Review

New Data on the Isomorphism in Eudialyte-Group Minerals. 2. Crystal-Chemical Mechanisms of Blocky Isomorphism at the Key Sites

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Abstract: The review considers various complex mechanisms of isomorphism in the eudialyte-group minerals, involving both key positions of the heteropolyhedral framework and extra-framework components. In most cases, so-called blocky isomorphism is realized when one group of atoms and ions is replaced by another one, which is accompanied by a change in the valence state and/or coordination numbers of cations. The uniqueness of these minerals lies in the fact that they exhibit ability to blocky isomorphism at several sites of high-force-strength cations belonging to the framework and at numerous sites of extra-framework cations and anions.

Keywords: eudialyte group; crystal chemistry; blocky isomorphism; peralkaline rocks

1. Introduction

Eudialyte-group minerals (EGMs) are typical components of some kinds of agpaitic igneous rocks and related pegmatites and metasomatic assemblages. Crystal-chemical features of these minerals are important indicators reflecting conditions of their formation (pressure, temperature, fugacity of oxygen and volatile species, and activity of non-coherent elements [1–9]).

A unique crystal-chemical diversity of EGMs is determined by a wide variability of their chemical composition involving more than 30 main elements and complex mechanisms of homovalent, heterovalent, and, especially, blocky isomorphism involving groups of atoms having different valency and coordination. The uniqueness of these minerals lies in the fact that they exhibit ability to blocky isomorphism at several sites of high-force-strength cations belonging to the framework and at numerous sites of extra-framework cations and anions.

According to the recommendation of the Commission on New Minerals, Nomenclature, and Classification of the International Mineralogical Association [3], the general formula of EGMs is $\text{N}_1\text{N}_2\text{N}_3\text{N}_4\text{N}_5\text{M}_1\text{M}_2\text{M}_3\text{M}_4\text{Z}_3(\text{Si}_{24}\text{O}_{72})\text{O}_4\text{X}_2$. In this formula, most symbols denote split sites (i.e., groups of closely spaced sites). The “rigid” part of the structures of eudialyte-type minerals (Figure 1) is a 3D quasi-framework consisting of $\text{IVSiO}_6$, $\text{IVSiO}_8$, and $\text{VI}_1\text{OSi}_8$ rings ($\text{M}_1 = \text{Ca}, \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Na}, \text{Lu}, \text{Y}, \text{Sr}$; coordination numbers are denoted by Roman numerals) connected via $\text{M}_2\text{O}_{4–7}$ polyhedra and $\text{Z}_0\text{O}_6$ octahedra ($\text{M}_2 = \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mn}^{2+}, \text{Mn}^{3+}, \text{Mg}, \text{Zr}, \text{Ta}, \text{Na}; \text{Z} = \text{Zr}, \text{T}, \text{Nb}$) and containing additional $\text{M}_3$ and $\text{M}_4$ sites which are situated at the centers of two nonequivalent $\text{SiO}_{27}$ rings and can be occupied by $\text{IVSi}$, $\text{IVNb}$, $\text{VTi}$, and $\text{VW}$, as well as subordinate $\text{Al}$, $\text{Na}$, and other components whose charges vary from +1 to +6 [1,2] (Figure 1). In the structures of most EGMs, including eudialyte s.s., $\text{M}_1$ cations can be disordered, but in some representatives of this mineral
group they alternate in the ring of octahedra, which results in its transformation into the ring 
(M1.1M1.2O6) and symmetry lowering from the space group R3m or R-3m to R3. In some samples, 
a splitting of the M1 site [10] or one of the M1.1/M1.2 sites [11] into two sub-sites located at short 
distance of ~0.2 Å from each other takes place. The M1–M4 sites are considered as the main 
species-defining “key sites” in the nomenclature of EGMs [3,6,7,12,13].

Extra-framework cations (Na+, K+, Ca2+, Mn2+, Sr2+, Pb2+, Y3+, Ln3+, and H3O+) and (in some 
samples) water molecules occupy five sites, N1–N5, which are typically split and can be partly 
vacant. Cations other than Na+ show a tendency to concentrate at the N3 and N4 sites. Some of these 
cations (K+, Ca2+, Mn2+, Sr2+, Ce3+, and H3O+) are species-defining ones in several representatives of the 
eudialyte group. The Ø anions (Ø = O, OH) coordinate the M2, M3, and M4 sites. Additional anions 
(Cl-, F-, OH-, S2-, SO42-, and CO32-) and water molecules occur at the X1 and X2 sites located on the 
three-fold axis.

Blocky isomorphism is defined as the ability of groups of atoms or ions having different 
configurations to replace each other in crystal structures [14]. Such substitutions are known for a 
large number of alkaline zircono- and titanosilicates [9]. In EGMs this kind of isomorphism is 
realized at the key sites M2, M3, and M4, as well as at the N and X sites. The eudialyte group is the 
only group of minerals in which blocky isomorphism is realized at several sites containing 
high-force-strength cations. Below we will use the symbols N1–N5, M2, M3, M4, and X to denote 
corresponding cavities (i.e., micro-regions which can contain several closely spaced sites).

Figure 1. Arrangement of key sites in the eudialyte-type structures viewed along (210).

In addition to EGMs with the rhombohedral unit-cell parameters a ~ 14.2 Å, c ~ 30 Å, members 
of the eudialyte group with modular structures and doubled c parameter are known. Their unit cells 
contain two eudialyte-type modules which differ from each other by local situations around key sites [4].

