CRYSTAL STRUCTURE OF EUDIALITE

V. M. Golyshev, V. I. Simonov,
and N. V. Belov

Institute of Crystallography, Academy of Sciences of the USSR

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In rhombohedral eudialite, along the very large period c = 30.018 Å, there are 12 steps separated by O atoms. These are divided into three mica-like packets in which there are cores of Zr (+Na) octahedra, clothed on both sides with silicon–oxygen armor sectioned into rings: three-fold [Si_3O_9] and nine-fold [Si_9O_{27}]. As in micas, large Ca cations are centered between the packets in octahedra which are linked into six-fold rings. The structure of eudialite, which is derived from an alkaline magma, is saturated with Na atoms located in three main layers in the mica-like packet, i.e., in the core of Zr octahedra and between the silicon–oxygen rings. In zeolite-like eudialite these constant components form a three-dimensional skeleton with the formula $Na_{12}Ca_6Zr_3Fe_3 \cdot [Si_3O_9]_2 [Si_9O_{27}]_2$, with large holes in which, in addition to accessory K, Na, Cl, and OH atoms usual for zeolites, there are also accessory (25th and 26th) Si tetrahedra centering the nine-fold rings.

The raspberry red crystals, frequently having a rich fiery appearance, of "Lapp blood" – Ca, Na, Fe zirconium silicate or eudialite – occupy one of the central positions in the mineralogy and geochemistry of zirconium, especially in the Lovozerskii and Khibinskii alkali massifs where minerals of the eudialite–eucolite group may be rock-forming in pegmatite pockets. The mineralogical crystallography of eudialites and eucolites and their chemistry has been worked out in great detail [1, 2], but nevertheless the chemical formula of the mineral cannot be considered to be established. This follows from the formula variants proposed in recent years, in very general forms: $Na_4Ca_2Zr[Si_3O_9]_2$ [3]; (Na, Ca, Fe)$_6$Zr[Si_6O_{18}](OH, Cl) [4, 5]; Na, Ca)$_6$Zr · [Si_6O_{17}] (O, OH, Cl) [6], and (Na, Ca, Fe)$_6$Zr[Si_3O_9]$_2$ · (OH, Cl) [7]. The metasilicate radical is quite obvious in three of the formulas, and only Betekhtin [6] proposes something different, with an Si:O ratio similar to that in xonotlite [8]. Although the ratio of the total number of cations to silicon is 7:6 in all the above formulas, this ratio is decreased to 1:1 in the formula of eudialite, (Na, Ca)$_5$ (Zr, Fe, Mn) (Si_6O_{17}) (O, OH, Cl), given in the fundamental monograph [9]. Borneman-Starynkevich believes that the changing ratio of the number of cations to silicon is characteristic for eudialites and creates principal difficulties in attempts to give a generalized "ideal" chemical formula of the mineral before the complete atomic structure of this complex silicate is known. The structure in particular should help solve the problems of isomorphous grouping.

M. D. Dorfman kindly provided the eudialite crystals for the x-ray structural study. These were from a pegmatite crossed by the Yuksporskii railroad tunnel. The chemical analysis (Z. M. Goroshchenko) is given in Table 1. Laue patterns, rotation photographs, and x-ray goniometric scans corresponded to the rhombohedral macrosymmetry of the mineral and the x-ray group 3mR– –, with which three space groups are associated: R$\bar{3}$m, R3m, and R32. The unit cell parameters of eudialite were refined on the DRON-1 diffractometer (CuK_α radiation):

Hexagonal (H) aspect	Rhombohedral (R)
$a_{hex} = 14.252$ Å	$a_{rh} = 12.955$ Å
$c_{hex} = 30.018$ Å	$\alpha_{rh} = 66°44'$

The experimental set of intensities was obtained

TABLE 1. Chemical Composition of the Eudialite Studied, Determined by Z. M. Goroshchenko

