

## THE ESSAYS ON FUNDAMENTAL AND GENETIC MINERALOGY: 4. EUDIALYTE-EUCOLITES AND PROBLEMS ON TYPOMORPHISM OF MINERALS

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The present paper is a sequel to the previously published (Borutzky, 2008) essay on the minerals of variable composition with variable structure (MVCVS) with an example of eudialyte-eucolites. The characteristic feature of this typical mineral from alkaline complexes is the unique ability to include up to one third of The Mendeleev's Periodic Table of the chemical elements in its composition. This is entailed by a partial realignment of the crystal structure in response to changing chemistry and evolution of the mineral-forming environment with time. According to the author, the detailed typomorphous analysis of eudialyte-eucolites is more informative and useful in terms of genetic mineralogy rather than formal determination of dozens of independent mineral species. 3 tables, 48 references

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### What is typomorphism and its issues

*«We have to distinguish two types of prospecting features: one is related to the nature of the objects sought for (minerals and elements) that result from ion and lattice structure features. The second is related to an external environment and determine factors due to concentration of the chemical elements»*

Alexander E. Fersman

The term "typomorphism of minerals" was first introduced in 1903 by Friedrich Becke (1855–1931), Austrian mineralogist and petrologist, the foreign corresponding member of the Emperor Petersburg Academy of Science. This problem was resumed in Russia in the 1930s by Alexander E. Fersman. In the 1970s the doctrine on typomorphism of minerals was created under the direction of Fedor V. Chukhrov and other outstanding Soviet scientists; and the talks on it were included in the Programme of XI IMA meeting held in Novosibirsk (Scientific foundations., 1980). The fundamentals of this doctrine lie in observations and revelations of the most typical (typomorphous) minerals, their associations or crystal and mineral morphology (typomorphous = "typical shape"), typical features of a chemical composition, crystal structure and physical properties of a mineral. All these characteristic features have to correspond with the geological and physical-chemical (including kinetics) conditions of the geological structures formation. In other words, Soviet mineralogy did not aim only to discover new

natural chemical compounds, but worked towards determination of the relationship between composition, structure, mineral properties and conditions of formation, i.e. its genetic features in order to use them as the mineralogical indicators for solving problems of rock- and ore-formation.

The investigation of typomorphism is carried out in different ways. Some scientists insist on the universal, global sense of the *typomorphous* features which in this case are the "rules" and not the "particular case". These scientists often consolidate or generalise the geological objects or deposits and rock types without good reason. They are carried away by the "blind" mathematical statistics, create comprehensive world-wide "databases" where only one specimen represents the Khibiny massif in whole, with no indication of the host rocks type, its location and conditions of formation. Such an approach to our point of view is a formal one. This hypertrophied "disadvantage" can be illustrated with the following statement: "nepheline is a typomorphous mineral of the nepheline syenites", which is true but senseless for the further application.

On the other hand, some generalized thesis are quite useful. For example, the occurrence of  $\beta$ -quartz which cannot be formed over 573°C (at normal pressure) or occurrence of microcline which stability field is below  $500 \pm 50^\circ\text{C}$  – are reliable geo-thermometers applied to judging the temperatures of the rocks and ores formation. The point of inversion  $\alpha \rightarrow \beta$  in quartz was widely applied by Alexander E. Fersman for derivation of his

*geo-phases*. The phase conversion sanidine  $\rightarrow$  microcline<sup>1</sup> has an important significance. The presence of microcline, for instance, make conclusions on the high temperature formation of some microcline-containing apgaitic nepheline syenites, doubtful. Thus, according to the experimental data obtained by Liya N. Kogarko (1977), the average melting temperature of the stratified rock complex of foyaites-lujavrites-urtites from the Lovozero massif is 1070°C in dry conditions or 910°C at  $P_{H_2O} = 1$  kbar. For the rock complex of eudialyte-lujavrites these are 990 and 872°C respectively. As microcline crystallisation was impossible at such a high temperatures, it is absolutely obvious that the mineral indicators were ignored. They indicate the post-crystallisation transformations within these rocks, and the possibility of another (rather than direct crystallisation from the melt) interpretation of a genesis of industrial rare-metal apgaitic mineralisation in association with microcline, was not considered.

As pointed out before, the typomorphous features can be not only shapes of the crystals and other mineral formations (proper *typomorphism*), but also peculiarities of the mineral chemical composition (*typoschemism*) and crystal structure (*structural typomorphism* which we would like to name similarly "*typostructurism*"). From the critique articles by my opponents (Rastsvetaeva, Chukanov, 2006; Rastsvetaeva, 2007) we find that "*structural typomorphism* is a concept about the close relationship between fine peculiarities of the mineral crystal structure and conditions of its formation – the new and rapidly developing line of geological science". At the XI meeting of the IMA (Scientific fundamentals., 1980) diverse research papers on structural typomorphism were presented by V.A. Frank-Kamenetsky, V.A. Drits, B.B. Zvyagin, A.P. Zhukhlistov, S.V. Soboleva, B.M. Shmakin, G.G. Afonina, M.T. Dmitrieva, O.V. Rusinova and V.L. Rusinov. The above mentioned examples of  $\alpha \rightarrow \beta$  inversion in quartz and sanidine  $\rightarrow$  microcline transformation, are typical investigations on the structural typomorphism of these minerals, as they reflect exactly "the close relationship between fine peculiarities of the mineral crystal structure and conditions of its formation".