2. Blocky Isomorphism at the M2 Site

The most complex blocky isomorphism is realized in the M2 micro-region situated between 
rings of octahedra, M1O6 [15]. This micro-region can be populated by cations having different radii, 
charges, and coordination (from flat square formed by edges of octahedra belonging to two
neighboring $M_1O_8$ rings to a 7- or 8-fold polyhedron: $\text{IV}^{\text{Fe}^{2+}}$, $\text{V}^{\text{Fe}^{3+}}$, $\text{VI}^{\text{Fe}^{3+}}$, $\text{VI}^{\text{Mn}^{2+}}$, $\text{VII}^{\text{Zr}}$, $\text{IV}^{\text{Ta}}$, $\text{IV}^{\text{Na}}$, $\text{V}^{\text{Na}}$, $\text{VI}^{\text{Na}}$, $\text{V}^{\text{K}}$, $\text{VII}^{\text{K}}$, and $\text{VIII}^{\text{K}}$. The $M_2$-cations occur in the plane of the six-membered rings which is perpendicular to the threefold axis (Figure 2). The coordination polyhedra $M_2O_5$ and $M_2O_7$ can have different orientations with respect to the plane of the square. Some examples of $M_2$-centered polyhedra are shown in Figure 3.

![Figure 2](image)

**Figure 2.** Six-membered ring composed of $M_1$ octahedra (a) and positions of some components in the $M_2$ micro-region between neighboring rings of $M_1$ octahedra (b).

The fourfold (nearly, flat-square) coordination is most typical for $\text{Fe}^{2+}$ and, to a less extent, for Na. In particular, eudialyte s.s. is $M^{\text{IV}(\text{Fe}^{2+})}$-dominant [16,17]. The crystal structures of $M^{\text{IV}(\text{Na})}$-dominant minerals are described in [11,18–24]. Some other components (Zr, Hf, and Ta) can occur in the $M_2O_5$ polyhedron in subordinate amounts [1]. The mean $M_2$–O distances vary from 2.04 Å for $M_2 = \text{Fe}^{2+}$ to 2.29 Å for $M_2 = \text{Na}$ (Table 1).

| Cation | $M_2$–O Distances, Å (Ranges) | O–O Distances, Å | Reference |
|--------|--------------------------------|------------------|-----------|
| Na$^+$ | 2.29–2.29                      | 3.28, 3.28, 3.13×2 | [22]      |
| Zr$^{4+}$ | 2.040–2.117                  | 2.78, 2.81, 3.03, 3.08 | [25]      |
| Ta$^{5+}$ | 2.035–2.116                 | 2.95, 3.11, 2.85×2 | [26]      |
| Fe$^{2+}$ | 2.03–2.06                   | 2.95, 2.98, 2.80×2 | [27]      |

![Table 1](image)
The fivefold M2-centered polyhedron is a square pyramid $M2O_4\Theta$ (Figure 3) where O atoms belong to the neighboring $M1O_6$ rings and $\Theta$ is OH group of the $M3O_3(OH)_3$ or $M4O_3(OH)_3$ octahedron or H$_2$O molecule. Kentbrooksite (Na,REE)$_{15}$(Ca,REE)$_6$V$_2$Zr$_3$Si$_2$Nb$_3$Si$_{48}$O$_{74}$F$_2$·2H$_2$O (Figure 4a) was the first EGM in which such polyhedron was identified [29]. Later, $^\gamma$M2 site was found in different EGMs [30–48]. Mn-dominant $^\gamma$M2 site occurs in the structure of andrianovite [30,31]. In the ilyukhinite structure [47,48] the M2 site has a fourfold flat-square coordination with the M2–O distances of 2.11–2.51 Å and is predominantly occupied by Mn with a minor Fe admixture. The replacement of manganese with iron at the fivefold M2 site has been established in a number of minerals close in structure to kentbrooksite including ferrokeentbrooksite [32], georgbarsanovite [33,34], taseqite [35,36], feklichevite [37], golyshevite [38,39], as well as some varieties of other EGMs [1]. In the M2 micro-region of so-called “eucolite” (a variety of ferrokeentbrooksite [40]), Fe atoms occupy two sites located at the distance of 0.49 Å from each other and having a joint occupancy about 100%. In most cases, differently oriented square pyramids occur in the M2 micro-region [1,41–43]. In siudaite [49], the M2 site is split into the M2a and M2b sub-sites which are located on both sides from the M2 square at the distance of 0.99 Å from each other and have fivelfold square pyramid coordination. The population of the $M2aO_4\Theta$ and $M2aO_6\Theta$ polyhedra ($\Theta = O$, OH) is $Fe^{3+}_{0.6}Mn^{2+}_{0.4}$ and $Fe^{3+}_{0.2}$, respectively. This conclusion was confirmed by means of Mössbauer spectroscopy. In some EGMs, $M2O_6\Theta$ octahedra (Figure 3) are formed involving OH groups (or H$_2$O) situated on both sides from the $M2O_4$ square where M2 is Mn$^{2+}$ (in manganoeudialyte) or Fe$^{3+}$ (in ikranite: Figure 4b).

**Figure 3.** Different polyhedra in the structures of eudialyte-group minerals: square (a), tetragonal pyramid (b), and octahedron (c), all viewed along (210), and the arrangement of 7-fold $^{40}$Na-centered polyhedra in a high-sodium EGM [28] (d).