Oxide	Wt.%	Oxide	Wt. %
SiO_2	50.14	MnO	0,60
TiO_2	0.46	SrO	0.47
ZrO_2	11.83	TR_2O_3	0,37
Al_2O_3	0.07	$(Ta, Nb)_2O_5$	0.11
Fe_2O_3	0.50	H_2O^-	0.12
FeO	5,32	H_2O^+	1,07
MgO	0,24	S	0,04
CaO	11.18	Cl	1,82
Na_2O	14.06	$O{=}Cl_2$	0,41
K_2O	1,39		

$\Sigma = 99{,}38$

from a spherical sample (ϕ = 0.32 mm, MoKα radiation, Zr filter, equi-inclination x-ray goniometer), which was oriented along the twice-centered body diagonal of the H cell. This agrees with the edge in the R cell (3 × 12.955 Å). From 10 layer lines (hk0-hk9), 783 independent, nonzero reflections were obtained (max sin θ/λ = 0.94). Their intensities were estimated with an intensity strip graduated in steps of $\sqrt[4]{2}$. The three-dimensional Patterson function was calculated, and this served as the basis for solving the atomic structure of eudialite. For a specific gravity of 2.87, the contents of the rhombohedral cell, calculated from Goroshchenko's analysis by the Borneman-Starynkevich method, is (Table 1): $(Na, Ca, Sr, TR, K)_{21-22}$ $(Zr, Fe^{\cdot\cdot}, Fe^{\cdot\cdot\cdot}, Mn, Mg, Ti, Al, Nb)_6Si_{25-26}O_{75-76}$ $(OH, Cl)_4$, i.e., 131-135 atoms. The procedure for solving such a complex structure was prolonged and difficult. The details of the structure determination of eudialite are the subject of a special paper in the journal "Kristallografiya." Here we will give the tables with the coordinates of all atoms (the parameters) and the interatomic distances.

The complex relationships between the cation and anion constituents of the structure of eudialite appear most sharply in its description as a layered structure (along the three-fold axis, but the cleavage perpendicular to this axis is very imperfect). In analogy with the normal layered silicates, the chemical and mineralogical base of the zirconosilicate eudialite may be taken as a layer of ZrO_6 octahedra which are not joined to each other. It is covered on both sides, along the three-fold axis, with silicon–oxygen armor which is broken up into one-step island metasilicate radicals of two types: three-fold rings $[Si_3O_9]$, and nine-fold $[Si_9O_{27}]$, which have been found for the first time in eudialite. Figure 1 shows the Zr core of a three-layer packet and its upper silicon–oxygen armor: the three-fold ring is in the center of one half of the unit rhomb and the nine-fold ring is in the center of the other half. In the latter ring, a purely crystallographic distinction can be made between "orthotetrahedra" in the inner part of the ring and pairs of Si tetrahedra – "diorthogroups"[1] – along the edges of the large external triangle. Three diorthogroups from three neighboring rings $[Si_9O_{27}]$ form very large spaces at the vertices of the cell. The armoring packets are interspersed with Ca cations, which are linked into six-fold rings by sharing edges of their octahedra. Further linkage is accomplished through single Fe tetrahedral vertices to form an open cation network (Fig. 2). In the period c = 30.018 Å there are three such Zr, Si packets which are separated by Ca, Fe cation layers. The 12 layers are related by the diagonal translations of the rhombohedral cell, i.e., the two types of rings in Fig. 1 and the large holes at the cell vertices are "threaded" onto three-fold axes, creating a wreath of spaces of varying sizes and configurations (Fig. 3) for the other components to fit into. As eudialite is the product of an alkaline magma, its structure contains quite remarkable quantities of Na. There are twice as many Na atoms in the layer of Zr octahedra, and the same number of Na atoms is found in the layer of the silicon–oxygen rings. Complete neutralization (and stability, one might think) of the eudialite skeleton is thus achieved without additives and compensations: $Na_{12}Ca_6Fe_3 \cdot Zr_3[Si_3O_9]_2\ [Si_0O_{24}(OH)_3]_2$. But the large spaces on the three-fold axes give eudialite a zeolitic, or more exactly a feldspar-like character.[2]

