

The eudialyte group: a review

Ole Johnsen, Joel D. Grice and Robert A. Gault

The eudialyte group of complex Na, Ca, Zr silicates encompasses a wide range of compositions in which all the main elements Si, Zr, Ca, Fe and Na vary, and many relatively minor elements such as Mn, REE, Sr Nb, K, Y and Ti are present. For most members of the group the empirical formula is $\text{Na}_{15}[\text{M}(1)]_6[\text{M}(2)]_3\text{Zr}_3[\text{M}(3)](\text{Si}_{25}\text{O}_{73})(\text{O},\text{OH},\text{H}_2\text{O})_3(\text{Cl},\text{F},\text{OH})_2$ and the best method of formula calculation is on the basis of 29 (Si, Al, Zr Ti, Hf, Nb, W, Ta) *apfu* ($Z = 3$), which are the elements assigned to the Zr, M(3) and all Si sites in the structure. The commonest substitutions are found with the solid solution series eudialyte *sensu stricto* (enriched in Si, Ca, Fe and Cl) and kentbrooksit (enriched in Nb, REE, Mn and F), but recent studies show that the series extends beyond kentbrooksit to an exceptionally Ca-deficient eudialyte now named oneillite. Most eudialytes are trigonal $R\bar{3}m$ or $R3m$ but oneillite is $R\bar{3}$. Additional members of the group are khomyakovite and manganokhomyakovite.

O.J., *Geological Museum, University of Copenhagen, Øster Voldgade 5–7, DK-1350 Copenhagen K, Denmark*. E-mail: oj@savik.geomus.ku.dk

J.D.G. & R.A.G., *Canadian Museum of Nature, P.O. Box 3443, Station D, Ottawa, Ontario, K1P 6P4 Canada*.

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Eudialyte (Fig. 1), a Na-rich zirconosilicate with varying amounts of Ca, Fe, Mn, rare-earth elements (REE), Sr, Nb, K, Y and Ti, was first described from the Kangerluarsuk area within the Ilímaussaq alkaline complex (Stromeyer 1819). There, it is widespread as a major constituent of the nepheline syenites and their pegmatites; locally in Kangerluarsuk up to 1 m thick continuous layers of almost pure eudialyte are found (Ussing 1912; Bøggild 1953). A particularly impressive occurrence of eudialyte in Kangerluarsuk is a rhythmic sequence of layered rocks (kakortokites) with black, red and white layers in which the varying concentrations of the main constituents arfvedsonite, eudialyte and alkali feldspar result in the banded appearance of the rocks (Fig. 2; Bohse *et al.* 1971; see Sørensen 2001, this volume).

Since the first analysis of eudialyte by Stromeyer (1819) many more from other localities have been published which display a wide range of compositions, much of which is real, but at least some variation was due to errors inherent in the analytical methods in use at the time. The result is considerable doubt about

the formula of eudialyte, and even after the basic structural features of eudialyte became known (Giuseppetti *et al.* 1971; Golyshev *et al.* 1971), ambiguity has remained with regard to the number and types of atomic sites in the mineral.

This paper reviews the recent literature on this complex mineral with special emphasis on the relationship between chemical and physical properties and crystal structure. Eudialyte has now developed into a group of several distinct mineral species including kentbrooksit from the Amdrup Fjord, Kangerdlugssuaq intrusion in East Greenland.

Structure overview

Eudialyte-group minerals are trigonal with $a \sim 14 \text{ \AA}$ and $c \sim 30 \text{ \AA}$, crystallising in space groups $R\bar{3}m$, $R3m$ or $R\bar{3}$. The most characteristic property of the eudialyte structure is the unique combination of three- and nine-membered rings of $[\text{SiO}_4]$ tetrahedra (Golyshev *et al.* 1971; Giuseppetti *et al.* 1971). These



Fig. 1. Eudialyte from Kangerluarsuk, the Ilímaussaq complex. Crystals are dominated by $\{10\bar{1}1\}$ and $\{0001\}$. Edge of large crystal 35 mm. Sample GM 1912.274 (Geological Museum, Copenhagen).