**Figure 4.** Fragnments of the crystal structures of kentbrooksite (a) and ikranite (b) viewed along (001).
The \(\text{VII}M2\)-centered sevenfold polyhedra are based on the flat square and include O atoms of the framework and large X anions. Positions of large cations (K\(^+\), Sr\(^{2+}\), or Ce\(^{3+}\)) occurring in the \(M2\) micro-region, are located at large distances from the plane of the O\(_4\) square. In these cases, the coordination polyhedron is supplemented by two inner O atoms of the SiO\(_2\) ring and one or two (statistically) species anions (Cl, F, or H\(_2\)O) situated at the X site on the threefold axis. As a result, a 7- or 8-fold polyhedron is formed. The coordination number of Na\(^+\) occurring in the \(M2\) micro-region can vary from 4 to 7. The \(\text{VII}\text{Na}\)-centered polyhedron dominates in the \(M2\) micro-region of some samples [28,44]. As a subordinate component, \(M3(\text{VII}\text{Na})\) occurs in the structures of intermediate members of the manganoeudialyte–ilyukhinite [45] and eudialyte–sergevanite [46] solid-solution series, with the Na–O distances of 2.23(4)–2.96(3) and 2.33(1)–3.01(1) Å, respectively. Rarely, the \(\text{VII}M2\) polyhedron is centered by Mn or Zr.

### 3. Blocky Isomorphism at the M3 and M4 Sites

The micro-regions M3 and M4 at the centers of two nonequivalent SiO\(_2\) rings can be vacant, but usually they contain tetrahedra (SiO\(_4\) rarely AlO\(_4\)) or octahedra (typically, NbO\(_6\); rarely, TiO\(_6\), WO\(_6\), MnO\(_6\), and NaO\(_6\)) [1] (Figure 5). The positions of M3 and M4 cations are located on the threefold axis, and their charge can vary from +1 (Na\(^+\)) to +6 (W\(^+\)). When SiO\(_4\) tetrahedron occurs in the M3 or M4 micro-region, corresponding SiO\(_2\) ring transforms into a 10-membered disc consisting of three 5-membered rings (Figure 5b).

![Figure 5](image)

**Figure 5.** Local situations at the centers of the SiO\(_2\) rings viewed along (001). (a) A ring with vacancy at the M3 site, (b) a ring centered with the SiO\(_4\) tetrahedron, (c) a ring centered with the NbO\(_6\) octahedron.

Three O atoms which form the base of each Si-centered tetrahedron occurring in the M3 or M4 micro-region are common with O atoms of the SiO\(_2\) ring. The fourth O atom of this tetrahedron belongs to OH group. The \(M3,M4\text{Si}\) atoms can occur either above or below the triangular base of the tetrahedron, and OH groups belonging to the tetrahedra can be located on both sides of the SiO\(_2\) ring in such a way that apical vertices of the neighboring tetrahedra are oriented in opposite directions. Different options involving M3 and M4 tetrahedra are shown in Figure 6. It is to be noted that the M3a and M3b tetrahedra, as well as M4a and M4b tetrahedra cannot exist in corresponding micro-regions simultaneously because of short \(\text{M3}\text{Si}^{1+}\text{M3}^{2+}\text{Si}\) and \(\text{M4}\text{Si}^{1+}\text{M4}^{2+}\text{Si}\) distances. The option (b) corresponds to a centrosymmetric structure, and the options (d) and (e) correspond to non-centrosymmetric ones.

The option (c) is most common, but corresponding local situation cannot be realized due to unacceptably short OH–OH distance of 1.4–1.5 Å between the vertices of the tetrahedra. However, this option can be realized statistically.

An example of the option (a) is the crystal structure of a high-silicon EMG from the Kovdor massif, Kola Peninsula, described as “low-iron eudialyte 2” [50]. In this sample, the M3 and M4 sites occupied by Si are split into pairs of partially occupied sub-sites located at short distances from each other: \(M3a–M3b = 0.92(6)\) Å and \(M4b–M4c = 1.04(1)\) Å. As noted above, a local situation when both
M₃b and M₄a sites are occupied is impossible due to a short distance (of 1.41 Å) between OH groups belonging to corresponding tetrahedra.

Figure 6. (a–e) A scheme showing different options of mutual orientation of the M₃ and M₄ tetrahedra.

Our investigations carried out on a large selection of EGMs [5,51] (Table 2) have shown that the total amount of Si atoms at the M₃ and M₄ sites (ΣT) varies in wide ranges, from 0.88 to almost 2 atoms per formula unit (apfu) (Z = 3). The ratio of the amounts of differently oriented tetrahedra (ΣTₐ/ΣTₐ) varies from 0 to 2.31; only in two structures this ratio is equal to 1 which corresponds to the existence of center of symmetry. Both centrosymmetric structures are characterized by rather low ΣT values of 1.12 and 1.39 apfu, and only one of them corresponds to the option (a).

Table 2. Population of tetrahedral sites in the M₃ and M₄ micro-regions, total amounts of the IVM₃ and IVM₄ components (ΣT, Z = 3) and atomic ratios of the contents of (IVM₃a,IVM₄a) and (IVM₃b,IVM₄b) cations (ΣTₐ/ΣTₐ). The samples are listed in the order of lowering of the ΣT value.

