NEW MINERALS

Dualite, Na$_{30}$(Ca,Na,Ce,Sr)$_{12}$(Na,Mn,Fe,Ti)$_6$Zr$_3$Ti$_3$MnSi$_{51}$O$_{144}$(OH,H$_2$O,Cl)$_9$, a New Zircono–Titanosilicate with a Modular Eudialyte-Like Structure from the Lovozero Alkaline Pluton, Kola Peninsula, Russia[1]

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Abstract—Dualite has been found at Mount Alluaiv, the Lovozero Pluton, the Kola Peninsula in peralkaline pegmatoid as sporadic, irregularly shaped grains up to 0.3–0.5 mm across. K–Na feldspar, nepheline, sodalite, cancrinite, aegirine, alkaline amphibole, eudialyte, lovozerite, lomonosovite, vuonnemite, lamprophyllite, sphalerite, and villiaumite are associated minerals. Dualite is yellow, transparent or translucent, with conchoidal fracture. The new mineral is brittle, with vitreous luster and white streaks. The Mohs hardness is 5. The measured density is 2.84(3) g/cm^3 (volumetric method); the calculated density is 2.814 g/cm^3. Dualite dissolves and gelates in acid at room temperature. It is nonfluorescent. The new mineral is optically uniaxial and positive; ω = 1.610(1), ε = 1.613(1). Dualite is trigonal, space group $R3m$. The unit cell dimensions are a =14.153(9), c = 60.72(5) Å, V = 10533(22) Å, Z = 3. The strongest reflections in the X-ray powder pattern [d, Å (I,%)(hkl)] are as follows: 7.11(40)(110), 4.31(50)(0.2.10), 2.964(100)(1.3.10), 2.839(90)(048), 2.159(60)(2.4.10, 0.4.20), 1.770(60)(2.4.22, 4.0.28, 440), 1362(50)(5.5.12, 3.0.42). The chemical composition (electron microprobe, H$_2$O calculated from X-ray diffraction data) is as follows, wt %: 17.74 Na$_2$O, 0.08 K$_2$O, 8.03 CaO, 1.37 SrO, 0.29 BaO, 2.58 MnO, 1.04 FeO, 0.79 La$_2$O$_3$, 1.84 C$_2$O$_3$, 0.88 Nd$_2$O$_3$, 0.20 Al$_2$O$_3$, 51.26 SiO$_2$, 4.40 TiO$_2$, 5.39 ZrO$_2$, 1.94 Nb$_2$O$_5$, 0.58 Cl, 1.39 H$_2$O, –O = 0.13 Cl$_2$; they total is 99.67. The empirical formula calculated on the basis of 106 cations as determined by crystal structure is (Na$_{29.79}$Ba$_{0.1}$K$_{0.10}$)$_{\Sigma 30}$(Ca$_{8.55}$Na$_{1.39}$REE$_{1.27}$Sr$_{0.79}$)$_{\Sigma 12}$ · (Na$_{3.01}$Mn$_{1.35}$Fe$^{2+}_{0.87}$Ti$_{0.77}$)$_{\Sigma 6}$(Zr$_{2.61}$Nb$_{0.39}$)$_{\Sigma 3}$(Ti$_{2.52}$Nb$_{0.48}$)$_{\Sigma 3}$(Mn$_{0.82}$Si$_{0.18}$)$_{\Sigma 1}$(Si$_{50.77}$Al$_{0.23}$)$_{\Sigma 51}$ O$_{144}$[(OH)$_{6.54}$(H$_2$O)$_{1.34}$ · Cl$_{0.98}$]$_{\Sigma 8.86}$). The simplified formula is Na$_{30}$(Ca,Na,Ce,Sr)$_{12}$(Na,Mn,Fe,Ti)$_6$Zr$_3$Ti$_3$ MnSi$_{51}$O$_{144}$(OH,H$_2$O,Cl)$_9$). The name dualite is derived from Latin *dualis* (dual) alluding to the dual taxonomic membership of this mineral, which is at the same time zirconosilicate and titanosilicate. The crystal structure is characterized by two module types (alluivite-like and eudialyte-like) alternating along a threefold axis with a doubled c period relative to eudialyte and close chemical affinity to rastsvetaevite (Khomyakov et al., 2006a) and labyrinthite (Khomyakov et al., 2006b). According to the authors' crystal chemical taxonomy of the eudialyte group, the new mineral belongs to one of three subgroups characterized by a 24-layered structural framework. Dualite is a mineral formed during the final stages of peralkaline pegmatite formation. The type material of dualite is deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow.

