	–	(H ₃ O) _{1,47} (H ₂ O) _{0,72}
4	Eudialyte-3400, Baruum Makhani	14.156 28.956 <i>R</i> 3	Na _{1,95} (H ₃ O) _{1,05}	(H ₃ O) _{1,5} Na _{1,15} K _{0,3} Sr _{0,55}	Na _{2,15} (H ₃ O) _{0,66} Y _{0,19}	(H ₃ O) _{2,37} Ce _{0,63}	(OH) _{0,75}	(O, OH) _{1,77} (H ₂ O) _{1,34}
5	Eudialyte-1593/4, Khibiny	14.173 30.226 <i>R</i> 3	Na _{2,4} (H ₃ O) _{0,6}	(H ₃ O) _{2,31} Sr _{0,48} K _{0,21}	(H ₃ O) _{3,0}	(H ₃ O) _{1,76} Na _{0,9} Ce _{0,2} Y _{0,1} Ba _{0,04}	(H ₃ O) _{1,11}	(H ₃ O) _{2,07} (H ₂ O) _{1,8}

Table 4. (Contd.)

Sample number	Mineral and pluton	$a, \text{\AA}$ $c, \text{\AA}$ Space group	$N(1)$	$N(2)$	$N(3)$	$N(4)$	$N(5)$	$N(6) + N(7)$
6	Eudialyte-1593/5, Khibiny	14.156 30.488 $R3$	$(\text{H}_3\text{O})_{1.5}\text{Na}_{1.5}$	$(\text{H}_3\text{O})_{2.37}\text{Sr}_{0.63}$	$(\text{H}_3\text{O})_{3.0}$	$\text{Na}_{1.5}(\text{H}_3\text{O})_{1.0}\text{Ce}_{0.22}\text{K}_{0.2} \cdot \text{Y}_{0.05}\text{Ba}_{0.03}$	$(\text{H}_3\text{O})_{1.11}(\text{OH})_{0.57}$	$(\text{H}_3\text{O})_{0.87}(\text{OH})_{1.35} \cdot (\text{H}_2\text{O})_{0.48}$
Empirical (a) and crystallochemical (b) formulas of the minerals								
1. (a) $\text{Na}_{2.74}\text{K}_{1.20}\text{Sr}_{0.49}\text{Ba}_{0.46}\text{Ca}_{5.79}\text{REE}_{0.19}\text{Fe}_{0.23}\text{Mn}_{0.12}\text{Zr}_{2.92}\text{Ti}_{0.29}\text{Nb}_{0.03}\text{Al}_{0.19}\text{Si}_{25.57}\text{Cl}_{1.23}\text{O}_{66.6}(\text{H}_2\text{O})_{16.06}$								
(b) $[(\text{H}_3\text{O})_{8.84}\text{Na}_{2.17}\text{K}_{1.20}\text{Sr}_{0.44}\text{Ba}_{0.53}\text{Ce}_{0.07}][\text{Ca}_{2.88}\text{Ce}_{0.12}][\text{Zr}_{3.01}][\text{Na}_{0.73}][(\text{Fe}, \text{Mn})_{0.33}(\text{OH})_{0.67}][\text{Si}_{1.0}(\text{OH})_{1.0}][\text{Si}_{0.5}(\text{OH})_{0.5}][\text{Ti}_{0.25}(\text{Al}_{0.22}\text{Nb}_{0.03})] \cdot (\text{OH})_{1.5}][\text{Si}_3\text{O}_9]_2(\text{Si}_9\text{O}_{24}(\text{OH}, \text{O})_{3.0})_2\text{Cl}_{1.3}(\text{SO}_4)_{0.02} \cdot 0.72\text{H}_2\text{O}$								
2. (a) $\text{Na}_{7.42}\text{K}_{0.53}\text{Sr}_{0.63}\text{Ba}_{0.38}\text{Ca}_{5.23}\text{REE}_{0.16}\text{Fe}_{0.08}\text{Mn}_{0.13}\text{Zr}_{2.42}\text{Hf}_{0.02}\text{Ti}_{0.54}\text{Nb}_{0.02}\text{Al}_{0.06}\text{Si}_{25.44}\text{Cl}_{0.93}\text{O}_{67.18}(\text{H}_2\text{O})_{15.78}$								