| No. | Mineral                  | M₃a | M₃b | M₄a | M₄b | ΣT  | ΣTₐ/ΣTₐ | References                      |
|-----|-------------------------|-----|-----|-----|-----|-----|---------|---------------------------------|
| 1.  | Davinciite              | 0.5Si | 0.49Si | 0.41Si | 0.53Si + 0.04Al | 1.97 | 0.86    | [52,53]                         |
| 2.  | Fe-poor EGM             | 0.1Al | 0.4Si + 0.5Mn | 0.9Si | 1.9 | 0.05 | [41]                             |
| 3.  | Fe-poor EGM             | 0.24Si | 0.57Si | 0.48Si | 0.47Si | 1.76 | 0.69 | [50]                             |
| 4.  | H₂O-analogue of eudialyte | 0.45Si | 0.34Si | 0.57Si | 0.21Si + 0.19Al | 1.76 | 1.38 | [19]                             |
| 5.  | Aqualite                | 0.45Si | 0.55Si | 0.5Si | 1.72 | 2.13 | [21,54,55]                      |
| 6.  | Ta-bearing eudialyte    | 0.5Si + 0.3Si | 0.43Si | 0.35Si | 1.58 | 0.37 | [26]                             |
| 7.  | Sergevanite             | 0.55Si | 0.51Si | 0.49Si | 1.55 | 2.16 | [44]                             |
| 8.  | Sergevanite             | 0.5Si | 0.5Al | 0.5Si | 1.5 | 0.5 | [25,56]                         |
| 9.  | Raslakite               | 0.45Si + 0.1Al | 0.45Si + 0.1Al | 0.5Si | 1.5 | 2.0 | [42,57]                         |
| 10. | H₂O-analogue of eudialyte | 0.44Si + 0.06Si | 0.5Si | 0.5Si | 1.5 | 0.5 | [19]                             |
| 11. | Mangano-eudialyte       | 0.38Si | 0.25Al | 0.37Si | 0.44Si | 1.44 | 1.09 | [58]                             |
| 12. | H₂O-analogue of eudialyte | 0.29Si | 0.2Si | 0.41Si | 0.49Si | 1.39 | 1.01 | [19]                             |
| 13. | Taseqite                | 0.35Si | 1.0Si | 1.3 | 0 | [35,36,59–61]               |
| 14. | Na-rich eudialyte       | 0.56Si | 0.56Si | 1.12 | 1.0 | [28]                             |
| 15. | H₂O-rich and Si-deficient EGM | 0.5Si | 0.31Si | 0.07Al | 0.17Si | 1.05 | 1.19 | [19]                             |
| 16. | H₂O-rich and Si-deficient EGM | 0.44Si | 0.1Al | 0.23Si | 0.19Si | 0.96 | 2.31 | [19]                             |
| 17. | Andria-novite           | 0.25Si | 0.75Si | 0.95 | 0.27 | [30,31]                         |
| 18. | H₂O-rich and Si-deficient EGM | 0.18Si + 0.2Al | 0.5Si | 0.88 | 0.76 | [19]                             |
In Si-deficient EGMs, the $M_3$ and $M_4$ micro-regions contain vacancies (as e.g., in ikranite [57,62,63] and mogovidite [38,64]) and/or octahedra formed by three O atoms common with the SiO$_7$ rings and three OH groups. The $M_3$ and $M_4$ cations with octahedral coordination can occur in one of three sites located at short distances from the $M_3$ and $M_4$ sites which are usually occupied by Si. Consequently, the $M_3$ and $M_4$ sites, as well as the $M_4$ and $M_4$, cannot be occupied simultaneously in the same micro-region. In most cases, blocky isomorphism involving atoms with tetrahedral and octahedral coordination is realized in the $M_3$ and $M_4$ micro-regions. However, there are cases when these microregions contain only one type of polyhedra, namely, only tetrahedra (for example, in davinciite [52,53]), or only octahedra. The latter case is realized in the centrosymmetric high zirconium eudialyte described by Giuseppetti [65], in which the $M_3$ and $M_4$ sites have been refined with the same occupancy, $\frac{1}{6}$ and $\frac{1}{6}$. However, the possibility of the occurrence of Zr in the $M_3$ and $M_4$ micro-regions was not confirmed by subsequent investigations. In most cases, octahedral sites in these micro-regions are occupied by Nb. In three EGMs (khomyakovite and manganokhomyakovite [66], and johnsenite-(Ce) [67]) the $M_3$ site is occupied by W. Some examples of blocky isomorphism in the $M_3$ and $M_4$ micro-regions are presented in Figures 7–9.

Figure 7. A fragment of the crystal structure of davinciite.

Figure 8. A fragment of the crystal structure of andrianovite.
Unlike Si-centered tetrahedra, the NbO$_6$(OH)$_3$ octahedra located in the $M_3$ and $M_4$ micro-regions can be directed towards the $N_5$ cavity between the neighboring Si$_9$O$_{27}$ rings only in the case when the $N_5$ site is vacant. Otherwise this would result in unrealistic short distances between OH groups and $N_5$ cations.

The option when the octahedra are oriented both outward and inward of the $N_5$ cavity is extremely rare. This situation takes place in a low-silicon sample with high contents of niobium and titanium and a low content of zirconium, found in the Kovdor phlogopite deposit, Kola Peninsula (Figure 10). This centrosymmetric member of the eudialyte group was formed as the result of partial leaching of sodium from an earlier EGM [68]. In the micro-regions $M_3$ and $M_4$ of this mineral, there are two octahedral sites located at a distance of 2.19 Å from each other and populated by titanium with the occupancy factors of 50 and 30%, respectively. A TiO$_6$ octahedron with a population of 50% is directed inside the $N_5$ cavity, while the less populated one faces in the opposite direction from the 9-membered ring. At a distance of 0.29 Å from the Ti site, there is a site occupied by Si with the population of 20%. Thus, all positions in the $M_3$ and $M_4$ micro-regions are populated statistically.

Figure 9. Blocky isomorphism in the $M_3$ and $M_4$ micro-regions of golyshevite viewed along (210).