The author in his investigations of mineral typomorphism opposed a "formal" approach but advocated a maximum concrete definition. We called it (apparently poorly) "the concrete typomorphism" or "typomorphism of the minerals from the concrete geological objects". We believe that the factors of the mineral-forming process, both *external* and *internal* (according to the statement by Alexander E. Fersman, see epigraph) are diverse and their combinations within the specific geological objects of different scale are also diverse (Borutzky, 1986; 1988; 1997). Thus, to specify an example with nepheline above, in order to compare different rock types of the Khibiny massif – nepheline syenites, melteigite-urtites, juvites and ristschorrites we shall consider the typomorphous features and difference in the chemical composition of nepheline from the rock-forming nepheline. For comparison of different nepheline porphyres one should consider the composition of nepheline phenocrysts and matrix; and for the small bodies (for instance, individual pegmatite veins or apatite-nepheline ores with different structure etc.) and also consider the changing chemical composition within the crystal growth zones. The *external* and *internal* factors of the mineral-forming process reflect the typomorphous peculiarities of the minerals in a different way. The external factors – geological, thermodynamic and kinetic – determine the relationship of the crystallised mineral with its environment – equilibrium progress, individual mineral growth rules, mineral chemical composition and the number of micro-impurities allowed etc. Also they define the transformation in morphology and properties of the mineral in geological time scale in the post-crystallisation conditions with the changed conditions of the mineral-preserving medium, i.e. the phase transformations within the mineral, metamorphism, metasomatic replacements effected by the late solutions evolved during the change in geological conditions. The *internal* factors – is an ability of the mineral structure, as some sort of a "muzzle", that restrains chemical diversity in the mineral at certain conditions, and (if it is possible) which adjusts to possible chemical and physical-chemical changes of the mineral-preserving

<sup>1</sup> – It is relevant to remind that the high-temperature phases can be metastable crystallised within the low-temperature phases stability fields. But the low-temperature can not be crystallised otherwise. For instance, cristobalite transforms into tridymite at low pressure and 1470°C, tridymite transforms into the high-temperature  $\alpha$ -quartz at 870°C, and at 573°C  $\alpha$ -quartz transforms into the low-temperature  $\beta$ -quartz. However cristobalite and tridymite often occur in opals as globules. The metastable high-temperature potassium sanidine occurs in alpine veins and other low-temperature hydrothermal formations as a dularia. Besides, it is characterised by the less-ordered Si/Al-distribution than sanidine from volcanic rocks.

medium. It is absolutely obvious that these factors should be considered together, in interaction with each other and it is impossible either to contrast them or to consider something alone – typochemism or structural typomorphism. In this scope, it would be logical to speak about the *minerals of variable composition with variable structure (MVCVS)* and eudialyte-eucolites in particular, and also to study their “*structural-chemical*” (crystallochemical) typomorphism.

### **The features of the minerals of variable chemical composition with variable structure**

In the previous essay (Borutzky, 2008) the author gave arguments against unwarranted, from his point of view, “multiplication” of eudialyte into several dozens of individual mineral species. Eudialyte is considered as a single mineral species of a *mineral of variable chemical composition with variable structure (MVCVS)*. Its distinctive feature is a zeolite-like complex structure which allows simultaneous occupancy by multiple components (micro-impurities as a rule) in different site positions. However this does not change the individuality of eudialyte in the mineral-forming process, which remains calcium-sodium zirconium silicate with its stability field. Although under substitution there occur interstructure reorganisations: displacements of atomic coordinates, changes of the coordination polyhedra configuration, statistic occupancy of the positions followed by their “splitting” that leads to the changes in the general symmetry. In our opinion this “multiplication” is speculative, although it is based on recommendations accepted by the Commission on New Minerals, Nomenclature and Classification of International Mineralogical Association (CNMNC IMA) that allow the approval of a new mineral if the content of any component within any structural position exceeds 50 rel.% independently of its total content in the mineral (even if it is less than 1–5 wt.%). This formal approach allows one to consider any chemical composition varieties of eudialyte as independent mineral species.

From the point of view of typomorphism all these “new-born” eudialyte minerals are logically to be concerned as the eudialyte varieties. Then there is no need to puzzle over naming *potassium* (or even *potassium-bearing*) eudialyte as *rastsvetaevite*, *Nb-bearing eucolite* as *kentbrooksites*, *W-bearing as*

*khomyakovite*, *Sr-bearing as taseqite*. In *Ta-bearing eudialyte* the content of Ta is not dominant in a position with occupancy 3 unlike “lucky” Nb and W that occupy positions with occupancy 1. Also it is worthwhile to mention here that *eucolite* is historically understood as a variety of eudialyte enriched in a number of the heavy multivalent cations which cause maximum distortion of the crystal structure, disappearance of the symmetry centre, increase in density, refractive indices, change of optical sign from positive to negative, appearance of a piezo-effect and change in colour. Natural eucolitization of eudialyte and subsequent eucolite re-crystallisation occur quite often.