(b) $[(\text{H}_3\text{O})_{9.32}\text{Na}_{2.86}\text{K}_{0.53}\text{Ba}_{0.36}\text{Sr}_{0.15}][\text{Ca}_{5.22}\text{Sr}_{0.49}\text{Ce}_{0.16}\text{Mn}_{0.13}][\text{Zr}_{2.42}\text{Ti}_{0.54}\text{Hf}_{0.02}\text{Nb}_{0.02}][\text{Na}_{1.48}(\text{Fe}_{0.10}\text{H}_2\text{O}_{0.1})][\text{Si}_{1.0}(\text{OH})_{1.0}][\text{Si}_{0.44}\text{Al}_{0.06}(\text{OH})_{0.50}] \cdot [\text{Si}_3\text{O}_9]_2[\text{Si}_9\text{O}_{24}(\text{O}, \text{OH})_2]_2\text{Cl}_{1.0} \cdot \text{H}_2\text{O}$								
3. (a) $\text{Na}_{3.86}\text{K}_{0.06}\text{Sr}_{0.99}\text{Ba}_{0.15}\text{Ca}_{4.66}\text{REE}_{0.44}\text{Y}_{0.22}\text{Fe}_{0.37}\text{Mn}_{1.21}\text{Mg}_{0.07}\text{Zr}_{2.95}\text{Hf}_{0.03}\text{Ti}_{0.09}\text{Nb}_{0.13}\text{Si}_{25.41}\text{O}_{67.87}(\text{H}_2\text{O})_{16.38}$								
(b) $[(\text{H}_3\text{O})_{8.53}\text{Na}_{3.51}\text{Sr}_{0.55}\text{Ce}_{0.45}\text{Y}_{0.3}\text{Ba}_{0.15}\text{K}_{0.06}][\text{Ca}_{2.4}\text{Sr}_{0.45}\text{Na}_{0.3}][\text{Ca}_{2.4}\text{Mn}_{0.6}][\text{Zr}_{2.97}\text{Hf}_{0.03}][\text{Mn}_{0.64}\text{Fe}_{0.38}][\text{O}_{0.3}\text{H}_2\text{O}_{0.72}][(\text{Si}_{0.49})(\text{Si}_{0.41})(\text{Nb}_{0.1})(\text{OH})_{0.9}]] \cdot [(\text{Si}_{0.29})(\text{Si}_{0.2})(\text{Ti}_{0.1}\text{Mg}_{0.07}\text{Nb}_{0.02})(\text{OH})_{1.06}][\text{Si}_3\text{O}_9]_2[\text{Si}_9\text{O}_{24}(\text{O}, \text{OH})_2]_2 \cdot 2.12\text{H}_2\text{O}$								
4. (a) $\text{Na}_{4.78}\text{K}_{0.34}\text{Sr}_{0.05}\text{Ca}_{4.44}\text{REE}_{0.53}\text{Y}_{0.23}\text{Fe}_{0.34}\text{Fe}_{1.53}\text{Mn}_{1.55}\text{Zr}_{3.44}\text{Hf}_{0.04}\text{Ti}_{0.05}\text{Nb}_{0.36}\text{Al}_{0.20}\text{Si}_{24.75}\text{F}_{0.35}\text{Cl}_{0.20}\text{O}_{69.86}(\text{H}_2\text{O})_{11.69}$								
(b) $[(\text{H}_3\text{O})_{5.58}\text{Na}_{3.25}\text{Ce}_{0.63}\text{K}_{0.3}\text{Y}_{0.19}\text{Sr}_{0.05}][\text{Ca}_3][\text{Ca}_1]\text{Mn}_{1.29}[\text{Zr}_{2.96}\text{Hf}_{0.04}][\text{Fe}_{1.0}^{3+}\text{Fe}_{0.35}^{2+}][\text{Fe}_{0.57}^{3+}][\text{Zr}_{0.32}\text{Mn}_{0.22}][\text{O}, \text{OH}]_{1.77}\text{H}_2\text{O}_{1.34}[(\text{Zr}_{0.18})(\text{Si}_{0.5})(\text{OH})_{0.5}] \cdot [(\text{Nb}_{0.41})(\text{Al}_{0.2}\text{Ti}_{0.05})(\text{Si}_{0.18})(\text{OH})_{0.93}][\text{Si}_3\text{O}_9]_2[\text{Si}_9\text{O}_{24}(\text{O}, \text{OH})_2]_2\text{Cl}_{0.2} \cdot 1.45\text{H}_2\text{O}$								