Figure 10. The crystal structure of a Nb,Ti-rich EGM from the Kovdor phlogopite deposit viewed along (210) [68].
4. Blocky Isomorphism at N Sites

At the N1–N5 extra-framework sites occurring in large cavities of the structures of EGMs, positional isomorphism of a statistical nature is most often observed. Below we will use the symbols N1–N5 to denote corresponding cavities (i.e., micro-regions containing several closely spaced extra-framework sites). In most cases, these positions are split and occupied by sodium; the set of closely spaced Na sites is typically coordinated by anions belonging to the same polyhedron. However, if significant amounts of other large cations enter these sites, ordering of different elements among closely spaced sites may result in changes in their anionic environment.

Most frequently, extra-framework cations other than Na occur at the N3 and N4 sites (Table 3). For example, in the structure of davinciite [52], the N3 and N4 cavities contain pairs of partially populated sites with the distances N3a–N3b = 0.65(1) Å and N4a–N4b = 0.42(1) Å. The N3a and N3b sites are partially occupied by K and (K + Na) and have 7- and 6-fold coordination, respectively. The 6-fold polyhedron is formed solely by O atoms of the framework, whereas the 7-fold polyhedron contains one H2O molecule. The N4a and N4b sites are partially occupied by (Na + Sr) and Sr and have 8- and 7-fold coordination, respectively. The larger Sr-centered 8-fold polyhedron involves two Cl atoms, and smaller one contains only one Cl atom.

A remarkable example of blocky isomorphism at the N sites is presented in a Fe- and Na-deficient EGM [41,50,69]. In this sample, sodium deficiency of almost 50% compared to eudialyte s.s. is mainly compensated by hydronium groups H3O+, as well as subordinate K+, Sr2+, and Ce3+. These cations occur in the N3 cavity and are statistically distributed over four sites, located at distances of 0.32(1) to 0.95(1) Å from each other. The coordination numbers and cation–anion distances (Å) for these sites are 10 and 2.91 for H3O, 10 and 2.87 for K, 9 and 2.73 for Ce, and 7 and 2.61 for Sr.

In most samples of EGMs, including eudialyte, manganoeudialyte, kentbrooksite, ferrokenbrooksite, carbokeenbrooksite, voronkovite, raslakite, sergevanite, and oneillite, the N3 and N4 sites are Na-dominant. However, in some members of the eudialyte group the N4 site is predominantly occupied by other cations: Sr (in taseqite), REE (in zirsilite-(Ce) and johnsenite-(Ce)), Mn (in georgbarsanovite and siudaite), and K (in andrianovite: Figure 8), etc.

Large N4-cations form triads of edge-sharing polyhedra. The coordination number of the N4 site in kentbrooksite, taseqite, and georgbarsanovite is equal to 10 (Figure 11) and is characterized by the cation–anion distances from 2.471 to 2.943 Å. The N4 site in andrianovite has 8-fold coordination and the cation–anion distances from 2.557 to 2.980 Å. Mixed population is typical for the N4 site. For example, the composition of the N4 micro-region in georgbarsanovite and andrianovite is (Mn1.07Sr0.72Ca0.33K0.25Y0.16)23 and (K1.45Sr1.05Ce0.5)23, respectively.

![Figure 11. The layer formed by the Mn2+, Sr2+, Ca2+, and Mn2+ polyhedra in “eucolite” (Sr- and Mn-rich EGM viewed along (001) [27,34]).](image-url)
In the majority of eudialyte-related minerals, the crystal chemical formula \((Z = 3)\) contains 6 Ca atoms, which enter into the composition of the six-membered ring of octahedra, and the N3 and N4 sites are predominantly occupied by Na (Figure 12a). However, in specific environments, EGMs of a different stoichiometry are formed. In particular, there are three representatives of this group with a high content of calcium of 9 to 10 Ca apfu: feklichevite, golyshhevite, and mogovidite (Table 1).

An example of EGM with an unusually high Ca content is feklichevite, Na\(_{11}\)Ca\(_5\)Fe\(_7\)Zr\(_2\)Nb\(_2\)Si\(_6\)O\(_{37}\)(OH\(_4\),H\(_2\)O,Cl\(_3\))\(_{[37]}\). In this mineral, Ca completely occupies the M1 site in the ring of octahedra and dominates at the neighboring N3 site. A cluster formed by three Ca-centered polyhedra sharing common vertices occurs at the threefold axis completed by six M1 octahedra (Figure 12b).

Golyshhevite and mogovidite are the most Ca-rich EGMs (Table 3). In these minerals, Ca occupies the M1 site in the ring of octahedra and dominates over Na at N(4) (in golyshievite \([39]\), Figure 12c) or at both N(3) and N(4) (in mogovidite \([38]\)). In the latter case, a double layer of Ca-centered polyhedra is formed (Figure 12d).

The N3- and N4-centered polyhedra share common edges with the M1O\(_6\) octahedra. As a result, the substitution of Na by bi- or trivalent cations at the N3 and N4 sites results in changes of local situations in the M2 micro-region and formation of rigid layers formed by the M1-, M2-, N3-, and N4-centered polyhedra. Acentric character of the georgbarsanovite crystal structure is especially obvious because of the presence of bi- and trivalent cations at the N4 site. As a result, this mineral demonstrates a pronounced piezo-effect.