INTRODUCTION

Despite the similarity in ion radii and chemical properties of titanium and zirconium, these elements differ sharply in their crystallochemical functions, as is especially evident from striving of Ti-octahedrons for association, whereas of Zr-octahedrons, for isolation in crystal structures of natural and synthetic compounds (Pyatenko and Voronkov, 1977). This circumstance significantly limits isomorphic substitution of these elements and explains why only sporadic zirconium minerals have titanium analogues and vice versa. This feature may be exemplified in the eudialyte group, which combines zeolite-like alkaline zircono- and titanosilicates with the heteropolyhedral framework {Ca$_6$(Zr,Ti)$_3$[Si$_9$O$_{27}$]$_2$[Si$_3$O$_9$]$_2$}$^{24-}$. In spite of expansion of this group of up to 20 mineral species during the last years, only one titanium mineral, alluaivite

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Table 1. Comparative characteristics of dualite, rastsvetaevite, labyrynthite, and alluivaite

Mineral	Dualite	Rastsvetaevite	Labyrynthite	Alluivaite
Formula	$Na_{30}(Ca,Na,Ce,Sr)_{12} \cdot (Na,Mn,Fe,Ti)_6 Zr_3 \cdot Ti_3 MnSi_{51}O_{144}(OH, H_2O,Cl)_9$	$Na_{27}K_8Ca_{12}Fe_3Zr_6 \cdot Si_{52}O_{144}(O,OH,H_2O)_6C_{12}$	$(Na, K, Sr)_{35}Ca_{12}Fe_3 \cdot Zr_6TiSi_{51}O_{144}(O,OH, H_2O)_9C_{13}$	$Na_{38}(Ca,Mn)_{12}(Ti,Nb)_6 Si_{52}O_{148}Cl_2 \cdot 4H_2O$
Symmetry	Trigonal	Trigonal	Trigonal	Trigonal
Space group	$R3m$	$R3m$	$R3$	$R\bar{3}m$
a, Å	14.153	14.249	14.239	14.046
c, Å	60.72	60.969	60.733	60.60
V, Å^3	10533	10720	10664	10354
Z	3	3	3	3
D, g/cm^3	2.84	2.86	2.88	2.76
Strong reflections in the X-ray powder pattern: $d(I)(hkl)$	2.964(100)(1.3.10) 2.839(90)(048) 2.159(60)(2.4.10) 1.770(60)(440) 4.31(50)(0.2.10) 1.362(50)(5.5.12) 7.11(40)(110) 2.675(30)(140) 2.599(30)(3.0.18) 1.477(30)(3.5.22) 1.338(30)(280)	2.987(100)(1.3.10) 4.345(81)(0.2.10) 2.861(73)(048) 3.249(57)(0.2.16) 6.48(47)(018) 3.565(41)(220) 2.695(40)(140) 3.196(37)(0.3.12) 2.619(36)(3.0.18) 5.72(33)(024) 3.189(32)(1.2.14)	2.977(100)(1.3.10) 2.853(88)(048) 4.324(68)(0.2.10) 3.230(44)(0.2.16) 3.550(39)(220) 2.685(38)(140) 3.049(36)(1.1.18) 2.605(36)(3.0.18) 5.70(34)(024) 3.173(34)(1.2.14) 6.45(33)(018)	2.960(100)(1.3.10) 2.825(100)(048) 7.14(80)(110) 1.762(80)(440) 4.30(70)(0.2.10) 2.148(70)(0.4.20) 1.358(70)(900) 3.36(50)(312) 2.664(50)(3.1.14) 2.583(50)(3.0.18) 3.77(40)(306)
Optical sign	+	+	+	+
ω	1.610	1.598	1.597	1.618
ε	1.613	1.600	1.601	1.626
Color	Yellow	Pink	Pink	Colorless
Source	This study	Rastsvetaeva and Khomyakov (2001a), Khomyakov et al. (2006a)	Rastsvetaeva and Khomyakov (2001b), Khomyakov et al. (2006b)	Khomyakov et al. (1990), Rastsvetaeva et al. (1990)

(Khomyakov et al., 1990), has been identified therein; all other species are zirconium minerals.

A titanium-rich, and at the same time Zr-bearing, mineral from the eudialyte group found in peralkaline pegmatites at Mount Alluaiv, in the Lovozero alkaline pluton, the Kola Peninsula, Russia, is described in this paper. The new mineral was named dualite[2] after the Latin *dualis* (dual) due to the combination of two types of mixed anion radicals $\{Zr_3[Si_9O_{27}]_2[Si_3O_9]_2\}^{36-}$ and $\{Ti_3[Si_9O_{27}]_2[Si_3O_9]_2\}^{36-}$ in the mineral structure, which determine the role of dualite as an interlink between zircono- and titanosilicates.

The mineralogical description of dualite and characteristics of the main features of its crystal structure are combined with a discussion on the position of this new mineral in the crystallochemical taxonomy of the eudialyte group. It was substantiated that dualite belongs to the high-ordered eudialyte pleiad with a double *c* period, which also includes alluaivite, rastsvetaevite, and labyrynthite (Khomyakov et al., 1990, 2006a, 2006b). Typomorphism of this eudialyte type is considered. The importance of the discovery of this pleiad is determined by the fact that all minerals of this pleiad are endemics of peralkaline rocks accompanying the world's largest rare-metal–phosphate deposits in the Khibiny–Lovozero Complex. Therefore, we regard these minerals as indicators of highly productive ore-forming processes related to alkaline magmatism (Khomyakov, 2002a, 2004; Khomyakov, 2006).

MODE OF OCCURRENCE, COMPOSITION, AND PROPERTIES OF DUALITE

Dualite was discovered in a core sample taken from a depth of 322 m in the eudialyte lujavrite pegmatite of

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[2] Dualite was provisionally characterized as a new Ti-rich member of the eudialyte family in a paper describing its crystal structure (Rastsvetaeva et al., 1999).