5. (a) $\text{Na}_{4.51}\text{K}_{0.22}\text{Sr}_{0.51}\text{Ba}_{0.04}\text{Ca}_{4.47}\text{REE}_{0.20}\text{Y}_{0.10}\text{Fe}_{0.13}\text{Fe}_{1.36}^{3+}\text{Mn}_{0.93}\text{Zr}_{0.97}\text{Hf}_{0.03}\text{Ti}_{0.22}\text{Nb}_{0.24}\text{Al}_{0.09}\text{Si}_{24.79}\text{Cl}_{1.31}\text{O}_{67.04}(\text{H}_2\text{O})_{10.78}$								
(b) $[(\text{H}_3\text{O})_{10.85}\text{Na}_{3.3}\text{Sr}_{0.48}\text{K}_{0.21}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Ba}_{0.04}][\text{Ca}_{2.1}\text{Na}_{0.9}][\text{Ca}_{2.4}\text{Na}_{0.3}\text{Mn}_{0.3}][\text{Zr}_{2.97}\text{Hf}_{0.03}][\text{Fe}_{1.32}][\text{Mn}_{0.6}][\text{O}_{1.44}\text{H}_2\text{O}_{1.80}][(\text{Ti}_{0.22}\text{Nb}_{0.02})(\text{Si}_{0.23})(\text{Si}_{0.19})(\text{OH})_{0.42}] \cdot [(\text{Si}_{0.44})(\text{Nb}_{0.1}\text{Al}_{0.1})(\text{Nb}_{0.04})(\text{OH})_{0.44}][\text{Si}_3\text{O}_9]_2[\text{Si}_9\text{O}_{24}(\text{O}, \text{OH})_2]_2\text{Cl}_{1.0} \cdot 1.19\text{H}_2\text{O}$								
6. (a) $\text{Na}_{3.72}\text{K}_{0.21}\text{Sr}_{0.64}\text{Ba}_{0.04}\text{Ca}_{4.63}\text{REE}_{0.20}\text{Y}_{0.05}\text{Fe}_{0.65}\text{Mn}_{1.20}\text{Mg}_{0.03}\text{Zr}_{2.96}\text{Hf}_{0.02}\text{Ti}_{0.16}\text{Nb}_{0.18}\text{Ta}_{0.005}\text{Al}_{0.07}\text{Si}_{25.00}\text{Cl}_{1.17}\text{O}_{65.68}(\text{H}_2\text{O})_{11.04}$								
(b) $[(\text{H}_3\text{O})_{11.61}\text{Na}_{3.0}\text{Sr}_{0.63}\text{Ce}_{0.22}\text{K}_{0.2}\text{Y}_{0.05}\text{Ba}_{0.03}][\text{Ca}_{2.25}\text{Na}_{0.75}][\text{Ca}_{2.4}\text{Mn}_{0.6}][\text{Zr}_{2.98}\text{Hf}_{0.02}][\text{Fe}_{0.66}^{3+}][\text{Mn}_{0.3}][\text{Mn}_{0.3}][\text{H}_2\text{O}_{1.43}\text{OH}_{0.79}][(\text{Ti}_{0.16}\text{Al}_{0.07}\text{Mg}_{0.03})(\text{Si}_{0.17})(\text{OH})_{0.17}] \cdot [(\text{Si}_{0.50})(\text{Si}_{0.31})(\text{Nb}_{0.18}\text{Ta}_{0.01})(\text{OH})_{0.81}][\text{Si}_3\text{O}_9]_2[\text{Si}_9\text{O}_{24}(\text{O}, \text{OH})_2]_2\text{Cl}_{1.1} \cdot 0.63\text{H}_2\text{O}$								