$[\text{Si}_3\text{O}_9]^{6-}$ and $[\text{Si}_9\text{O}_{27}]^{18-}$ rings are arranged in layers perpendicular to $[001]$ with the configuration shown in Fig. 3. Two such layers, related by a centre or a pseudocentre of symmetry, embrace a layer of discrete rings of six $[M(1)\text{O}_6]$ octahedra linked together by $[M(2)\text{O}_n]$ polyhedra forming a 2:1 composite layer. The site notation adopted here is taken from Johnsen & Grice (1999). The 2:1 composite layers are cross-linked by Zr in octahedral co-ordination and related to one another in accordance with the rhombohedral symmetry. This open structure is filled with $[\text{Na}\phi_n]$ polyhedra having various coordinations (where ϕ indicates ligands of O, OH, and F).

In the stacking sequence of the 2:1 layers and the layers with $[\text{ZrO}_6]$ octahedra, twelve levels can be rec-

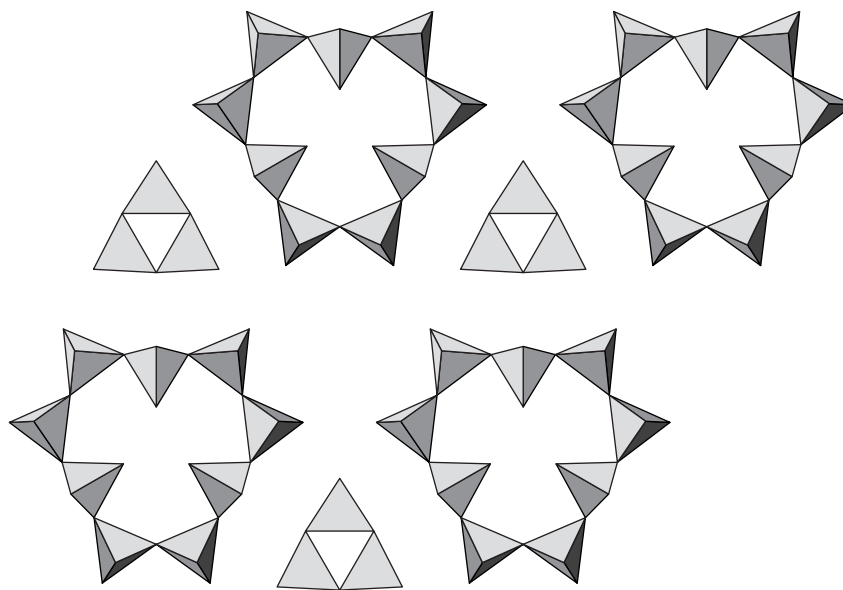
ognised within the repeat distance of the c cell dimension. Figure 4 gives a simplified representation of these levels from one sixfold ring of $[M(1)\text{O}_6]$ octahedra to the next ring. Oblong cages exist along the triad axes reaching from one constriction made by a $[\text{Si}_3\text{O}_9]^{6-}$ ring up through the layer sequence to the next $[\text{Si}_3\text{O}_9]^{6-}$ ring constriction including nine of the twelve levels. In these cages the central level comprises a region surrounded by six $[\text{ZrO}_6]$ octahedra (only four of them are shown in Fig. 4) and on either side followed by (1) an intra- $[\text{Si}_9\text{O}_{27}]^{18-}$ ring level, (2) a level with a region surrounded by $[M(1)\text{O}_6]$ and $[M(2)\text{O}_n]$ polyhedra, (3) an inter- $[\text{Si}_9\text{O}_{27}]^{18-}$ ring level and (4) a level with a region surrounded by three $[\text{ZrO}_6]$ octahedra.

Na dominates the $[\text{ZrO}_6]$ octahedra levels and other



Fig. 2. View of Kringlerne, Kangerluarsuk, the Ilímaussaq complex. Kringlerne is a rhythmic sequence of black, red and white layers of kakortokite in which the varying concentrations of the main constituents arfvedsonite, eudialyte and alkali feldspar result in the banded appearance of the rocks. The plateau above the rhythmic layering is about 400 m above the fjord. Photo: Henning Bohse.

Fig. 3. The nets of threefold and ninefold silicate rings in eudialyte seen along [001]. From Johnsen & Grice (1999).



cavities in or at the border of other levels. Cl, F, OH and H₂O are accommodated in the inter-[Si₉O₂₇]¹⁸⁻ ring levels while the central parts of the [Si₉O₂₇]¹⁸⁻ rings offer space for a cation in tetrahedral (*Si*(7)) or octahedral (*M*(3)) co-ordination pending the occupation or not of the *O*(19) site. *M*(2) is either fourfold co-ordinated in an almost planar arrangement or fivefold co-ordinated in a distorted square pyramid when *O*(19) is involved. Finally, *O*(19) is also ligand to the *Na*(4) site, which adds to the capability of this site to carry stronger bonding atoms such as REE or Sr. Table 1 gives a full list of cation sites in eudialyte structures.