Table 2. Chemical composition, wt % of dualite

Component	Content in five grains	
	range	average
Na_2O	17.49–18.22	17.74
K_2O	0.07–0.10	0.08
CaO	7.86–8.18	8.03
SrO	1.31–1.52	1.37
BaO	0.26–0.44	0.29
FeO	0.84–1.21	1.04
MnO	2.43–2.70	2.58
La_2O_3	0.62–0.97	0.79
Ce_2O_3	1.74–2.07	1.84
Nd_2O_3	0.81–0.98	0.88
Al_2O_3	0.20–0.20	0.20
SiO_2	50.82–51.37	51.26
ZrO_2	5.13–5.45	5.39
Nb_2O_5	1.67–2.39	1.94
TiO_2	3.92–4.58	4.40
Cl	0.52–0.77	0.58
H_2O		1.39
$-O=Cl_2$		0.13
Total		99.67

Note: Electron microprobe data, analyst G.N. Nechelystov. The water content was calculated from the results of X-ray diffraction data.

the third intrusive phase of the Lovozero pluton. This sample is a strongly mineralized peralkaline pegmatoid composed of an aggregate of K–Na feldspar, nepheline, sodalite, cancrinite, aegirine, alkaline amphibole, lovozerite, lomonosovite, vuonnemite, lamprophyllite, sphalerite, and villiaumite. The new mineral occurs as very rare irregularly shaped grains up to 0.3–0.5 mm across, which are occasionally intergrown with crystals of common eudialyte containing no more than 0.40–0.55 wt % TiO_2.

The small amount of the new mineral did not allow a complete study of its properties. The most important results are given in Table 1, where they are compared with the respective data for other eudialyte-like minerals with high-ordered structure.

Physical and optical properties. Dualite is yellow, with conchoidal fracture and vitreous luster. The streak is white. The new mineral is transparent or translucent and brittle. The cleavage or jointing is not distinct. The Mohs hardness is 5. The measured density is 2.84(3) g/cm^3 (microvolumetric method); the density calculated from the empirical formula is 2.814 g/cm^3. Dualite is uniaxial and positive. The refractive indexes were determined by immersion (λ = 589 nm): ω = 1.610(1) and ε = 1.613(1). The new mineral is not ple-

ochroic and is fluorescent in UV light (λ = 240–400 nm). It dissolves and gelates in 50% solutions of HCl and HNO_3 at room temperature. After 2-h ignition at 500°C, dualite retains its transparency and the refractive indexes of the primary grains.

The chemical composition of dualite (Table 2) was studied by G.N. Necheluystov with a Superprobe-733 electron microprobe operating at 15 kV and 20 nA. The composition of five grains (five point analyses for each grain) was determined by the following standards: chkalovite (Na), $K_2ZrSi_2O_7$ (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), $LiNbO_3$ (Nd), chlorapatite (Cl). Iron was conditionally deemed as bivalent. The water content is calculated from X-ray diffration data.

Taking into account the crystal structure of dualite (see below), the empirical formula calculated from the average chemical composition of five analyzed grains on the basis of 106 cations (Z = 3) is $(Na_{29.79}Ba_{0.11}K_{0.10})_{\Sigma 30}(Ca_{8.55}Na_{1.39}REE_{1.27}Sr_{0.79})_{\Sigma 12}(Na_{3.01}$ $Mn_{1.35}Fe^{2+}_{0.87}Ti_{0.77})_{\Sigma 6}(Zr_{2.61}Nb_{0.39})_{\Sigma 3}(Ti_{2.52}Nb_{0.48})_{\Sigma 3}(Mn_{0.82}$ $Si_{0.18})_{\Sigma 1}(Si_{50.77}Al_{0.23})_{\Sigma 51}O_{144}[(OH)_{6.54}(H_2O)_{1.34}Cl_{0.98}]_{\Sigma 8.86}.$ The simplified formula is $Na_{30}(Ca,Na,Ce,Sr)_{12}$ $(Na,Mn,Fe,Ti)_6Zr_3Ti_3 MnSi_{51}O_{144}(OH,H_2O,Cl)_9.$

The X-ray powder pattern of dualite (Table 3) is individualized but remains similar to the patterns of other minerals from this group (Table 1). The unit cell dimensions (hexagonal aspect) calculated from the X-ray powder pattern are a = 14.152(3), c = 60.71(2) Å and coincide with parameters obtained from X-ray single crystal study: a = 14.153(9), c = 60.72(5) Å. Unfortunately, because of the low resolution of the Gandolfi method used in this study, weak reflections that double parameter c of the mineral cell in comparison with typical eudialyte were not recorded.

THE POSITION OF DUALITE IN THE CRYSTALLOCHEMICAL TAXONOMY OF EUDIALYTE GROUP AND ITS CRYSTAL STRUCTURE

According to the modern concept of the crystal chemistry of eudialyte group minerals (Johnsen and Grice, 1999; Johnsen et al., 2003; Khomyakov, 2002b, 2005; Rastsvetaeva and Khomyakov, 2003; Khomyakov et al., 2006a), this group comprises trigonal zircono- and titanosilicates with the general formula $A(1)_3A(2)_3A(3)_3A(4)_3A(5)_3B_{3-6}CD\{M_6Z_3[T_{24}O_{72}]\}$ $(O,OH)_{2-6}X_2$ (Khomyakov, 2002a, 2004a). The base of their zeolite-like structure is a heteropolyhedral framework (in braces) formed by (001) sheets alternating along axis c in the running order *MTZT*, where *M* sheets are six-member rings consisting of Ca- and more complex octahedrons, *T* sheets are isolated rings $[Si_9O_{27}]$ and $[Si_3O_9]$, and *Z* sheets are discrete Zr- and/or Ti-octahedrons. In the array cavities, there are cations with