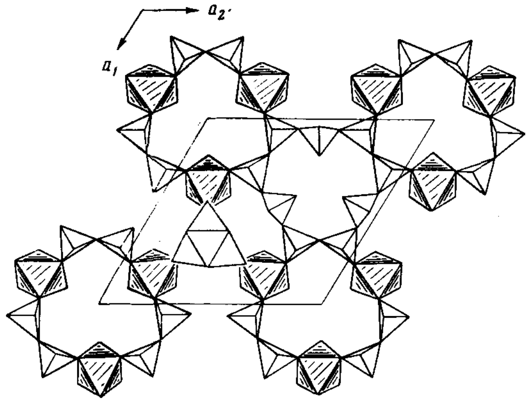

Fig. 1. Eudialite. The Zr core (discrete octahedra) of the three-layer eudialite packet and its upper silicon–oxygen armor of three-fold and nine-fold rings.

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[1] Correspondingly, the formula of the nine-fold ring can be represented in the form $[Si_{2+1}O_9]_3$. The wollastonite chain $[Si_{2+1}O_9]_\infty$, broken up into discrete rings, can thus be seen.

[2] This similarity to zeolites is reflected in its Greek name, which emphasizes the fact that eudialite is readily decomposed in a blowtorch in analogy with zeolites.

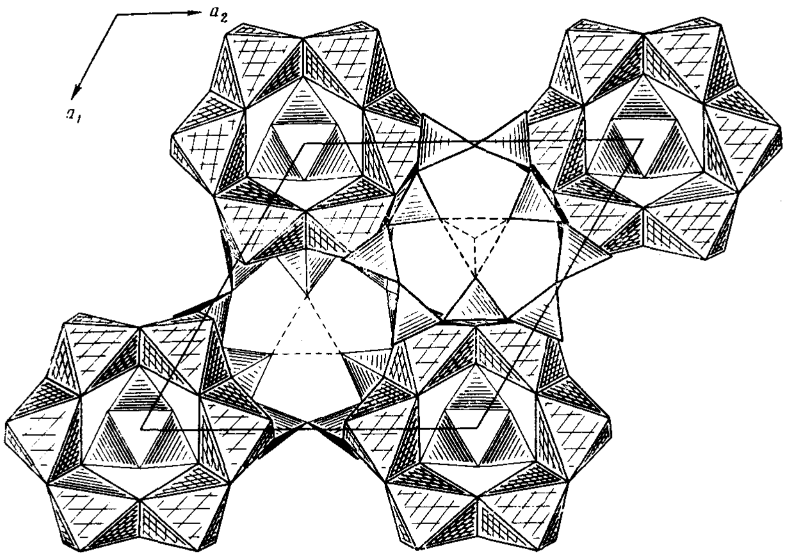

Fig. 2. Eudialite. At the vertices of the unit rhomb are six-fold rings of Ca octahedra linked together by the three-fold silicon–oxygen rings. Between the Ca rings are the nine-fold silicon–oxygen rings in two orientations, with additional Si tetrahedra (dashed lines).

This results in the variations or relative discrepancies in the chemical formulas of different eudialite samples, as mentioned at the beginning of this paper. Three Na polyhedra from the Zr core and three from the layer of Si rings are joined at a common vertex on the three-fold axis, in the middle of the bulge corresponding to the breaks in the skeleton at the vertices of the cell (Fig. 1). The distances from this vertex to the six Na atoms may change, depending on whether OH or large Cl atoms (as in sodalite) are located in it. There are two such positions in the rhombohedral skeleton, in correspondence with the material content given.