The eudialyte structure is more or less centrosymmetric depending on the degree of disorder and the chemical content of certain sites. Eudialyte *sensu stricto* rich in Si, Fe and Ca, such as eudialyte from Ilímaussaq, represents the most centrosymmetric structures and as substitutions of the type Si → (Nb,W), Fe → Mn, (Ca,Na) → (REE,Sr) take place, the structures become progressively less centrosymmetric as in the case of kentbrooksitite (Johnsen & Grice 1999).

Chemistry

A comprehensive survey of all published analyses of eudialyte minerals is outside the scope of this paper. References to a large number of eudialyte papers containing information on chemistry and paragenesis are found in Deer *et al.* (1986) and Sørensen (1974), and a number of more recent papers are quoted by Johnsen & Gault (1997).

Johnsen & Gault (1997) focus on chemical variation by investigating a large suite of eudialyte minerals of different provenance by microprobe analysis performed under uniform conditions. The differences in chemical composition observed in this study reflect most of what has been noted previously in the literature and the following discussion is principally based on this work and subsequent studies based on single-crystal structure data (Johnsen & Grice 1999).

Practically all the main elements, Si, Zr, Ca, Fe and Na vary in concentration and a large number of the relatively minor elements such as Mn, REE, Sr, Nb, K, Y and Ti can enter the eudialyte structure in different quantities. The anions Cl and F, determined by microprobe analysis, also show variations, and indications that the total number of anions do vary in eudialyte minerals are confirmed by single-crystal data. In spite of this Johnsen & Gault (1997) found that the most reliable procedure was to calculate the atoms per formula unit (*apfu*) on the basis of 78 anions and *Z* = 3 for all analyses.

Al is rarely found in significant amounts in eudialyte. This fact, combined with the absence of other tetrahedrally co-ordinated elements like Be that could substitute for Si, suggests that the variation of Si is a very special chemical property of eudialyte. The Si contents are consistently above 24 *apfu*, i.e., more than required to build the ring network. Regression analysis of the Si *apfu* versus other elements show a strong negative correlation with Nb *apfu*. Nb varies from zero up to ~ 1 *apfu*; the highest Nb content hitherto reported is from the Pilanesberg complex, South Africa