Table 3. X-ray powder diffraction data for dualite

I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl
40	7.11	7.08	110	5	1.716	1.717	3.2.28
20	6.50	6.45	018			1.714	0.2.34
10	6.02	6.01	202	5	1.689	1.689	624
20	5.63	5.68	024			1.686	0.0.36
10	5.08	5.06	0.0.12	10	1.670	1.670	4.4.12
50	4.31	4.31	0.2.10	20	1.639	1.640	1.1.36
20	4.10	4.12	1.1.12			1.637	6.2.10
		4.09	0.1.14	20	1.613	1.614	1.4.30
		4.08	300			1.613	0.4.32
20	3.79	3.79	036	10	1.582	1.583	2.4.28
20	3.54	3.54	2.0.14			1.582	2.6.14
		3.54	220			1.581	1.3.34
20	3.37	3.38	312	10	1.572	1.573	2.3.32
20	3.17	3.18	0.3.12	20	1.545	1.545	5.1.28
		3.17	1.2.14			1.544	360
100	2.964	2.966	1.3.10	10	1.525	1.526	636
90	2.839	2.841	048			1.526	3.4.26
30	2.675	2.675	3.1.14			1.524	084
		2.674	140	10	1.501	1.502	808
30	2.599	2.601	3.0.18			1.500	5.0.32
10	2.531	2.532	1.3.16	30	1.477	1.478	3.5.22
		2.530	0.0.24			1.478	7.0.22
10	2.443	2.443	502			1.477	3.6.12
		2.441	2.2.18			1.476	4.3.28
20	2.358	2.359	330			1.476	4.5.14
10	2.309	2.309	422	10	1.439	1.442	2.1.40
60	2.159	2.164	2.4.10			1.438	0.6.30
		2.156	0.4.20	10	1.418	1.421	0.8.16
10	2.063	2.063	2.3.20			1.416	1.1.42
10	2.043	2.044	0.2.28			1.415	550
		2.043	4.2.14	10	1.402	1.404	3.6.18
		2.043	600			1.404	642
10	1.979	1.977	2.4.16			1.400	464
10	1.946	1.947	348	50	1.362	1.363	5.5.12
		1.946	1.1.30			1.363	3.0.42
10	1.896	1.894	0.6.12			1.362	1.8.14
10	1.868	1.866	612			1.360	4.0.40
20	1.833	1.838	1.4.24	30	1.338	1.338	5.0.38
		1.830	5.2.12			1.338	2.2.42
60	1.770	1.774	2.4.22			1.338	6.2.28
		1.770	4.0.28			1.337	6.4.14
		1.769	440			1.337	280

Note: Operating conditions: Gandolfi camera, D 114.6 mm, FeK_α radiation.

valences ranging from 1+ to 6+ (Na, K, H_3O^+, Ca, Sr, Mn, Fe^{2+}, Fe^{3+}, REE, Si, Ti, Nb, W), additional anions (Cl, F, O, OH, SO_4, CO_3), and water molecules. Currently, more than 20 mineral species of the eudialyte group are known. All are attributed to trigonal symmetry and space groups $R\bar{3}m$, $R3m$, or $R3$. Most species, including eudialyte proper, have a relatively low-ordered 12-layered structure described by the unit cell with $a \approx 14.2$ and $c \approx 30$ Å.

The peculiar "Chapter Two" in the mineralogy and crystal chemistry of the eudialyte group was the discovery in the Khibiny–Lovozero Complex of an entire pleiad of megaeudialytes with 24-layered structure distinguished from the eudialytes of "Chapter One" by their high-ordered structure, doubled c period, and more complex alteration of structural sheets in the running order ($MTZT$) ($M^* T^* Z^* T^*$), which defines their structures (Khomyakov, 2002a, 2002b, 2005; Rastsvetaeva and Khomyakov, 2003). In addition to dualite, three crystallochemically unique minerals are members of this pleiad: alluaivite $Na_{38}(Ca,Mn)_{12}(Ti,Nb)_6Si_{52}O_{148}Cl_2 \cdot 4H_2O$ (Khomyakov et al., 1990; Rastsvetaeva et al., 1990), rastsvetaevite $Na_{27}K_8Ca_{12}Fe_3Zr_6Si_{52}O_{144}(O,OH,H_2O)_6Cl_2$ (Rastsvetaeva and Khomyakov, 2001a; Khomyakov et al., 2006a), and labyrynthite $(Na,K,Sr)_{35}Ca_{12}Fe_3Zr_6TiSi_{51}O_{144}(O,OH,H_2O)_9Cl_3$ (Rastsvetaeva and Khomyakov, 2001b; Khomyakov et al., 2006b).