Investigations of typomorphism of the minerals should be directed not only to accepting the typical distinctive features but also to the reasons that caused these distinctions. In eudialyte-eucolites, one component is discovered in several different structural positions. For instance, in *kentbrooksites* REE occupy both sodium position *N(4)* and calcium ring *M(1)*, and Mn occupies both *M(1)* and “iron” position *M(2)*. In *carbokentbrooksites* Mn also occupies positions *M(1)* and *M(2)*, and Ca – positions *M(1)*, *N(2)* and *N(3)*. Why do they so occur? In Table 1 in the previous essay (Borutzky, 2008) we gave several similar examples. On the other hand, the same “iron” position *M(2)* in *low-ferruginous eudialyte* can be statistically simultaneously occupied by  ${}^4\text{Na}$  (Na-“square” *Na4b*),  ${}^5\text{Na}$  (Na-half-octahedron *Na4a*),  ${}^5\text{Fe}^{3+}$  and  ${}^5\text{Mn}$  (five-end polyhedra), and  ${}^6\text{Nb}$  and  ${}^6\text{Ti}$  (octahedra). In *alluaivite* the same “iron” position can be occupied by sodium in different coordination polyhedra:  ${}^4\text{Na}(11)$  (“square”),  ${}^7\text{Na}(12)$  and  ${}^7\text{Na}(13)$  (seven-end polyhedra); in *hyper-zirconium eudialyte* – by  ${}^6\text{Zr}$  (octahedron); in *Mn,Na-ordered eudialyte* – by  ${}^4\text{Fe}^{2+}$  (“square”), [ ${}^5\text{Zr}$ ,  ${}^5\text{Na}$ ] and [ ${}^5\text{Ti}$ ,  ${}^5\text{Nb}$ ] in two types of the five-end polyhedra *M(2a)* and *M(2b)*; in *Ca,Fe-ordered eudialyte* – by  ${}^4\text{Zr}$  (“square” *M(2,4)*),  ${}^5\text{Mn}$  (five-end polyhedra *M(2,5a)*) and  ${}^5\text{Na}$  (five-end polyhedra *M(2,5b)*); in *eudialyte enriched in tantalum* by  ${}^4\text{Ta}$  (“square”) or  ${}^6\text{Ta}$  (octahedra) and  ${}^5\text{Fe}$  (five-end polyhedron). Why are such modifications possible? Crystallographers cannot answer these questions and consequently are more tempted to register data arising from structure decoding as a new mineral species.

We assume that in terms of successful *structural* typomorphism (Rastsvetaeva, Chukanov, 2006; Rastsvetaeva, 2007) prior to revealing “the close interrelation of the fine

features of a mineral crystal structure with its formation conditions" one should try to understand and explain the reason for these structural mechanisms. Why such complex compounds as *MVCVS* occur in nature, and why eudialyte-eurolite in particular includes up to one-third of The Mendeleev's Periodic Table of chemical elements without being disintegrated into a number of simple and more equilibrium minerals? We are convinced that the answer to these questions is in the complex approach to the unique eudialyte crystal structure and consideration of eudialyte as a single complex mineral.

### The typomorphism of eudialyte-eurolites in the Khibiny massif

Anyway, the variations in the chemical composition of eudialyte-eurolites can be a sensitive indicator for comparison between different types of rocks and other geological formations and help in solving debatable genetic questions. However one should remember that typomorphism investigation is to be undertaken in relation to all geological-petrological-geochemical data on a certain geological object; and both data and conclusions obtained will result in progressing a better understanding of the nature and geological history of the objects studied. We shall consider it as applied to an example of the Khibiny alkaline massif, Kola peninsula.

The very first work on typomorphism of eudialyte-eurolites from Khibiny was fulfilled by the field expeditions by Alexander E. Fersman (Kostyleva, 1929; 1936; Minerals of Khibiny... 1937). The eudialyte from pegmatites within nepheline syenites were studied in detail. It was concluded that sodium eudialyte is typical for khibinite rocks zones, and eurolite enriched in Ca, Fe and Mn – is typical for foyaitite zones. The chemical composition of eudialyte was concluded as corresponding to the chemical composition of the host rocks: eudialyte occurs in sodium rocks of the Lovozero massif, and eurolite occurs in the enriched in calcium rocks of the Khibiny

massif. This conclusion regarding eudialyte from khibinite rocks and foyaitite was later confirmed by Igor P. Tikhonenkov (1963).