Note: Sources: (1) Rastvetaeva et al. (2002) and this study; (2–6) Rozenberg et al. (2005). Numerals (2–6) for the hydrated eudialytes correspond to the authors' numeration of the samples.

position and structural features of the six studied samples are presented in the same table.⁵ While considering the results obtained, it should be kept in mind that the crystallochemical data for aqualite presented in the table pertain to its structure at room temperature (Rastsvetaeva and Khomyakov, 2002) and markedly differ from the data reported by Rozenberg et al. (2005) at the temperature of liquid nitrogen. In connection with the revealed and inexplicable inconsistency between these results, the data from the former publication that seem to be more reliable are discussed in this paper.

According to Table 4, all minerals differ from typical eudialytes in a significantly reduced Na concentration and a high hydration. The substantial distinctions of the particular samples are pointed out below. Samples 1 and 2 from the Inagli pluton are characterized by an extremely low Fe content; sample 3 from the Konder pluton is high-Sr and Cl-free; sample 4 from the Baruun Makhon pluton is high-Mn and Cl-free; and samples 5 and 6 from the Khibiny pluton are high-Fe and Mn-Fe, respectively. The representative set of the samples different in chemical composition, origin, and crystallochemical characteristics allowed us to ascertain some general features in the distribution of H_3O^+ ions by structural sites of the minerals.

However, it should be noted that X-ray diffraction analysis provides only indirect evidence for the occurrence of H_3O -groups, because its high mobility prevents the localization of H-atoms, so that only O-atoms are recorded in the maps of the electron density in the respective sites. At the same time, a significant deficiency in the positive charges of out-of-framework cations does not admit the interpretation of O-atoms in *N* sites as neutral H_2O molecules. The oxonium groups may be established more strictly with the vibrating spectroscopy (Plyusnina, 1977). According to the cited article, IR spectra of minerals containing H_3O groups are characterized by absorption in the band 1680–1800 cm^{-1} that is not overlapped with the absorption bands of the OH groups and H_2O molecules. Taking into account this fact, the band at 1750 cm^{-1} in the IR spectrum of aqualite and bands with close values in spectra of the other studied samples may be considered as reliable experimental evidence for the presence of H_3O^+ in the examined structures.⁶

According to the data presented in Table 4, all studied samples are fairly close to one another in the degree of hydration. The amount of H_3O groups per mineral

formula ranges from 5.6 to 11.6. These groups play the role of monovalent cations that replace low-charge, primarily alkaline cations and compensate for the deficiency of the positive charge in structures of decationized eudialytes. Oxonium is the main species of mineral hydration and occupies all *N* sites in variable amounts. At the same time, the rate of affinity of *N* sites to the H_3O^+ ions is specific for each structure. Sites *N*(2) and *N*(4) containing oxonium in dominant or significant amounts in all of the studied minerals demonstrate the greatest affinity to these ions. Site *N*(1) does not contain oxonium in samples 2 and 3 only, and site *N*(3), only in sample 2. Other *N* sites are partly occupied by oxonium ions: site *N*(5) in samples 2, 5, and 6 and sites *N*(6) + *N*(7) in all samples except sample 4. Site *N*(8), which is not shown in Table 4, is distinguished by the lowest oxonium content. This site is located in the center of a closed cavity in the middle of a six-member ring of Ca-octahedrons covered from above and below by three-membered rings [Si_3O_9]. In all previously described structures, site *N*(8) remained vacant except for alluaivite (Rastsvetaeva et al., 1990b), where it is occupied by K and H_2O . The insignificant occupation by oxonium ions and water molecules was detected only in H-eudialites 3 and 5, respectively.

The general increase in the oxonium content in sites *N*(1)–*N*(4) detected in most studied structures is caused by the absence of steric constraints for large oxonium groups therein. The presence of oxygen atoms or OH groups and H_2O that coordinate cations in sites *M*(3) and *M*(4) by tetrahedron or octahedron on the 3-fold axis in the middle of the nine-membered rings [Si_9O_{27}] is the limiting factor for the maximum occupation of sites *N*(5), *N*(6), and *N*(7) by oxonium. While sites *M*(3) in samples 1, 2, and 3 and *M*(4) in samples 2 and 6 are completely occupied, sites *N*(5)–*N*(7) either are not realized or are occupied by oxonium to a much lesser extent. The occupation of sites *N*(6) and *N*(7) is correlated with the amount of vacancies in site *M*(2), which can enter into the polyhedral cluster in combination with either *M*(3) or *M*(4), or both positions together. Thus, although oxonium does not replace small and medium-sized cations in sites *M*(2)–*M*(4), its total content in minerals is inversely correlated with the concentration of these cations.