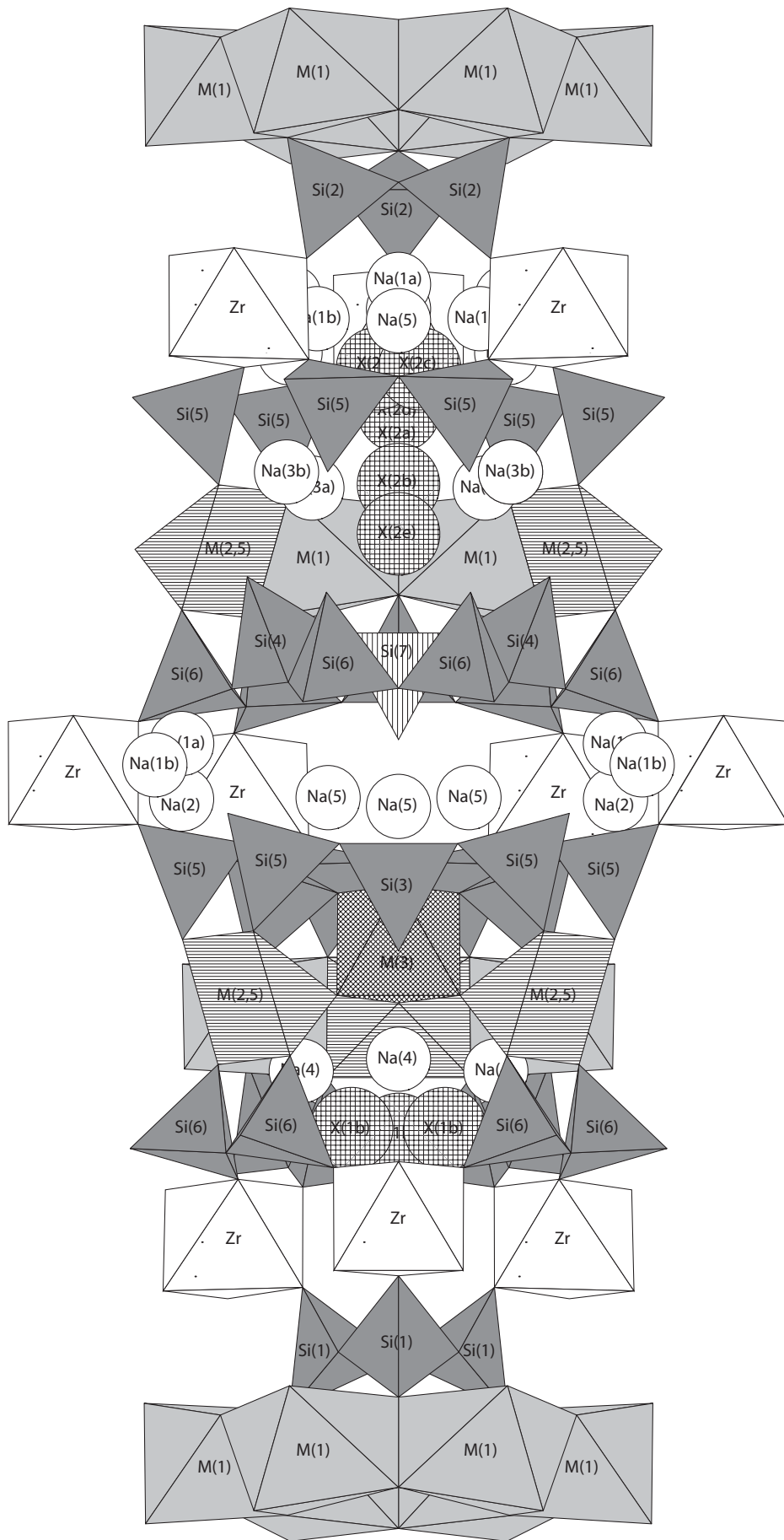


Fig. 4. A simplified polyhedral model of a non-centrosymmetric eudialyte (*sensu lato*) viewed approximately along [010]. From Johnsen & Grice (1999).

Table 1. The major rock types of the Innaussaq alkali complex

Rock type	Texture	Essential minerals*	Minor minerals
Augite syenite	hypidiomorphic to xenomorphic granular, massive or layered, medium to coarse	alkali feldspar, hedenbergite, titanomagnetite, ferropargasite, olivine, biotite	ternary feldspar, apatite, pyrrhotite, nepheline
Pulaskite and foyaite	massive, medium to coarse, platy feldspars	alkali feldspar, nepheline, hedenbergite, fayalite, aegirine-augite to aegirine, katophorite	titanomagnetite, apatite, aenigmatite, biotite, fluorite, eudialyte
Sodalite foyaite	foyaitic, coarse	alkali feldspar, nepheline, sodalite, aegirine-augite to aegirine, katophorite, arfvedsonite	fayalite, hedenbergite, apatite, aenigmatite, titanomagnetite, eudialyte, rinkite, fluorite, biotite
Naujaite	poikilitic, coarse to pegmatitic	sodalite, alkali feldspar, nepheline, aegirine, arfvedsonite, eudialyte	aenigmatite, hedenbergite, aegirine-augite, fayalite, apatite, katophorite, rinkite, polyolithionite, biotite, sphalerite, pectolite, villiamite, fluorite, titanomagnetite
Kakortokite	laminated, layered, medium to coarse	alkali feldspar, nepheline, aegirine, arfvedsonite, eudialyte	sodalite, aenigmatite, magnetite, rinkite, fluorite, löllingite, sphalerite, galena
Lujavrite [†]	laminated, fine-grained; sometimes layered or massive, medium to coarse	microcline, albite, nepheline, sodalite, analcime, naujakasite, aegirine, arfvedsonite, eudialyte,	monazite, britholite, villiamite, sphalerite, pectolite, steenstrupine, lovozerite, vitusite, polyolithionite, ussingite, lueshite, neptunite
Alkali granite, quartz syenite	hypidiomorphic granular, medium to coarse	alkali feldspar, quartz, aegirine, arfvedsonite	aenigmatite, elpidite, zircon, ilmenite, pyrochlore, neptunite, fluorite, sphalerite

* Analcime and natrolite are secondary minerals in most rocks.

† There are several types of lujavrites. Three major groups may be distinguished: *aegirine or green lujavrite* with aegirine being the dominant mafic mineral; *arfvedsonite or black lujavrite*, fine grained, often laminated with arfvedsonite as the dominant mafic mineral; *medium- to coarse-grained lujavrite (M-C lujavrite)* with arfvedsonite as the dominant mafic mineral and generally showing foyaitic textures. *Naujakasite lujavrite* is a variety of arfvedsonite lujavrite containing naujakasite instead of nepheline and with steenstrupine instead of eudialyte.