Notable progress in typomorphism investigation was made by Vladimir G. Feklichev (1973) who studied distribution of Zr, Hf, Nb, Ta, Sr, *REE*, Be, Ga, Sc, Ba, Li in the Khibiny eudialyte using the detailed geological foundation of detailed zonation of the rocks within the Khibiny massif. According to these data some rare element contents vary widely and irregularly within one and the same rock complex: for example  $Ta_2O_5$  ( $0.018 \div 1.027$ , in eudialyte from albitites in foyaitites the content detected was 1.61%). Other rare elements, such as  $ZrO_2$ ,  $HfO_2$  and SrO, are distributed equally; and the others are typomorphous for eudialyte from the different rock complexes (Table 1). Thus, the minimum Be content in eudialyte is typical for khibinite rocks; the minimum  $Nb_2O_5$ , *REE* and maximum yttrium content are typical for ijolite-urtites and ristschorrites of Poachvumschorr type; the maximum  $Nb_2O_5$ , *REE* and maximum cerium content are typical for ijolite and ristschorrites of Yukspor type. The data on *REE* and Y behavior corresponds with ours (Varshal *et al.*, 1967; Borutzky *et al.*, 1975): the maximum content of  $\Sigma REE$  and cerium rare earth were determined in eudialyte from nepheline syenites (more in foyaitites rather than in khibinites), and the minimum contents were found in eudialyte from ristschorrites, ijolite-urtites and pegmatites within apatite-nepheline rocks. These variations are inversely proportional to those of yttrium and yttrium rare earth content.

In the region of Bolshoy and Maliy Vudiyav Lakes where most of the Khibiny massif rock types have outcrops, Vladimir G. Feklichev (1975) carried out mineralogical mapping on the basis of typomorphous features of eudialyte: average refractive index  $(2n_o + n_e)/3$ , optical sign and colour. Among 124 specimens of eudialyte 17 were from the coarse-grained trachytoid khibinites, 50 – from the medium-grained trachytoid khibinites, 9 – from melteigite-urtites, 17 – from ristschorrites

Table 1. The average content of rare earth elements in eudialyte from Khibiny, after Vladimir G. Feklichev (1973) (wt.%)

Rocks	Li <sub>2</sub> O	BaO	TR <sub>2</sub> O <sub>3</sub>	TR <sub>v</sub> /TR <sub>ce</sub>	Nb <sub>2</sub> O <sub>5</sub>	Be	Ga	Sc <sub>2</sub> O <sub>3</sub>
Khibinites	0.001	0.03	0.62	0.069	0.59	0.0001	0.0004	0.003
Ijolite-urtites	0.002	—	0.23	0.260	0.12	0.0001	0.0004	0.001
Ristschorrites of Poachvumschorr type	0.003	0.38	0.25	0.145	0.61	0.0005	0.0006	0.008
Ristschorrites of Yukspor type	0.001	0.01	2.88	0.041	1.78	0.0024	0.0002	0.004
Foyaites	0.002	0.12	2.24	0.041	1.76	0.0009	0.0008	0.011

and 19 – from foyaites. It was determined that brown eudialyte with increasing refractive index (1.611–1.612) is typical for the coarse-grained khibinites; red eudialyte with lower refractive index (1.609–1.610) is typical for trachytoid khibinites; raspberry-pink eudialyte with the lowest refractive index (1.606–1.608 and less than 1.605) is typical for melteigite-urtites and ristschorrites of Poachvumtschorr type; and brownish-red with medium and high refractive index (1.611–1.614 and over 1.616) is typical for foyaites.

Let us return to the question of the “formal” and “specific” approaches in mineral typomorphism investigation. The maximum specification in the petrological-geochemical research includes comparison of the chemical composition and the structure and features of the mineral from different geological-petrological rocks of a massif complex. During this the most specific details are normally emasculated, as petrologists and geochemists usually disregard mineralogical data. Quite often they made general conclusions or consolidations according to practiced petrogenetic methodology and schemes. Thus, many scientists consider the Khibiny massif as a *single unit*, as an isolated magmatic system which crystallized from its periphery to centre, with crystallization or gravity-crystallization differentiation of the alkali melt (Galakhov, 1975). Describing this system, petrologists calculate the *average* composition of the Khibiny magma prior to its differentiation (Kukharensko *et al.*, 1968), determine the *average* age (Kogarko *et al.*, 1981<sub>1</sub>) and speak about the single mineral-forming process within the massive, caused by the sinusoidal change in alkalinity and increasing relative acidity at the end (Khomyakov, 1990). Alexander P. Khomyakov also assumes the integration of the Khibiny and Lovozero massifs into the unit “Khibiny-Lovozero complex”.

This all affects the methodology of the eudialyte typomorphism studies. It is especially annoying when mineralogists have been involved. Thus, in the monograph by Viktor N. Yakovenchuk (Yakovenchuk *et al.*, 2005) recently published in English with excellent illustrations, all the types of nepheline syenites from the Khibiny massif were combined into one called *foyaites*, obviously to please petrologists. After that they divided the 30 km radial section through the Khibiny massif into 6 statistic intervals and analyzed correlation of  $\text{Si}/(\text{Si} + \text{Nb})$ ,  $\text{Fe}/(\text{Fe} + \text{Mn})$  and  $\text{Ca}/(\text{Ca} + \text{REE})$  in eudialyte. As a result they

formally conclude that from the periphery to the centre of a massif the content of Na, REE, Sr, Fe, Nb and Cl decrease; but near “the central arch” the content of Mn, Zr and Nb increase, there eudialyte-Mn, ferrokentbrooksite and ikranite occur; and eudialyte-Fe is typical for urtites and ristschorrites of “the central arch” itself. The reasons for such trends are not discussed.