The following local situations around the M2 micro-region are possible in Na-deficient EGMs:

1. IV\(_{M2}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\)
2. IV\(_{M2}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\)
3. VI\(_{M2}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\)
4. VI\(_{M2}\) + VI\(_{M2}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M3}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\)
5. IV\(_{M2}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\)
6. IV\(_{M2}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\)
7. VI\(_{M2}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\)
8. VI\(_{M2}\) + VI\(_{M2}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M3}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\)
9. IV\(_{M2}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\)
10. IV\(_{M2}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\)
11. IV\(_{M2}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\) + VI\(_{M4}\)
12. VI\(_{M2}\) + VI\(_{M1}\) + VI\(_{M1}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\) + VI\(_{M3}\)

| Mineral               | N3   | N4   | Reference |
|-----------------------|------|------|-----------|
| Golyshhevite          | Na   | Ca   | \([38,39]\) |
| Mogovidite            | Ca   | Ca   | \([38,64]\) |
| Feklichevite          | Ca   | Na   | \([37]\)   |
| “Ferrofeklichevite”   | Ca   | Na   | \([70]\)   |
| Taseqite              | Na   | Sr   | \([35,36]\) |
| Georgbarsanovite      | Na   | Mn   | \([33,34]\) |
| Zirsilite-(Ce)        | Na   | Ce   | \([71]\)   |
| Johnsenite-(Ce)       | Na   | REE  | \([67]\)   |
| Abidianovite          | Na   | K, Sr| \([30]\)   |
| Davinciite            | K    | Na   | \([52]\)   |
5. Blocky Isomorphism at the X Sites

In the structures of EGMs, the extra-framework X1 and X2 sites located on the threefold axis can be occupied by different anions (Cl, F, S²⁻, SO₄²⁻, and CO₃²⁻) and H₂O molecules which coordinate large N and (in some samples) M2 cations. The most common X-components are Cl⁻ (e.g., in eudialyte s.s.) and H₂O (e.g., in feklichevite). Carbonate anion is a significant component in five EGMs: golyshevite, mogovidite, carbokentbrooksite, johnsenite-(Ce), and zirsilite. The only EGM with species-defining F⁻ is kentbrooksite. S-bearing anions can occur at the X sites in subordinate amounts.

In zirsilite-(Ce) and carbokentbrooksite, the X1 site is split into two sub-sites, one of which is partly occupied by CO₃²⁻ and another one contains Cl⁻. The total population of the X1 site is C₀.6Clₒ.₄ in zirsilite-(Ce) and C₀.₃₈Clₒ.₆₂ in carbokentbrooksite. The X2 site in these minerals is occupied by H₂O.

In golyshevite, the X1 site is split into two sub-sites located at the distance of 0.55 Å from each other and occupied by CO₃²⁻ (with the total occupancy close to 100%), and the X2 site is occupied by H₂O and subordinate Cl⁻. Both carbonate groups are flat triangles whose O atoms coordinate cations of the N4 micro-region (Figure 9).

In most S-bearing EGMs, sulfur occurs in the sulfate form. In these minerals, isolated SO₄ tetrahedra occur at the sites located on the threefold axis (see Figures 10 and 13). A potentially new EGM containing sulfur in the sulfide form has been discovered recently in the Lovozero alkaline
massif, Kola Peninsula [72]. Hypothetically, this mineral crystallized at a low activity of oxygen. Its end-member formula is \((Na\text{I}_{14}Sr)Ca(Mn\text{II}Na)Zr\text{[Si\text{II}O\text{VII}]}(OH)\text{Si\text{II}O\text{VII}}\cdot 2H\text{\textsubscript{2}O}\). In the sulfide EGM, the \(X_1\) and \(X_2\) sites are split into pairs of closely spaced sub-sites with the following occupancies: \(X_1a = 0.41(S^{2-} + \text{Cl})\), \(X_1b = 0.39\text{H\textsubscript{2}O}\), \(X_2a = 0.33(S^{2-} + \text{Cl})\), \(X_2b = 0.30\text{H\textsubscript{2}O}\). The \(S^{2-}\) anions belonging to the \(X_1\) and \(X_2\) micro-regions coordinate triads of \(\text{Sr}^{2+}\) and \(\text{Na}^{+}\) cations with the \(\text{Sr-S}\) and \(\text{Na-S}\) distances of 2.322 and 2.541 Å, respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure13.png}
\caption{The crystal structure of aqualite viewed along (210).}
\end{figure}

6. Ordered Blocky Isomorphism in Modular EGMs

Heteropolyhedral frameworks of EGMs consist of layers containing \(\text{Si\text{O\text{IV}}}\) and \(\text{Si\text{O\text{VII}}}\) rings of tetrahedra (\(T\)-layer), \(\text{VI}\text{M\text{I\text{II}}}\text{O\text{IV}}\) rings of octahedra (\(M\)-layer), and isolated \(\text{ZO\text{VII}}\) octahedra (\(Z\)-layer) alternating in the order \(\ldots TMTZ\ldots\). Most EGMs have 12-layer structures, with the 2D repeat unit \(\text{TMTZ}\), unit-cell parameters \(a \sim 14\ \text{Å}\), \(c \sim 30\ \text{Å}\), and space groups \(R\bar{3}m\), \(R\bar{3}m\), or \(R3\). However, in several members of the eudialyte group (so-called “megaeudialytes”), additional cation ordering takes place which results in the formation of the doubled 2D repeat units \([(TMTZ)\text{TMTZ}\\text{\ldots}] \) with the ordered 1:1 alternation of two nonequivalent \(TMTZ\) modules and doubling of the \(c\) parameter \((c \sim 60–61\ \text{Å})\). Megaeudialytes are characterized by the same space groups as common 12-layer EGMs. Unlike crystalline compounds with superstructures, in megaeudialytes \(R\)-translation remains, and the unit-cell doubling is due to blocky isomorphism in the 30 Å module.