The above-mentioned findings made it possible to elaborate the crystallochemical taxonomy of the eudialyte group covering all natural species (Khomyakov, 2004a; Khomyakov, 2005; Khomyakov et al., 2006a) in contrast to the previous classification adopted for 12-layered eudialytes (Johnsen and Grice, 1999). The new taxonomy described in the above-cited papers is based on the division of this group into six crystallochemical subgroups distinguished by combinations of 12- and 24-layered structure motifs with each of the three space groups identified for eudialytes. The subgroups were named after the most fully characterized minerals, whereas the subgroups so far consisting of only one mineral were named after this mineral. The list of the recognized subgroups and alphabetic lists of minerals (in parentheses) attributed to each subgroup are as follows: (1) eudialyte subgroup (eudialyte s.s.);[3] (2) kentbrooksite subgroup (georgbarsanovite, goloyshevite, ikranite, johnsenite-(Ce), carbokentbrooksite, kentbrooksite, manganokhomyakovite, mogovidite, taseqite, feklichevite, ferrokentbrooksite, khomyakovite, zirsilite-(Ce), eudialyte s.l.); (3) oneillite subgroup (aqualite, oneillite, raslakite); (4) alluaivite subgroup (alluaivite); (5) rastsvetaevite subgroup (dualite, rasts-

vetaevite); and (6) labyrynthite subgroup (labyrynthite). Subgroups 1–3 are 12-layered eudialytes, whereas subgroups 4–6 are 24-layered eudialytes. The order of the listing of subgroups within each triad corresponds to the order of decreasing symmetry of space groups in the series $R\bar{3}m$—$R3m$—$R3$.

Dualite pertains to the rastsvetaevite subgroup that combines eudialytes with a 24-layered structure motif and space group $R3m$. According to recommendations of the Subcommittee on Eudialytes of the Commission on New Minerals and Mineral Names, International Mineralogical Association (Johnsen et al., 2003), the composition of minerals from this subgroup can be broadly described by the general formula (where $Z = 3$): $[N(1)N(1)^*N(2)N(2)^*N(3)N(3)^*N(4)N(4)^*N(5)N(5)^* N(6)N(7)]_3[M(1)M(1)^*]_3[M(2)M(2)^*]_3M(3)M(3)^*M(4)M(4)^*Z_3Z_3^*[Si_{24}O_{72}][Si_{24}O_{72}]^*\varphi_4\varphi_4^*X_2X_2^*$, where the same symbol with and without m asterisk designates the homologous position of the first and second modules of the structure, respectively (see below). According to statistical data on the composition of atoms occupying key sites of eudialytes with determined structure, sites $N(1)$–$N(7)$ and $N(1)^*$–$N(5)^*$ are occupied, as a rule, by Na; some of them can also be occupied by REEs, Sr, Ca, K, Mn, and H_3O^+, while positions $N(6)$ and $N(7)$ can contain K and Sr; $M(1)$ and $M(1)^* = $ Ca, K, Mn, Sr, REE, Y, and Na; $M(2)$ and $M(2)^* = Fe^{2+}$, Fe^{3+}, Mn, and Na; $M(3)$ and $M(3)^* = $ Nb, Ti, W, Mn, and Si; $M(4)$ and $M(4)^* = $ Si; Z and $Z^* = $ Zr, Ti; φ and $\varphi^* = $ O, OH, and H_2O; X and $X^* = $ Cl, F, H_2O, OH, CO_3, and SO_4.

The crystallochemical basis of the 24-layered eudialytes is a heteropolyhedral framework consisting of M, T, and Z sheets alternating along [001] in the running order ($MTZT$) ($M^* T^* Z^* T^*$), where parentheses comprise pairs of nonequivalent 4-layered modules, which form an eight-layered stack about 20 Å thick. The first module of stack corresponds to a fragment of an independent part of the structure within a range of z from −0.025 to 0.14, and the second one, to the homologous fragment within a range of z from 0.14 to 0.31. The individuality of the first and second modules is determined by topological features of M and M^* sheets. In M sheets, the rings consisting of six edge-shared octahedrons $[M(1)O_6]$ are bound with one another by the pairs of face-shared seven-vertex polyhedrons $[N(6)O_7]$ and $[N(7)O_7]$ to form 12-member heteropolyhedral rings. For the first time, M sheets with similar topology were identified in the structure of alluaivite (Rastsvetaeva et al., 1990) and therefore, they are designated according to our nomenclature of structural units of minerals belonging to this group as cationic heteropolyhedral sheets of the alluaivite-like type (Khomyakov et al., 2006a); modules containing M sheets are two noted alluaivite-like, respectively. In contrast to M sheets, the rings consisting of six octahedrons $[M(1)^*O_6]$ in M^* sheets are linked by polyhe-