(Olivo & William-Jones 1999). The crystallochemical explanation for the strong Si–Nb correlation can be expressed by the substitution $M^{VI}(3) + Si^{IV}(7) \leftrightarrow 2Si^{IV}(7)$ where $M(3)$ and $Si(7)$ are the two central sites of the two crystallographically distinct nine-membered silicate rings.

The amount of Zr is generally close to the ideal value of 3 *apfu*. Nb plays a subordinate role in this site and Ti is the only element that substitutes for Zr to any significant degree; usually only up to ~0.5 *apfu*. Recently, a eudialyte with about one-half of Zr substituted by Ti has been found in Lovozero, Kola Peninsula (A.P. Khomyakov, personal communication 1999). This eudialyte is thus halfway towards the Ti end-member alluaivite (Khomyakov *et al.* 1990).

Ca is the dominant element in the general site $M(1)$ which amounts to 6 *apfu*. Mn is the most important substitutional element in this site followed by REE and Y. About half of Ca can be replaced until an ordering of the elements into two distinct sites, $M(1a)$ and $M(1b)$, occurs. Ca is also found in the *Na* sites but only in limited amounts, and the $Ca \leftrightarrow Na$ substitution often reported (e.g. Deer *et al.* 1986) is insignificant in comparison with other substitutions in eudialyte.

Fe is accommodated in $M(2)$. The main replacing element in this site is Mn and in most cases the substitution is of the type $Fe^{IV} \leftrightarrow Mn^V$. Full occupation of $M(2)$ gives 3 *apfu*, but most often this site is only partly occupied, typically in the range of 2–3 *apfu*. Fe and Mn are generally present as Fe^{2+} and Mn^{2+} (Pol'shin *et al.* 1991; Johnsen & Grice 1999). In rare cases Al or Ti are accommodated in $M(2)$.

All five *Na* sites are special sites and add up to 15 *apfu*. The *Na* sites can to some degree accommodate other elements such as Ca, K, REE, Sr, Y, H₂O or even H₃O⁺ (Rastsvetaeva *et al.* 1990). In a few remarkable cases, a *Na* site – primarily the *Na(4)* site – is dominated by one of the replacing elements such as in khomyakovite and manganokhomyakovite (Johnsen *et al.* 1999a) where Sr constitutes ~ 2.6 out of 3 *apfu*.

Based on a number of simple correlations between individual elements or small groups of elements, Johnsen & Gault (1997) suggested a solid solution series between eudialyte *sensu stricto* rich in Si, Ca, Fe and Cl, and kentbrooksitite (Johnsen *et al.* 1998) rich in Nb, REE, Mn and F. Single-crystal studies (Johnsen & Grice 1999) largely confirmed this series with minor modifications, one of them being that the anion part is of insignificant importance in this context, another

is that Nb in the kentbrooks site component may be substituted by other elements such as W, and finally, that the series extends beyond kentbrooks site up to an exceptionally Ca-deficient eudialyte crystallising in *R3*, now established as an independent mineral species by the name of oneillite (Johnsen *et al.* 1999b).

Johnsen & Grice (1999) present a detailed crystallochemical discussion of the substitutions and their interactions in the eudialyte group. A summary of elements assigned to the various sites in eudialyte-group minerals is shown in Table 1.

Formula calculation

In the general case where single-crystal structure data are not available, a formula must be calculated from the chemical analysis alone. As most chemical information is based on microprobe analysis, a H₂O determination is generally not available which is a serious disadvantage when calculating a formula based on the number of anions. The use of this method without further corrections results in *apfu* values of cations systematically too high; by way of example, in a typical eudialyte the *apfu* of Si will drop from 25.90 to 25.30 by the incorporation of 1 wt% H₂O.