The hydration unrelated to the incorporation of oxonium groups into the structure and caused by the presence of proton–oxygen clusters in H-eudialytes is of subordinate importance. For example, the absence of Na atoms in site *N*(5) located in the cage between [Si_9O_{27}] rings results in the partial occupation of this cage with OH-groups that frame tetrahedral and octahedral cations on the 3-fold axis, in particular, “zeolite” Ti-octahedrons in site *M*(4) of the aqualite structure. Another type of hydration is realized in the sites of out-of-framework anions *X*(1) and *X*(2) on the 3-fold axis usually occupied by Cl-ions. In the studied samples, Cl-ions are replaced either completely (Cl-free samples 3 and 4) or partially with H_2O molecules. The ordering of Cl in *X*(1) and H_2O in *X*(2) was detected only in sample 5.

⁵ Empirical formulas were calculated on the basis of $\text{Si} + \text{Ti} + \text{Zr} + \text{Hf} + \text{Nb} + \text{Al} = 29 - x$ apfu, where *x* is the sum of the vacancies in the sites *M*(3) and *M*(4) (Johnsen et al., 2003). The number of H_2O molecules in the formulas corresponds to the water content detected with the Penfield method in samples 1, 4, 5, and 6 (9.93, 6.96, 6.63, and 6.72 wt %, respectively) and in samples 2 and 3 on the basis of the deficiency in the totals of the microprobe analyses (9.80 and 9.99 wt %, respectively).

⁶ This criterion was applied successfully for the first time to the eudialyte-group minerals as evidence for the occurrence of H_3O^+ in the structure of potassium–oxonium eudialyte (Rastsvetaeva et al., 1990a; Sokolova et al., 1991).

To estimate the possibility of the hydration of the eudialyte-group minerals by the substitution of oxygen atoms with OH-groups in the framework of an eudialyte structure, the local valence balance on the basis of 18 oxygen atoms of the framework for typical eudialyte has been calculated (Rozenberg et al., 2005). According to the results obtained, 14 of 18 atoms that make up the bridges of Si–O–Si, Si–O–Zr, and Si–O–2Ca cannot be replaced with OH-groups, because their bonds are locally balanced almost completely by positive charges of Si, Zr, and Ca cations. At the same time, the other four oxygen atoms can be partially replaced by OH-groups, because a contribution of the framework cations to the compensation of their charges is only about 1.3 for O(15)–O(16) and about 1 for O(17)–O(18). However, this possibility can be realized only if the remaining deficiency in the positive valence efforts focused on either the first or the second pair of oxygens, which are incorporated simultaneously into the coordination sphere of the out-of-framework sites *M*(2) and *M*(3)–*M*(4), respectively, will not be compensated by the contribution of cations occupying these sites, i.e., in the case of a vacancy in these positions. Otherwise, the sum of the valence efforts focused on these oxygens will be close to 2 like on oxygens O(1)–O(14) making their substitution with OH-groups impossible. In most structurally studied eudialyte-group minerals, sites *M*(2), *M*(3), and *M*(4) are characterized by the partial occupation that provides the possibility of the partial replacement of oxygen atoms in sites O(15)–O(18) with OH-groups. All of these relationships pertain to the samples described in this paper. However, according to the calculation of the local valence balance (Rozenberg et al., 2005), the role of the OH-groups in these sites is very limited for other types of proton–oxygen clusters revealed in the structures of the studied samples.

In conclusion, we emphasize that, although all of the above features were established for samples of the eudialyte-group minerals with a 12-layered structural motif, they are undoubtedly valid for the highly ordered 24-layered H-eudialytes as well. In the latter case, oxonium ions remain the major agent of hydration as in the 12-layered eudialytes. This is confirmed by the results of the X-ray diffraction analysis of two samples of high-ordered H-eudialytes from the Khibiny pluton (Rastsvetaeva et al., 2002), which require a special discussion.