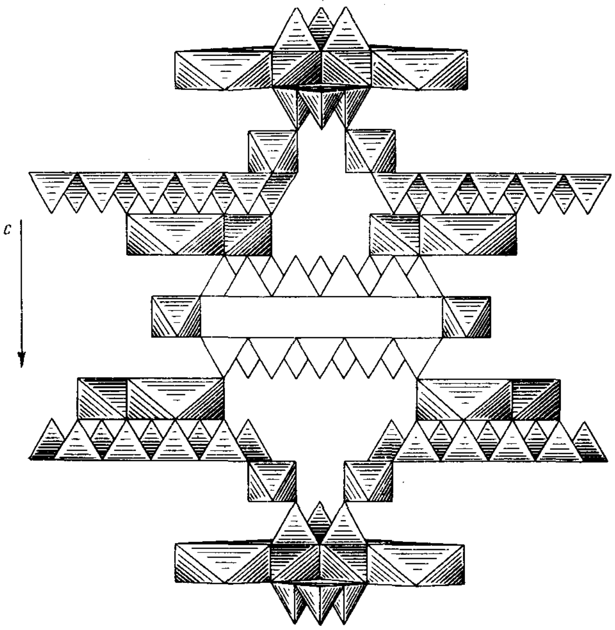

Fig. 3. Eudialite. The wreath of spaces along the rhombohedral axis.

Each of the nine O atoms in the three-fold rings and 24 O atoms in the nine-fold rings are in the nearest surroundings of either two Si, one Si and one Zr, or one Si and two divalent Ca and Fe atoms. The balance of valences is unsaturated in the three anions inside the nine-fold ring; these anions have been designated hydroxyl groups in the formula given for the skeleton, and they are bonded to only one Si. The distances from these vertices to the three-fold axis can easily be varied by rotating the tetrahedra about the corresponding side of the oxygen nonagon. The proximity of the active vertices of three Si tetrahedra to the three-fold axis, with the formation of a triangle having a side of ~2.65 Å, permits the main skeleton of eudialite to accomodate an additional atom of Si in the special positions on the three-fold axes.[3] This atom, in order to complete its tetrahedron, attracts an additional anion (OH) on the same three-fold axis with the simultaneous liberation of three H atoms at the base of the tetrahedron. The nine-fold ring,

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[3] And this is the 25th Si atom in the formula of eudialite which Borneman-Starynkevich [9] always insisted on after considering a very large number of accurate chemical analyses for this zirconosilicate.

TABLE 2. Eudialite. Coordinates of the Basis Atoms (Hexagonal Aspect)

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Zr (9)	—0.166	0.166	0.1676	O_4 (9)	0.097	—0,097	0,8659
Fe (9)	0.162	—0.162	0,3339	O_5 (9)	—0,223	0.223	0.2886
Ca (18)	—0,072	0.332	0.3334	O_6 (9)	0,210	0.210	0.7130
Si_1 (9)	—0.069	0,069	0,079	O_7 (18)	0,296	0.369	0,3721
Si_2 (9)	0,071	—0,071	0.915	O_8 (18)	—0.282	—0.362	0.6217
Si_2 (9)	—0,127	0,127	0.4107	O_9 (18)	0.288	0.236	0.4393
Si_4 (9)	0.125	—0,125	0,5920	O_{10} (18)	—0.289	—0.237	0.5601
Si_5 (18)	0,335	0.272	0,5703	O_{11} (9)	0,163	—0,163	0,4497
Si_6 (18)	—0.339	—0,277	0.4313	O_{12} (9)	—0.153	—0,153	0,5487
Na_1 (9)	0.249	—0.249	0,4984	O_{13} (18)	0.439	0,375	0.5443
Na_2 (9)	—0.221	0.221	0.4895	O_{14} (18)	—0.453	—0,381	0.4570
Na_3 (9)	0.115	—0.115	0,7216	O_{15} (9)	0.154	—0.154	0.6364
Na_1 (9)	—0,099	0.099	0.2838	O_{16} (9)	—0,153	0,153	0.3678
O_1 (9)	—0,273	0.273	0,4005	O_{17} (9)	—0,059	0,059	0.3971
O_2 (9)	0.268	—0.268	0.5834	O_{18} (9)	0,061	—0,061	0.5861
O_3 (9)	—0,095	0,095	0,1283	(OH, Cl)$_1$ (3)	0	0	0,2339
				(OH, Cl)$_2$ (3)	0	0	0,7530

modified by the additional Si tetrahedron (dashed lines in Fig. 2), is transformed into the planar botryoidal radical $[Si_{10}O_{27}OH]$. The formula with two nine-fold rings corresponds to the volume which is sectioned out of the eudialite skeleton by the rhombohedral cell, and consequently up to two (25th and 26th) additional Si atoms can be put in the formula ("in a side chain" according to V. I. Vernadskii).[4]