At present investigations of typomorphism should be fulfilled on the basis of more reliable facts and methods. The behaviour of minerals, as well as rocks, do not end with their crystallisation. As usual, they undergo changes during the long geological history, they can form in several stages, change their chemical composition and structure during changes in the mineral-forming and mineral-preserving medium, undergo metasomatic replacements and post-crystallisation alterations. Eudialyte is not an exception and all this reflects in its typomorphous features.

Liya N. Kogarko (1977) considers eudialyte as a magmatic mineral which crystallised from alkaline agpaite magma (Kogarko *et al.*, 1980; 1981<sub>2</sub>) – the dry one (although her own experiments reveal that in such a melt up to 10% of water can be dissolved), the high-temperature one, 1000–800°C (although the gap between the liquidus and solidus curves can reach several hundreds of degrees), the one occurred in reductive conditions. On the contrary, we consider that eudialyte was formed in a typical paragenesis with aenigmatite, rinkite, lamprophyllite, aegirine (enriched in  $\text{Fe}^{3+}$ ) and microcline (that cannot be formed at temperatures higher than 500–550°C) during the late, auto-metasomatic, relatively low-temperature stage of formation of nepheline syenites and their pegmatites, i.e. with the alkaline solutions involved. Obviously, the process does not end here and later, during the low-temperature stage eudialyte undergoes *eucolitization*. The details of this process were described earlier (Borutzky, 2008).

Igor V. Pekov (2001) postulates the change from sodium conditions of alkalinity to potassium conditions during the final stages of evolution of the agpaite alkaline rock complexes. Unlike him, we repeatedly showed that at least in the Khibiny massif the high-alkaline paragenesis with adularia-like orthoclase, kalsilite and rare ultra-alkaline accessory minerals were formed during the infiltrating metasomatic effect of the nepheline-syenite magma fluids onto the chemically contrasting basic rocks from “the central arch” (meltei-

gite-urtites) captured within the massif as a huge relic. According to the principle of Dmitry S. Korzhinsky (1955; 1993), the drastically increasing potassium activity is caused by the acidic-basic interaction of the fluids with the matrix being replaced, and is variable depending on the temperature and equilibrium of metasomatic reactions. Giving accord to Alexander P. Khomyakov (1990) opinion on the trend of a sinusoidal change of alkalinity and increasing acidity towards the end of the process, we nevertheless insist on the detailed investigation of this phenomenon in different formations, and show that in the case of eudialyte it leads to distinctive results (Ageeva, 1999; 2002; Ageeva *et al.*, 2002<sub>1</sub>; 2002<sub>2</sub>; Azarova, 2005).

Discussing one or other specific problems of the Khibiny massif geology, petrology and mineralogy, we constantly face the fact that our concept of its geological history, understanding its nature and its rock-forming process is not adequately known. Most likely it happens because petrologists are unfamiliar with the mineralogical literature or do not realise the validity and reliability of mineralogical indicators as solutions for petrological problems.

We consider Khibiny as a composite *volcanic-plutonic* complex, formed by a succession of caldera subsidences. They were composed of: (1) nepheline-syenite magma with a large quantity of relicts and xenoliths of Archean-Proterozoic frame host rocks, and (2) Paleozoic volcanic rocks (varying in composition from alkaline picrites, augite-porphyrals to phonolites and rhomb-porphyrals), and also (3) ancient foliated fine-medium-grained stratified melteigite-urtites. The relict and xenolith rocks have more or less undergone metamorphism, syenitisation and fenitisation influenced by the fluids derived from nepheline-syenite magma. These processes were most intensive within the so-called "central arch" of the massif, where the relicts of the fine-medium-grained melteigite-urtites were transformed into giant-grained agpaitic metasomatic rocks (fenites) of malignite, urtite, juvite and nepheline-syenite (ristschorrites) composition, considerably enriched in potassium (Mineralogy of Khibiny... 1978; Borutzky *et al.*, 1978; 1980; Borutzky, 1988; 1997). The rocks of "the central arch" are obviously situated in the lowermost, shattered and heated part of the massif and differ from the rocks of "the western arch" by their increased basicity (Table 2) which increases activity of the most basic components in the fluid solutions. The

most basic replaced substrate corresponds to the fine-grained urtites dated to the middle part of a section of the stratified rocks. This is exactly how the giant-grained urtites, underlying apatite-nepheline ore bodies, have been formed. The relative potassium enrichment in nepheline indicates the considerable role of this element in the mineral-forming system. During fenitisation the fluid solutions composition evolves into a nepheline syenite one. According to this, the role of silicon is increasing and the leucocratic metasomatic rocks forming, transform in the sequence: urtite → feldspar urtite → juvite → ristschorrite. The melanocratic metasomatic rocks transform in the sequence: feldspar ijolite → malignite. Mineralogically it appears as replacement of nepheline by kalsilite (Ageeva, Borutzky, 2004), and later – replacement of nepheline and pyroxene by structurally disordered adularia-like orthoclase (Mineralogy of Khibiny..., 1978; Borutzky, 1988; 1997).