Megaeudialytes are known only in the Lovozero and Khibiny alkaline massifs, Kola Peninsula [1,4,73–79]. Four of them (alluaivite, dualite, labyrinthite, and rastsvetaevite) have been approved by the Commission on New Minerals, Nomenclature, and Classification of the IMA as valid mineral species (see Figures 14 and 15).
Figure 14. Ordered isomorphism at the Z site in dualite [73] (a), at the M2 and N3 sites in rastsvetaevite holotype [23,74] (b), and at the M2 and N4 sites in hydrated rastsvetaevite [8,75] (c), viewed along (210).
Figure 15. The crystal structures of alluaivite (differently oriented SiO$_4$ tetrahedra at the M3 and M4 sites are shown with red) (a) and Mn-rich “megaeudialyte” with the alteration of $^{IV}$(Na) and $^{IV}$Mn$^{2+}$ in neighboring modules [24] (b).

Unlike zirconium, titanium rarely forms isolated octahedra in structures of silicate minerals [80]. The main cause of this distinction between the behavior of these elements is a different degree of distortion of Zr- and Ti-centered octahedra. As a result, the isomorphism between Ti and Zr is usually significantly restricted. Minerals of the eudialyte group are one of exceptions to this rule. In EGMs, titanium can occur at the M2, M3, and M4 sites (Table 4).

Table 4. Ordered blocky isomorphism at the M2 and M3/M4 sites of EGMs with modular structures and doubled c parameter ($Z = 3$).

| No. | Mineral          | Module I          | Module II        | References |
|-----|------------------|-------------------|------------------|------------|
|     |                  | $M3+M4$ | $M2$ | $M3^*+M4^*$ | $M2^*$ |
| 1   | Alluaivite holotype ($Z = Ti$) | Si$_2$↑ | $^{IV}$Na$_{2.34}$ $^{IV}$Na$_{0.66}$ | Si$_2$↓ | $^{IV}$Na$_3$ | [81] |
| 2   | Alluaivite ($Z = Ti$) | Si$_2$↑ | $^{IV}$Na$_{1.64}$ $^{IV}$Mn$_{1.4}$ | Si$_2$↓ | $^{IV}$Na$_3$ | [18] |
| 3   | Dualite holotype | $^{IV}$Mn$_{1.64}$ | $^{IV}$Na$_{1.3}$ $^{IV}$Ti$_{1.0}$ | Si$_2$ | $^{IV}$Na$_{1.7}$ $^{IV}$Mn$_1$ | [43,73] |
Alluaivite (Sample 1 in Table 4; Figure 15) [81] is the first megaeudialyte whose crystal structure was solved. In this mineral zirconium is absent, and the Zr and Nb sites are occupied by Na. All Na in the M3 and M4 micro-regions; in each module, both additional SiO₄ tetrahedra have the same orientation, but their orientation is different in different modules.

In the structure of dualite (Sample 3 in Table 4; see Figure 14a) [43], alternation of Zr and Ti in the modules I and II takes place. The M3 + M4 and M3* + M4* micro-regions of dualite are dominated by Mn and Si, respectively. There are also significant differences in the populations of the Na-dominant M2 and M2* sites of dualite.

The unit-cell doubling of rastsvetaevite (Sample 4 in Table 4; see Figure 14b) [78] is mainly due to the blocky isomorphism in the M2 and M2* micro-regions: in M2, Na has fourfold flat-square coordination and is surrounded by K atoms having sevenfold coordination; the micro-region M2* is predominantly occupied by Fe. There are also differences between the modules I and II of rastsvetaevite in the population of extra-framework sites. In particular, in the module I the N3 site is occupied by K, whereas in the module II all N sites are Na-dominant.

In most cases, the formation of megaeudialyltes is regulated by the ordering of the M2-cations. For example, in hydrated rastsvetaevite (Sample 10 in Table 4; see Figure 14c) [75], different population of the M2 and M2* micro-regions (by Na+²Fe³⁺ and Fe³⁺Mn⁰, respectively) is the main cause of the unit-cell doubling.

7. Combinations of Blocky Isomorphism at the M1–M4 Sites

The population of each of the M1–M4 micro-regions does not occur independently on the local situations at neighboring sites. Very often, M2-centered polyhedra share common edges with the M1O₆ octahedra and common vertices with the M3O₆ and M4O₆ octahedra. As a result, only specific kinds of clusters (i.e., combinations of local situations around neighboring M1–M4 cations) can be realized with their statistical alteration in different unit cells. The examples of different clusters
which can be involved in the combined blocky isomorphism in EGMs with the symmetry $R3m$ (1–4) and $R3$ (5–8) are

1. $^iv M2 + ^v M1 + ^v M1$
2. $^v M2 + ^v M1 + ^v M1 + ^v M3$
3. $^v M2 + ^v M1 + ^v M1 + ^v M4$
4. $^vi ^v M2 + ^v M1 + ^v M1 + ^v M3 + ^v M4$
5. $^iv M2 + ^v M1.1 + ^v M1.2$
6. $^v M2 + ^v M1.1 + ^v M1.2 + ^v M3$
7. $^v M2 + ^v M1.1 + ^v M1.2 + ^v M4$
8. $^vi ^v M2 + ^v M1.1 + ^v M1.2 + ^v M3 + ^v M4$

The $M1O_6$ octahedra can be occupied by different elements including Ca, Mn, Fe, Na, REE, Sr, and Y. For example, in one module of dualite, all the listed elements, except Y statistically substitute each other [43]. For each cluster involving the $M1$ and $M2$ polyhedra, only specific combinations of cations which answer the condition of local valence balance on the common O atom are possible. Some examples are presented in Figures 16 and 17.

**Figure 16.** Alternative variants of blocky isomorphism in the structure of manganoeudialyte [58], with the M2 micro-region occupied by differently oriented Mg- and Fe-centered square pyramids (a) and by Mn-centered octahedra (b) viewed along (001).