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[3] s.s. and s.l. stand for sensu stricto and sensu lato, respectively. Eudialyte s.s. is eudialyte proper with centrosymmetrical structure, whereas eudialyte s.l. is a dimorph of eudialyte s.s. having an acentric structure (Johnsen and Grice, 1999; Khomyakov et al., 2006a).
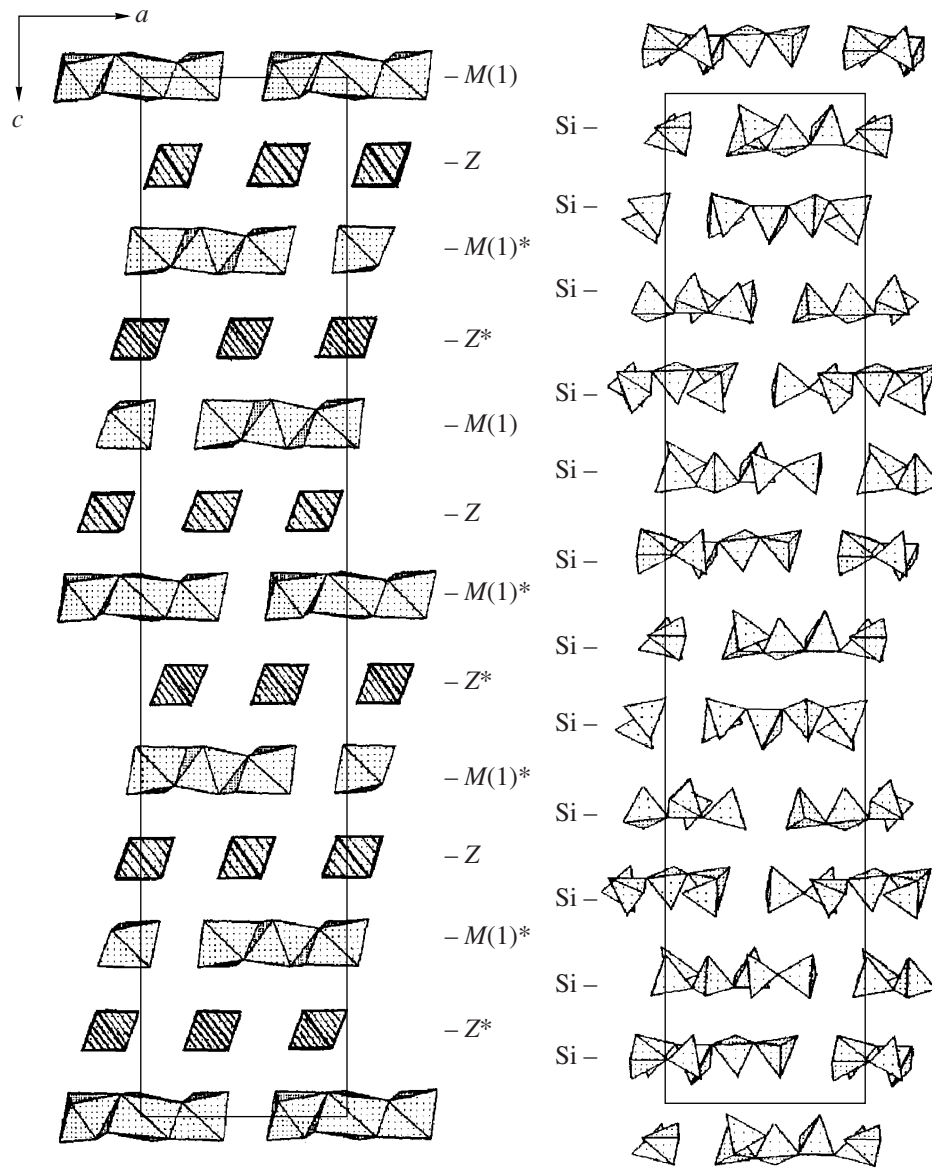
Intercalation of Si-, $M(1)$- and Z-polyhedrons along axis c in the crystal structure of dualite: $M(1) = 3.7Ca + 1.9Na + 0.4Ce$, $M(1)^* = 4.8Ca + 1.2Mn$, $Z = 2.0Zr + 0.7Ti + 0.3Nb$, $Z^* = 1.7Ti + 1.0Zr + 0.3Nb$. See text for explanations.

drons $[M(2)^*O_{4-6}]$ (four-, five- or less frequently six-vertex) to form 9-member heteroplyhedral rings. M^* sheets are similar in topology to corresponding sheets in the structure of eudialyte proper and therefore, they are designated as cationic heteropolyhedral sheets of the eudialyte-like type; modules containing M^* sheets are marked as eudialyte-like.

The crystal structure of dualite (see figure) is determined on the basis of the experimental dataset obtained with an Enraf-Nonius CAD4 4-circle single crystal diffractometer and specified for 3402 unique reflections $[Fo > 4\sigma(F)]$ to an R factor of 0.068 (Rastsvetaeva et al., 1999). The space group is $R3m$, $a = 14.153(9)$, $c = 60.72(5)$ Å, $V = 10533(22)$ Å, $Z = 3$. The following distribution of atoms by key cation sites

(without splitting into subsites) was established: $N(1) = Na_{0.3}$, $N(1)^* = (Na_{2.73}Ce_{0.27})_{\Sigma = 3.0}$, $N(2) = Na_{0.3}$, $N(2)^* = (Na_{2.68}Ce_{0.23})_{\Sigma = 2.91}$, $N(3) = Na_{3.0}$, $N(3)^* = (Na_{2.6}Sr_{0.4})_{\Sigma = 3.0}$, $N(4) = Na_{3.0}$, $N(4)^* = Na_{3.06}$, $N(5) = Na_{2.97}$, $N(5)^* = Na_{3.06}$, $N(6) = (Na_{1.46}Sr_{0.37})_{\Sigma = 1.83}$, $N(7) = (Na_{0.67}Ce_{0.23})_{\Sigma = 0.9}$, $M(1) = (Ca_{3.73}Na_{1.87}C_{0.4})_{\Sigma = 6.0}$, $M(1)^* = (Ca_{4.77}Mn_{1.23})_{\Sigma = 6.0}$, $M(2) = Fe_{0.27}$, $M(2)^* = (Na_{1.33}Ti_{1.00}Fe_{0.67})_{\Sigma = 3.0}$, $M(3) = (Si_{0.67}Al_{0.33})_{\Sigma = 1.0}$, $M(3)^* = (Mn_{0.9}SiO_{0.1})_{\Sigma = 1.0}$, $M(4) = Si_{1.0}$, $M(4)^* = Si_{1.0}$, $Z = (Zr_{2.0}Ti_{0.7}Nb_{0.3})_{\Sigma = 3.0}$, $Z^* = (Ti_{1.7}Zr_{1.0}Nb_{0.3})_{\Sigma = 3.0}$.