ABUNDANCE AND NATURE OF HYDRATED EUDIALYTES

Until recently, hydrated eudialytes with the ratio $H_3O/Na \geq 1$ have been found only in the Khibiny and Inagli plutons and regarded as mineralogical curiosities (Efimov et al., 1963; Feklichev, 1965, 1979; Kostyleva-Labuntsova et al., 1978; Sokolova et al., 1991). In recent years, the geography of H-eudialytes' occurrences was substantially expanded owing to thematic

studies performed by many researchers including the authors of this paper. The findings in the Konder pluton (South Yuakutia), the Baruun Makhon pluton (Mongolia), numerous repeated findings in the Khibiny pluton (Ageeva et al., 2002; Khomyakov et al., 2006), and the discovery of ikranite in the Lovozero pluton (Chukanov et al., 2003) should be mentioned in this respect as well as the mineral from the Konder pluton, which is close in composition to aqualite (Pekov et al., 2005).

A detailed examination (Rastsvetaeva and Khomyakov, 2002, 2003; Rastsvetaeva et al., 2002; Rozenberg et al., 2005) made it possible to recognize H-eudialytes with 12- and 24-layered structures. In all alkaline plutons except the Khibiny, the 12-layered H-eudialytes occur, whereas minerals with the 24-layered structural motif are predominant only in the Khibiny pluton. Such structural typomorphism of H-eudialytes was explained by Khomyakov et al. (2006), taking rastsvetaevite $Na_{27}K_8Ca_{12}Fe_3Zr_6Si_4[Si_3O_9]_4[Si_9O_{27}]_4(O,OH,H_2O)_6Cl_2$, a high-K eudialyte-group mineral with the 24-layered structure, as an example. This mineral was found only in the rocks of the central arc of the Khibiny pluton. Rastsvetaevite is distinguished by clearly expressed ion-exchange properties that provide a wide abundance of its hydrated analogues ("hydrorastsvetaevites") in the Khibiny. In particular, these are partly hydrated rastsvetaevite-like minerals with a doubled-period *c* found as the products of the late magmatic mineralization within the central arc of the pluton (Rastsvetaeva et al., 2002). The previously stated suggestion that some other, thus far poorly studied H-eudialytes from the Khibiny pertain to hydrorastsvetaevites (Khomyakov et al., 2006) has recently been confirmed by V.V. Bakakin and Yu.V. Seretkin who carried out experiments on sample 41 of potassium–oxonium eudialyte described by Feklichev (1979). Fragments of the original sample 41 kept by the first author of this paper (see footnote 3) were used for this experiment. The single-crystal X-ray imaging of these fragments confirmed that potassium–oxonium eudialyte recognized by Feklichev is actually characterized by a doubled-period *c* and is close to rastsvetaevite ($a = 14.25$, $c = 60.97$ Å) in the unit-cell dimensions ($a = 14.28$, $c = 60.53$ Å). The results obtained can be considered (with some reservations) as an experimental corroboration of our general statement that high-potassium H_3O -eudialytes from the Khibiny pluton examined both by the authors of this paper and other researchers (Feklichev, 1965, 1979; Kostyleva-Labuntsova et al., 1978; Sokolova et al., 1991; Ageeva et al., 2002) were formed as the products of hydration and decationization of rastsvetaevite and its analogues with the 24-layered structural motif (Khomyakov et al., 2006) rather than of the common eudialyte as was assumed in previous publications.

According to the current concept, the distinctions between the ion-exchanged properties of rastsvetaevite and typical eudialyte are caused by the dimensional heterogeneity of the rastsvetaevite structure containing two types of cation layers—alluaivite-like (*M*) and eud-

ialyte-like (M^*)—different in thickness (Khomyakov et al., 2006). While the thickness of layer M^* (2.70 Å) is practically indistinguishable from that of the cation layer of the eudialyte structure (2.69 Å), the thickness of layer M (2.92 Å) exceeds the latter by 0.23 Å. On these grounds, we suggest that the expansion of the rastsvetaevite M -layer up to 2.92 Å along the principal axis of symmetry provides a high permeability of the structure for exchanging cations owing to the prevalence of potassium cations within the zeolite cages of this layer. However, such an explanation hardly may be accepted as universal. For example, the thickness of the cation layer in aqualite (3.15 Å) is still greater (by 0.46 Å) than that of the eudialyte structure even at a moderate potassium content in this mineral (1.93 wt %). At the same time, the virtually complete absence of Fe atoms, which tighten the quaternions of oxygen atoms at junctions of the six-membered Ca-rings in the structure of a typical eudialyte, is a common feature of the aqualite cation layer and the M -layer of rastsvetaevite. Precisely this feature probably provides the untypical of eudialyte expansion of the above-mentioned layers in the aqualite and rastsvetaevite structures. Anyhow, the presence of an anomalously thick cation layer in the structure of aqualite is consistent with the principal crystallochemical attributes of this mineral and explains its ion-exchange properties.