**Figure 17.** Pairs of differently oriented $M2O_5$ pyramids in the structure of a $^{v}Na$-dominant sample viewed along (001) [15].
In kentbrooksite, barsanovite and some related EGMs, the $^{\text{M3}}$Mn$^{2+}$O$^{6-}$ and $^{\text{M2}}$Fe$^{2+}$O$^{5-}$ polyhedra are combined with the $^{\text{M3,3}}$Mn$^{3+}$O$^{5-}$ octahedra. In W-dominant EGMs related to kentbrooksite (i.e., khomyakovite, manganokhomakoyakite, and johnsenite-(Ce)), the $^{\text{M2}}$Mn$^{2+}$O$^{5-}$ and $^{\text{M2}}$Fe$^{2+}$O$^{5-}$ pyramids are combined with the $^{\text{M3,3}}$W$^{6+}$O$^{5-}$ octahedra. In these cases, local charge balance is regulated by the isomorphism between O and OH at the common vertex of the square pyramid and octahedron.

The charge of M2-cations, which occur in different polyhedra having common edges with the M10$^-$ octahedra, can vary from 1 to 5, but cations with high charges (Ti$^{4+}$, Zr$^{4+}$, and Ta$^{4+}$) cannot occupy the M2 micro-region in combination with trivalent M1 cations (Li$^{+}$, Y$^{3+}$). In high-calcium EGMs like mogovidite, feklichevite, golyshevite, and ferrofeklichevite, the M2 micro-region can contain bi-, tri-, tetra-, and pentavalent cations. In other cases, different combinations of uni-, bi-, and trivalent M1-cations with M2-cations having charges from +1 to +5 are realized.

A high degree of separation of different elements in the M2 micro-region is realized in a Fe-deficient sample from the Oleniy Ruchey deposit, Khibiny massif, Kola Peninsula [10]. Its crystal-chemical formula is ($Z = 3$):

$$
\text{M1}=[\text{Na}_{1.1}^{(2)}(\text{H}_2\text{O})_{4.4}^{(2)}]\quad \text{M2}=[\text{K}_{0.8}^{(2)}] \quad \text{M3}=[\text{Ca}_{1.9}^{(2)}(\text{Mn}_{1.1})] \\
\text{M3}=[\text{Si}_{1.8}\text{Nb}_{0.2}]^{(2)}[\text{Zr}_{2.4}\text{Ti}_{0.6}]^{(2)}[\text{Si}_{3.0}\text{O}_{12}^{2-}](\text{OH})_{5.6}\text{Cl}_{1.5}(\text{H}_2\text{O})_{7}1.5\text{H}_2\text{O}.
$$

In this mineral, four kinds of clusters (1 to 4 types) involving five kinds of M2-polyhedra are realized statistically.

A more complex situation takes place in Ca-depleted samples, in which ordering in the M2 micro-region is accompanied by the ordering in the M1 sites of the 6-membered ring of octahedra. In this case, the M1 site is transformed into two alternating sites, M1.1 and M1.2 (Figure 18), which are occupied differently (respectively, by Ca and Mn in onellite and sergamevanite, by Ca and Fe in raslakite, and by Mn and Na in voronkovite). Differently occupied octahedra have different sizes (Table 5) which results in variations of configurations of M2-polyhedra.

### Table 5. Cation-oxygen distances (Å) in the M1a- and M1b-octahedra of ordered EGMs with the R3 symmetry.

| No. | Mineral          | Dominant Cations | References |
|-----|-----------------|------------------|------------|
| 1   | Oneillite       | Ca 2.431, Mn 2.227 | [82]       |
| 2   | Raslakite       | Ca 2.311–2.400, Mn 2.225–2.351 | [57]       |
| 3   | Voronkovite     | Ca 2.132–2.278, Mn 2.393–2.497 | [83,84]    |
| 4   | Sergevanite     | Ca 2.331–2.438, Mn 2.257–2.384 | [85]       |
| 5   | Sergevanite     | Ca 2.320–2.420, Mn 2.230–2.386 | [20]       |
| 6   | Ca-deficient EGM| Ca 2.300–2.441, Mn 2.23–2.33 | [86]       |
| 7   | Ca-deficient EGM| Ca 2.27–2.411, Mn 2.211–2.38 | [86]       |
| 8   | Zr-rich EGM     | Ca 2.30–2.41, Mn 2.228–2.347 | [56,87]    |
| 9   | Zr-rich EGM     | Ca 2.297–2.38, Mn 2.211–2.38 | [88]       |
| 10  | Hydrated EGM    | Ca 2.28–2.50, Mn 2.23–2.41 | [89]       |

Note: Mean M1,2-O distances are given in brackets. The table includes holotypes of onellite (1), raslakite (2), voronkovite (3), and sergevanite (4). *Megaeudialyte with c = 60.33 Å.
8. Conclusions

The uniqueness of the eudialyte-group minerals lies in the combination of complexity and variability of their crystalline structures and various schemes of homovalent, heterovalent, and blocky isomorphism, in which at least 26 different elements are involved. From the crystal chemical point of view, the most interesting are the complex mechanisms of blocky isomorphism, when, in a given micro-region of a unit cell, the substitution of one group of atoms and ions by another one is accompanied by significant changes of the local structure, including splitting of cationic and anionic sites, changes in the valence state and coordination numbers of cations. Such substitution schemes are realized both around the key sites of rigid high-force-strength cations of the framework (\(M_2, M_3,\) and \(M_4\)), and in the \(N_1-5\) and \(X_1-2\) micro-regions, populated by extra-framework cations and anions, respectively.

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