Thus, returning to the problem of eudialyte-eucolite typomorphism, we see that it is closely related to the change in alkalinity conditions of the mineral-forming solutions and re-distribution of their components according to the principle of acidic-basic interaction by Dmitry S. Korzhinsky (1955; 1993).

### The typomorphism of eudialyte in "the central arch" rocks in the Khibiny massif

From the above mentioned publications (Rastsvetaeva, Chukanov, 2006; Rastsvetaeva, 2007) we found out that Alexander P. Khomyakov *et al.* determined that "rastsvetaevite formation in the Khibiny massif was carried out by *the solid-phase transformation of eudialyte under potassium metasomatosic conditions*" (italic type – by the author). "At present, along with the rastsvetaevite holotype described, similar high-potassium eudialyte containing over 5–6% K<sub>2</sub>O was discovered (Khomyakov *et al.*, 2006) in the several regions of the Khibiny massif in the poikilitic nepheline syenites (ristschorrites). This discovery is undoubtedly interesting for the full understanding of the typomorphism of potassium minerals in the Khibiny massif". We were surprised by this statement because we never saw any publications on eudialyte typomorphism by Alexander P. Khomyakov, and he never supported our concept on the metasomatic genesis of ristschorrites from the Khibiny massif (Mineralogy of Khibiny..., 1978; Borutzky *et al.*, 1978; 1980; Borutzky,

The essays on fundamental and genetic mineralogy:  
4. Eudialyte-eucolites and problems on typomorphism of minerals

103

Table 2. Petrochemical formulae of the Khibiny massif rocks and indexes of basicity  $\Delta Z_{298\text{K}}^{\text{H}_2\text{O}}$  calculated, after Alexey A. Marakushev (1979)