According to the results, the crystallochemical formula of dualite can be expressed, when $Z = 3$, as $\{[Na_{15.0}]^{VI-IX}(Na_{14.1}Ce_{0.5}Sr_{0.4})^{VI-X}\}\{(Ca_{3.73}Na_{1.87}Ce_{0.4})^{VI}(Ca_{4.77}Mn_{1.23})^{VI}\}\{(Na_{2.13}Sr_{0.37}Fe_{0.27}Ce_{0.23})^{IV-VII}$

$(Na_{1.33}Ti_{1.00}Fe_{0.67})^{IV-VII}\}\{(Zr_{2.0}T_{0.7}Nb_{0.3})^{VI}$ $(Ti_{1.7}Zr_{1.0}Nb_{0.3})^{VI}\}\{(Si_{0.67}Al_{0.33})^{IV,VI}(Mn_{0.9}Si_{0.1})^{IV}\}$ $\{(Si)^{IV}(Si)^{IV}\}[Si_{48}O_{144}](OH)_{6.2}(H_2O)_{1.5}Cl_{0.9}$, where coordination numbers are marked by Roman numerals. The formula emphasizes that mineral belongs to modular eudialytes. Cations occupying homologous key sites of alluaivite-like (*A*) and eudialyte-like (*B*) modules, respectively, are combined in pairs in braces. Both modules, taken together, make up an eight-layered stack 20.24 Å thick. Multiplied along the threefold axis of symmetry according to the *R*-lattice law, this stack forms a 24-layered structure with a *c* period of 60.72 Å.

The examined structure differs from the structures of 12-layered eudialytes by a distinct differentiation of atoms of various elements between homologous sites, as is characteristic of alluaivite, rastsvetaevite, and labyrynthite structures. However, if the octahedral sites *Z* and *Z** of the aforementioned analogues are dominated by only one cation (Ti in alluaivite and Zr in rastsvetaevite and labyrynthite), the described mineral has two different type of octahedrons $(Zr_{2.0}Ti_{0.7}Nb_{0.3})$ and $(Zr_{1.7}Ti_{1.0}Nb_{0.3})$. Each octahedron forms its own sheets alternating along the threefold axis and doubling the *c* period of the dualite unit cell.

The distribution of other cations between key homologous sites of the modules *A* and *B* in dualite is as follows:

	N4, N4	*M1, M1*	*N6, N7, N7*, M2, M2*	*M3, M3*, M4, M4*
A	Na_3^{VII}	$(Ca, Na, Ce)_6^{VI}$	$(Na, Sr)_{18}^{VII}(Na, Ce)_{0.9}^{VII}Fe_{0.3}^{IV}$	$(Si^{IV}, Al^{VI})Si^{IV}$
B	$(Na, Sr)_3^{VII}$	$(Ca, Mn)_6^{VI}$	$Na_{1.3}^{VII}Ti_{1.0}^{VI}Fe_{0.7}^{IV}$	$(Mn^{IV}, Si^{IV})Si^{IV}$

It is close to labyrynthite:

	N4, N4	*M1a, M1b, M1a*, M1b*	*N6, N7, M2, M2*	*M3, M3*, M4, M4*
A	Na_3^{VII}	$Ca_3^{VI}(Ca, Sr)_3^{VI}$	$(Na, Sr, Ce)_{1.6}^{VII}(Na, Sr, Ce)_{1.7}^{VII}Na_{1.2}^{IV}$	$(Ti^{VI}, Si^{IV}, \square)Si^{IV}$
B	$(Na, K, Sr)_3^{VII-VIII}$	$Ca_3^{VI}Ca_3^{VI}$	$(Fe^{IV}, Mn^V)_3$	$Si\ Si^{IV}$

Both minerals have much in common as concerns the composition of *A* modules, where cations are distributed by three sites *M*(2) (in a "square" of $[M(2)O_4]$), *N*(6), and *N*(7) (on both sides of the square). However, if Na occupies the *M*(2) site in labyrynthite, Fe occupies this site in dualite. Sites *N*(6) and *N*(7) in both minerals are Na-dominant with an admixture of Sr and Ce. However, these sites in dualite are drawn together to a greater extent (2.82 Å as opposed to 2.93 Å in labyrynthite), and in combination with site *M*(2) contain up to 9 atoms in total contrary to 18 atoms in labyrynthite. As a result, the total number of Na atoms in dualite is less than in labyrynthite.

One of the important differences of *B* modules as compared minerals is the predominance of Mn in tetrahedral site *M*(3)* in the structure of dualite, whereas in the labyrynthite structure, this site is occupied by silicon. The average cation–ligand interatomic distance in site *M*(3)* of dualite (2.0 Å) corresponds to the sum of ion radii $(Mn^{2+})^{IV}$ (0.66 Å) and O^{2-} (1.36 Å). Earlier, tetrahedral Mn^{2+} with a bond length of 1.5–1.93 Å was established in the *M*(3) site of feklichevite (Rastsvetaeva et al., 1999). The crystallochemical individuality of dualite is emphasized by a number of other features revealed by X-ray diffraction (Rastsvetaeva et al., 1999).