The wreath of zeolite-like holes which stretches along the three-fold axis narrows after every 12 layers because of the centrosymmetric rings of Ca octahedra located at the vertices of the cell. Above and below these rings are located $[Si_3O_9]$ rings which may be regarded as the tops and bottoms of the holes extending through nine layers. Between the neighboring silicon–oxygen three-fold rings, i.e., in the center of the Ca ring, there is a short hole which exactly corresponds to one large K cation. In the two halves of the long holes (divided in two by the internal Si tetrahedra in the nine-fold rings), it is not difficult to put in either two additional Si(OH) or two Cl(OH) and two Na atoms. The zeolite-like nature of eudialite appears, in particular, in the remarkable mobility of the central tetrahedra in the nine-fold ring, which permits not only an additional Si atom, but also cations with a radius of ~ 1 Å (i.e., Na, Ca, and rare earths) to rest on the three inseparable O (OH) atoms. The biggest bulge in the space (Fig. 1) on the level of the Ca rings permits the emplacement of a troika of three O(OH) anions, related by the three-fold axis, which increases the coordination of Fe to 5, i.e., to a hemi-octahedron. Thus, the basic skeleton of the eudialite zeolite (ion exchanger)[5] $Na_{12}Ca_6Fe_3 \cdot Zr_3[Si_3O_9]_2\,[Si_9O_{24}\,(OH)_3]_2$ can become quite complex with respect to the chemical composition by the "side groups" (V. I. Vernadskii), as a result of making use of the wreaths of spaces along the three-fold axes. The composition can vary up to A_5X_{10}, while of the five additional cations up to two can be Si atoms. The filling of the possible positions on the three-fold axes should be statistical and not follow any of the usual isomorphous (atom for atom) substitutions also in all positions of the main skeleton.

The first model of the eudialite structure, with a disagreement index R ~ 20%, was obtained in the framework of the centrosymmetric space group $R\bar{3}m$. Refinement of the model demanded lowering the symmetry to R3m, although the main skeleton retained a pseudoinversion center with $R < 15\%$ (for all 783 independent structure factors, with only the skeleton atoms considered). Table 2 gives the coordinates of the basis atoms of the skeleton along with some of the additional positions and types of the corresponding atoms which are indicated at the present stage of the refinement.

The interatomic distances in eudialite vary very little about standard averages. In the Zr octahedra, Zr–O = 2.02-2.17 Å; in the different types of SiO_4 tetrahedra Si–O = 1.53-1.70 Å; Ca–O= 2.31-2.41 Å; Fe–O = 2.00-2.07 Å; and, as usual, in the four types of Na polyhedra Na–O = 2.35-3.05 Å.

The relationship of eudialite with a series of zircono-silicate ion exchangers was indicated above. It may be noted that among the decomposition products of eudialite are catapleite $Na_2Zr[Si_3O_9] \cdot 2H_2O$ [10, 11], which inherits only the three-fold silicon–oxygen rings, and lovozerite $Na_2Zr\,[Si_6O_{12}(OH)_6]$ [12], which has the wollastonite chains joined into six-fold rings $[Si_{2+1}O_9]_2$ rather than nine-fold $[Si_{2+1}O_9]_3$.

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[4] The balance of valences is maintained accordingly: $3H^{1+} \rightarrow Si^{4+}(OH)^{1-}$.

[5] Synthetic zirconosilicates are mainly involved as ion exchangers.

We are obliged to M. D. Dorfman for the beautiful samples of eudialite from the depths of the Khibinskii pegmatite, I. D. Borneman-Starynkevich for the detailed discussion of the results in the light of her extensive card index with the chemical analyses of various eudialites, and also for valuable advice, particularly regarding the requirement for a 25th (and 26th) Si atom in the formula of eudialite, and Yu. A. Kharitonov for his great help with the work.

All of the calculations for the structure solution were carried out with the "Kristall" set of programs [13], and the help of one of its writers (A. V. Tovbis) and that of V. A. Mel'nikov was extremely useful.

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