Like hydrorastsvetaevite, aqualite and other H-eudialytes presented in Table 4 pertain with a high probability to the special genetic group of minerals defined as transformational mineral species that are formed as a result of the ion-exchange modifications of their full-cationic analogues during the late stages of mineral formation (Khomyakov and Yushkin, 1981; Khomyakov, 1990, 1995, 1996, 1999). This statement is supported by the structural data in combination with direct evidence for the pseudomorphous crystallization of H-eudialytes after high-alkaline analogues in the zones of hydrothermally altered pegmatites.

Most samples of the studied collection of H-eudialytes belong to the $R3$ symmetry, which is extremely rare in the full-cationic eudialyte-group minerals in comparison with $R3m$. Although five of the six $R3$ H-eudialytes in Table 4 formally pertain to the same subgroup as oneillite (see above), they are quite different in crystal chemistry from the latter mineral. As mentioned above, in full-cationic minerals of this subgroup, the lowering of the symmetry from $R3m$ to $R3$ is mainly caused by the breakdown of the six-membered octahedral rings [$M(1)_6O_{24}$] into triplets of nonequivalent octahedrons significantly differing from one another in both composition and size. For example, in oneillite, the mean cation–anion distances in these octahedrons are 2.227 and 2.431 Å, respectively (Johnsen et al., 1999), i.e., they differ by more than 0.2 Å.

The appreciable difference of the octahedrons in size testifies in favor of the initial crystallization of oneillite in the $R3$ symmetry. At the same time, all H-eudialytes with the same symmetry are characterized

by barely different sizes of nonequivalent octahedrons. For instance, in aqualite, the average cation–anion distances in these octahedrons are 2.33 and 2.35 Å, i.e., they differ only by 0.02 Å. This general structural feature of H-eudialytes (Table 4) suggests that, in contrast to oneillite, the preceding high-alkaline phases of the hydrated $R3$ eudialytes initially crystallized in symmetry group $R3m$ and then were decationed with a degradation of the symmetry to $R3$. This shift was caused by the deformation of the primary high-symmetry structure at the final stage of the structure formation under the effect of the specific behavior of oxonium ions rather than by cation redistribution between $M(1a)$ and $M(1b)$ sites.

In line with the data considered above, H-eudialytes were formed at a relatively low temperature owing to the transformation of full-cationic protoeudialytes during the postcrystallization period. This transformation was driven by an ion-exchange mechanism and accompanied by the inheritance of structural and compositional features of the mineral precursors by mineral successors.

With allowance for the published and unpublished original data, the genetic interpretation of H-eudialytes considered above may be spread with some reservations over the group of hydrated eudialytes as a whole, including their analogues with a 24-layered structural motif. Unfortunately, the problem of primary eudialytes, from which H-eudialytes have been derived, remains unsettled. Except for rastsvetaevite as an unambiguous protophase for hydrorastsvetaevite, the speciation of protophases for other H-eudialytes remains unknown. The typical eudialytes, which are extremely inert for hydration and retained in hydrothermally altered rocks as absolutely fresh relics, can hardly be candidates for such precursors. Since the overwhelming majority of the identified H-eudialytes belongs to mineralogical curiosities, eudialytes with exotic compositions may be protophases for, at least, some H-eudialytes. For example, as judged from the composition of aqualite, a protophase might be depleted in Fe and enriched in Ba (up to 2.5 wt % BaO), which is not characteristic of typical eudialytes. The leading role of the natural catalytic reactions in the formation of H-eudialytes cannot be ruled out as well. Precisely these reactions may be responsible for the highly endemic nature of mineralization, including eudialyte-bearing, in alkaline plutons (Khomyakov et al., 2002b, 2004).

The type material of aqualite is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow. The registration number is 2668/1.

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