In conclusion, it should be noted that in contrast to dualite, the main cause of *c* period doubling in both rastsvetaevite and labyrynthite is the occurrence of two cation sheets of *M* and *M** types distinct in composition and structure. In the case of alluaivite, the main cause of such doubling is the ordered distribution of additional Si-tetrahedrons embedded into nine-member rings of disklike clusters $\{[Si_9O_{27}]SiO\}$. One of these tetrahedrons is oriented like basic tetrahedrons in the ring, whereas the second one is oriented in the opposite direction.

TYPOMORPHIC FEATURES OF DUALITE AND MODULAR EUDIALYTES AS A WHOLE

Dualite is a late mineral that crystallized during the final stages of formation of peralkaline pegmatites. In contrast to rastsvetaevite characteristic of the potassium branch of such pegmatites, especially striking in the Khibiny pluton (Khomyakov, 1990; Ageeva et al., 2002a; Khomyakov et al., 2006a), both dualite and alluaivite are typomorphic of the sodium branch of peralkaline pegmatites, which are abundant in the Lovozero pluton. Taking into account the aforementioned geochemical difference of high-alkaline mineralization in the two compared plutons, it can be suggested that labyrynthite, a sodium analogue of rastsvetaevite found in the Khibiny pluton as a mineralogical rarity, is more abundant in the Lovozero pluton and the discovery of

labyrynthite therein was only a matter of time (Khomyakov et al., 2006b).

Modular eudialytes are unknown outside of the Khibiny–Lovozero Complex, where they are abundant and in some cases may be considered rock-forming minerals. In particular, these are rastsvetaevite and its still unnamed hydrated analogues that occur in rischorrite and related high-mineralized rocks of the Khibiny pluton (Khomyakov et al., 2006a). A number of potentially new minerals of the eudialyte group with a doubled c period have been described from these plutons (Rastsvetaeva and Khomyakov, 2003).

Currently, dualite and alluaivite have been reliably established only in the Lovozero pluton, although eudialyte-like minerals close to dualite and alluaivite in composition but poorly characterized in terms of crystal chemistry were identified in Khibiny (Ageeva et al., 2002a, 2002b). The distinct boundaries between the alluaivite and dualite grains in the examined Lovozero samples, on the one hand, and typical eudialyte, on the other, indicates that a miscibility gap exists between titanium and zirconium members of eudialyte group. The absence of an elevated titanium content in eudialytes associated with such titanium minerals as titanite and lorecenite supports this suggestion. Taking into account this fact, dualite may be likened to some extent to dolomite as an ordered intermediate member of the calcite–magnesite series. The idealized formula of dolomite can be written as $(Ca,Mg)CO_3$ rather than $CaMg(CO_3)_2$.

The genetic link between high-ordered eudialytes and its low-ordered analogues is strikingly expressed in the Khibiny pluton, where the relics of medium-K 12-layered eudialyte have been identified in cores of rastsvetaevite grains, while their margins are composed of the 24-layered hydrated eudialyte mentioned above (Khomyakov et al., 2006a). These three minerals are characterized by homoaxial relationships that are recorded in simultaneous extinction under crossed polars and may be regarded as a criterion for rastsvetaevite and hydrated eudialyte belonging to the special group of transformation mineral species (Khomyakov, 1980, 1999; Khomyakov and Yushkin, 1981; Yushkin et al., 1984; Khomyakov, 1996).

In terms of this concept, the abundance of rastsvetaevite in the Khibiny pluton was controlled by the distribution of eudialyte subsequently altered by potassium metasomatism, whereas the abundance of 24-layered hydrated eudialyte corresponds to areas where rastsvetaevite was modified by superimposed epithermal processes. This idea is consistent with published data (Ageeva et al., 2002a), according to which potassium metasomatism in the Khibiny pluton was accompanied by replacement of eudialyte of ordinary composition by its analogues enriched in potassium. These processes developed the most intensively close to the world's largest apatite deposits, making understandable they localization of rastsvetaevite segregations and its hydrated analogues in the high-potassium peralkaline pegmatoids accompanying these deposits along the central arc of this pluton for about 70 km.

The establishment of an intrinsic relationship between the structural ordering of the eudialyte group minerals and the degree of peralkalinity of host rocks is one of the most important implications of the discovery of unusual eudialyte-like minerals with a 24-layered structural motif in the Lovozero and Khibiny plutons. The low- and high-ordered members of this group are characteristic of moderate- and ultraperalkaline rocks, respectively. The abundance of minerals of this group in genetically distinct peralkaline complexes makes them the most important indicators of formation conditions and typification of alkaline rocks (Khomyakov, 2002a, 2002b, Khomyakov et al., 2006a). Because all discovered 24-layered eudialytes are endemic in ultraperalkaline rocks accompanying large rare-metal–phosphate deposits, they may be regarded as indicators of high-productive ore-forming processes related to alkaline magmatism (Khomyakov, 2004; Khomyakov, 2006).

The type material of dualite is deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow. The registration number is 2626/1.

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