An alternative method of formula calculation is proposed by Johnsen & Grice (1999). This method is based on the number of cations accommodated in the framework composed of the silicate rings and the Zr octahedra supplemented with the two sites (*M*(3) and *Si*(7)) in the centres of the nine-membered rings, i.e. Si + Al + Zr + Ti + Hf + Nb + W + Ta, ideally adding up to 29 *apfu* (*Z* = 3). This method is fully applicable without the determination of hydrogen or other cations. The main disadvantage of this method is that some of the elements involved (Al, Ti and Zr) occasionally also occur in other parts of the structure. However, these cases are exceptions and in the majority of cases the method works well. For the majority of the eudialyte-group minerals the empirical formula will be of the type: Na₁₅[*M*(1)]₆[*M*(2)]₃Zr₃[*M*(3)](Si₂₅O₇₃)(O,OH,H₂O)₃X₂ where *X* represents (Cl,F,OH). The following procedure is recommended when constructing the empirical formula for eudialyte based on a chemical analysis only:

1. Calculate the *apfu* based on 29 (sum of Si, Al, Zr, Ti, Hf, Nb, W, Ta) and with all Fe and Mn as divalent.
2. Assign all Si + Al to the 25 Si *apfu*. Any excess Si should be added to *M*(3).

3. Assign all Zr to the *Zr* site and if deficient make up the total to 3 atoms with Ti.
4. Assign all Nb and W to *M*(3).
5. Assign all Fe and Mn to *M*(2). Any excess Mn should be assigned to *M*(1).
6. Assign all Ca to *M*(1) and any remaining Mn then Y and REE to bring the total to 6 atoms. Any excess Ca should go into the *Na* sites.
7. Assign all Na, K, Sr and remaining Ca and REE to the *Na* sites.
8. Assign 73 of the O atoms to the silicate rings with the remaining anions partitioned into a O fraction and a halogen fraction.
9. The number of H atoms is based on charge balance.

Rare cases where Ca *apfu* is below 50% of the *M*(1) site or Na is below 50% in the *Na*(4) site will become evident during the course of formula calculation. In such cases crystal structure refinement data will be required in order to calculate a reliable formula.

Optical and physical properties

Johnsen *et al.* (1997) investigated the optical properties of a selection of eudialyte samples. The refractive indices measured are in the range of 1.60–1.64 thus covering the range previously reported in the literature, as do the birefringences. Most samples are optically negative showing great variation in refractive indices as well as in birefringences, whereas the few optically positive samples all have low refractive indices and both refractive indices and birefringences fall within narrow fields. Only a few samples are truly uniaxial; most samples show axial angles up to ~ 25°. The colour varies from brown through reddish-pink and yellow to colourless; pleochroism is, if at all present, insignificant. In a few samples a poor (001) cleavage has been observed.

Johnsen *et al.* (1997) examined the mean refractive indices and birefringencies and their correlation with the chemical composition and concluded that an isomorphous series between Na- and Ca-rich end-members, if it exists, is of no importance as a controlling factor in the variation of optical properties as suggested by, e.g. Deer *et al.* (1986). The overriding influence on the mean refractive indices comes from substitutions such as Si ↔ (Nb,W) and (Ca,Na) ↔ (REE,Sr) and as expected the mean refractive index increases as these substitutions go to the right. The

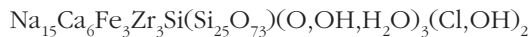
birefringence shows the best correlation to the Si ↔ (Nb,W) substitution. However, as this substitution is an integral part of the complex substitution between the two end-members eudialyte and kentbrooksit, it cannot be asserted as the only controlling factor in the birefringence. It is concluded that the term eucolite, which has been used for an optically negative and Ca-rich eudialyte, is meaningless and in some respects misleading, so the use of this term should be discontinued. Also, mesodialyte as a name for an optically isotropic intermediate member of an inferior, if existing, series should be abolished.

The density varies in the range 2.85–3.25 g/cm³. With eudialyte *sensu stricto* rich in Na, Ca, Fe and Si as a starting point, all major substitutions, except the Fe ↔ Mn substitution, go from a relatively light element towards a heavier element. Thus, the density increases as the series goes from eudialyte towards kentbrooksit and oneillite.

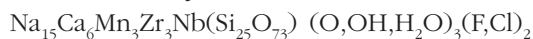
Members of the eudialyte group

Within the eudialyte group the following species can be recognised:

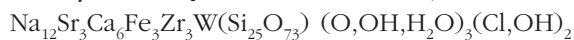
eudialyte (Stromeyer 1819):



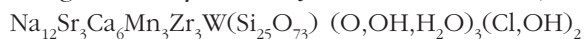
kentbrooksit (Johnsen *et al.* 1998):



khomyakovite (Johnsen *et al.* 1999a, b):



manganokhomyakovite (Johnsen *et al.* 1999a, b):



oneillite (Johnsen *et al.* 1999a, b):



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