№	Rocks	Formula	$\Delta Z_{298\text{K}}^{\text{H}_2\text{O}}$
<i>Nepheline syenites:</i>			
1	Khibinites (40 an.)	$\text{K}_{2.44}\text{Na}_{5.31}\text{Ca}_{0.55}\text{Sr}_{0.02}\text{Mg}_{0.28}\text{Mn}_{0.06}\text{Fe}_{0.78}^{2+}\text{Fe}_{0.51}^{3+}\text{Ti}_{0.24}\text{Al}_{7.22}\text{Si}_{16.06}\text{P}_{0.03}\text{O}_{49.87}\text{F}_{0.13}$	3.60
2	Lyavotschorrites (32 an.)	$\text{K}_{2.34}\text{Na}_{5.40}\text{Ca}_{0.74}\text{Sr}_{0.04}\text{Ba}_{0.01}\text{Mg}_{0.33}\text{Mn}_{0.08}\text{Fe}_{0.77}^{2+}\text{Fe}_{0.42}^{3+}\text{Ti}_{0.32}\text{Nb}_{0.03}\text{Al}_{7.27}\text{Si}_{15.79}\text{P}_{0.05}\text{C}_{0.11}\text{O}_{49.86}\text{F}_{0.14}$	3.69
3	Lujaurites (12 an.)	$\text{K}_{2.96}\text{Na}_{4.79}\text{Ca}_{1.15}\text{Mg}_{0.73}\text{Mn}_{0.06}\text{Fe}_{1.13}^{2+}\text{Fe}_{0.74}^{3+}\text{Ti}_{0.55}\text{Al}_{6.32}\text{Si}_{15.63}\text{P}_{0.04}\text{O}_{50.00}$	3.97
4	Foyaites (17 an.)	$\text{K}_{2.15}\text{Na}_{5.32}\text{Ca}_{0.44}\text{Sr}_{0.01}\text{Ba}_{0.02}\text{Mg}_{0.25}\text{Mn}_{0.04}\text{Fe}_{0.51}^{2+}\text{Fe}_{0.31}^{3+}\text{Ti}_{0.17}\text{Al}_{7.33}\text{Si}_{16.30}\text{P}_{0.06}\text{C}_{0.15}\text{O}_{49.93}\text{F}_{0.07}$	3.34
<i>Melteigite-urtites of stratified rock complex of "the central arch":</i>			
In total (109 an.)*			4.75
5	Ijolites medium-grained mesocratic from the upper strata (21 an.)*	$\text{K}_{1.71}\text{Na}_{6.46}\text{Ca}_{2.36}\text{Mg}_{1.29}\text{Mn}_{0.07}\text{Fe}_{1.02}^{2+}\text{Fe}_{1.22}^{3+}\text{Ti}_{0.74}\text{Al}_{6.74}\text{Si}_{13.79}\text{P}_{0.20}\text{O}_{50.00}$	4.62
6	Ijolites fine-grained mesocratic from the upper strata (9 an.)*	$\text{K}_{1.78}\text{Na}_{6.51}\text{Ca}_{2.10}\text{Mg}_{1.12}\text{Mn}_{0.07}\text{Fe}_{0.95}^{2+}\text{Fe}_{1.23}^{3+}\text{Ti}_{0.71}\text{Al}_{6.58}\text{Si}_{14.00}\text{P}_{0.18}\text{O}_{50.00}$	4.68
7	Ijolites fine-medium-grained mesocratic from the middle strata (21 an.)*	$\text{K}_{1.62}\text{Na}_{6.19}\text{Ca}_{2.51}\text{Mg}_{1.53}\text{Mn}_{0.06}\text{Fe}_{1.00}^{2+}\text{Fe}_{1.16}^{3+}\text{Ti}_{0.61}\text{Al}_{6.26}\text{Si}_{14.13}\text{P}_{0.13}\text{O}_{50.00}$	4.67
8	Trachytoidal urtites from the stratified band from middle strata (16 an.)*	$\text{K}_{1.85}\text{Na}_{7.23}\text{Ca}_{1.86}\text{Mg}_{0.84}\text{Mn}_{0.03}\text{Fe}_{0.86}^{2+}\text{Fe}_{1.04}^{3+}\text{Ti}_{0.39}\text{Al}_{8.20}\text{Si}_{13.20}\text{P}_{0.16}\text{O}_{50.00}$	5.05
9	Melteigites of the stratified band from middle strata (17 an.)*	$\text{K}_{0.75}\text{Na}_{3.55}\text{Ca}_{4.73}\text{Mg}_{2.71}\text{Mn}_{0.13}\text{Fe}_{2.39}^{2+}\text{Fe}_{2.41}^{3+}\text{Ti}_{1.33}\text{Al}_{3.04}\text{Si}_{12.70}\text{P}_{0.67}\text{O}_{50.00}$	3.91
10	Ijolites medium-grained mesocratic from the lower strata (10 an.)*	$\text{K}_{1.62}\text{Na}_{6.25}\text{Ca}_{2.64}\text{Mg}_{1.43}\text{Mn}_{0.08}\text{Fe}_{0.91}^{2+}\text{Fe}_{1.19}^{3+}\text{Ti}_{0.81}\text{Al}_{6.49}\text{Si}_{13.73}\text{P}_{0.16}\text{O}_{50.00}$	4.72
11	Ijolites fine-grained melanocratic with titanite from the lower strata (15 an.)*	$\text{K}_{1.75}\text{Na}_{6.60}\text{Ca}_{2.29}\text{Mg}_{1.17}\text{Mn}_{0.05}\text{Fe}_{1.02}^{2+}\text{Fe}_{1.04}^{3+}\text{Ti}_{0.76}\text{Al}_{7.26}\text{Si}_{13.32}\text{P}_{0.23}\text{O}_{50.00}$	4.57
<i>Agpaitic metasomatic rocks:</i>			
12	Massive giant-grained urtites (91 an.)*	$\text{K}_{1.94}\text{Na}_{6.80}\text{Ca}_{1.72}\text{Mg}_{0.54}\text{Mn}_{0.05}\text{Fe}_{0.67}^{2+}\text{Fe}_{0.82}^{3+}\text{Ti}_{0.44}\text{Al}_{8.22}\text{Si}_{13.48}\text{P}_{0.48}\text{O}_{50.00}$	4.73
13	Juvites (107 an.)*	$\text{K}_{3.4}\text{Na}_{5.97}\text{Ca}_{1.32}\text{Mg}_{0.54}\text{Mn}_{0.05}\text{Fe}_{0.63}^{2+}\text{Fe}_{0.76}^{3+}\text{Ti}_{0.48}\text{Al}_{7.87}\text{Si}_{14.26}\text{P}_{0.20}\text{O}_{50.00}$	4.73
14	Juvites (39 an.)**	$\text{K}_{2.73}\text{Na}_{5.96}\text{Ca}_{1.16}\text{Sr}_{0.03}\text{Ba}_{0.01}\text{Mg}_{0.43}\text{Mn}_{0.04}\text{Fe}_{0.38}^{2+}\text{Fe}_{0.74}^{3+}\text{Ti}_{0.51}\text{Al}_{7.90}\text{Si}_{14.41}\text{P}_{0.14}\text{C}_{0.15}\text{O}_{49.85}\text{F}_{0.15}$	4.42
15	Ristschorrites (46 an.)*	$\text{K}_{3.65}\text{Na}_{4.63}\text{Ca}_{0.51}\text{Mg}_{0.31}\text{Mn}_{0.04}\text{Fe}_{0.79}^{2+}\text{Fe}_{0.57}^{3+}\text{Ti}_{0.36}\text{Al}_{7.65}\text{Si}_{15.65}\text{P}_{0.07}\text{O}_{50.00}$	4.03
16	Ristschorrites (98 an.)**	$\text{K}_{4.16}\text{Na}_{4.24}\text{Ca}_{0.51}\text{Sr}_{0.02}\text{Ba}_{0.02}\text{TR}_{0.02}\text{Mg}_{0.27}\text{Mn}_{0.03}\text{Fe}_{0.56}^{2+}\text{Fe}_{0.50}^{3+}\text{Ti}_{0.23}\text{Zr}_{0.05}\text{Al}_{7.84}\text{Si}_{15.50}\text{P}_{0.05}\text{C}_{0.09}\text{O}_{49.91}\text{F}_{0.09}$	4.15
17	Kalsilite-bearing ristschorrites (epileucitophyes?) (3 an.)	$\text{K}_{6.70}\text{Na}_{1.96}\text{Ca}_{0.22}\text{Sr}_{0.00}\text{Ba}_{0.00}\text{Mg}_{0.06}\text{Mn}_{0.01}\text{Fe}_{0.24}^{2+}\text{Fe}_{0.49}^{3+}\text{Ti}_{0.10}\text{Al}_{8.32}\text{Si}_{15.86}\text{O}_{50.00}$	5.64
<i>Volcanic rocks of "the wester arch":</i>			
18	Picrite-porphyrates (2 an.)	$\text{K}_{0.28}\text{Na}_{1.36}\text{Ca}_{3.36}\text{Sr}_{0.02}\text{Mg}_{8.91}\text{Mn}_{0.06}\text{Fe}_{3.31}^{2+}\text{Fe}_{0.96}^{3+}\text{Ti}_{1.31}\text{Zr}_{0.01}\text{Al}_{1.75}\text{Si}_{13.04}\text{P}_{0.22}\text{C}_{0.06}\text{O}_{49.79}\text{F}_{0.21}$	3.81
19	Pyroxenites (2 an.)	$\text{K}_{0.68}\text{Na}_{0.76}\text{Ca}_{4.34}\text{Sr}_{0.02}\text{Mg}_{8.28}\text{Mn}_{0.07}\text{Fe}_{2.23}^{2+}\text{Fe}_{2.15}^{3+}\text{Ti}_{1.31}\text{Zr}_{0.01}\text{Al}_{1.66}\text{Si}_{12.70}\text{P}_{0.19}\text{C}_{0.06}\text{O}_{49.77}\text{F}_{0.23}$	3.89
20	Melteigites (2 an.)	$\text{K}_{0.86}\text{Na}_{1.36}\text{Ca}_{5.59}\text{Sr}_{0.05}\text{Ba}_{0.02}\text{Mg}_{5.78}\text{Mn}_{0.06}\text{Fe}_{1.39}^{2+}\text{Fe}_{1.93}^{3+}\text{Ti}_{1.29}\text{Zr}_{0.01}\text{Al}_{2.13}\text{Si}_{13.10}\text{P}_{0.28}\text{C}_{0.10}\text{O}_{49.68}\text{F}_{0.32}$	4.05
21	Melilitite	$\text{K}_{0.41}\text{Na}_{1.24}\text{Ca}_{9.50}\text{Sr}_{0.07}\text{Ba}_{0.01}\text{Mg}_{4.54}\text{Mn}_{0.10}\text{Fe}_{1.94}^{2+}\text{Fe}_{3.84}^{3+}\text{Ti}_{1.75}\text{Zr}_{0.01}\text{Al}_{1.93}\text{Si}_{9.79}\text{P}_{0.45}\text{C}_{0.07}\text{O}_{49.58}\text{F}_{0.42}$	5.10
22	Melilititic picrite	$\text{K}_{0.18}\text{Na}_{1.15}\text{Ca}_{6.52}\text{Sr}_{0.04}\text{Ba}_{0.01}\text{Mg}_{11.47}\text{Mn}_{0.12}\text{Fe}_{2.92}^{2+}\text{Fe}_{2.92}^{3+}\text{Ti}_{0.72}\text{Al}_{1.23}\text{Si}_{10.91}\text{P}_{0.03}\text{C}_{0.08}\text{O}_{49.87}\text{F}_{0.13}$	5.72
23	Augitite-porphyrates (3 an.)	$\text{K}_{0.96}\text{Na}_{2.53}\text{Ca}_{2.96}\text{Sr}_{0.04}\text{Ba}_{0.01}\text{Mg}_{4.07}\text{Mn}_{0.07}\text{Fe}_{2.75}^{2+}\text{Fe}_{2.75}^{3+}\text{Ti}_{1.22}\text{Al}_{3.99}\text{Si}_{14.12}\text{P}_{0.20}\text{C}_{0.13}\text{O}_{49.58}\text{F}_{0.42}$	3.25
24	Nephelinites (2 an.)	$\text{K}_{1.12}\text{Na}_{5.19}\text{Ca}_{2.43}\text{Sr}_{0.06}\text{Ba}_{0.03}\text{Mg}_{2.17}\text{Mn}_{0.14}\text{Fe}_{1.91}^{2+}\text{Fe}_{1.05}^{3+}\text{Ti}_{1.22}\text{Al}_{5.09}\text{Si}_{13.74}\text{P}_{0.30}\text{C}_{0.11}\text{O}_{49.25}\text{F}_{0.75}$	3.90
25	Feldspar nephelinites (4 an.)	$\text{K}_{1.94}\text{Na}_{4.04}\text{Ca}_{1.13}\text{Sr}_{0.07}\text{Ba}_{0.02}\text{Mg}_{1.17}\text{Mn}_{0.10}\text{Fe}_{1.64}^{2+}\text{Fe}_{0.76}^{3+}\text{Ti}_{0.65}\text{Zr}_{0.05}\text{Al}_{6.54}\text{Si}_{14.83}\text{P}_{0.20}\text{C}_{0.16}\text{O}_{49.60}\text{F}_{0.40}$	3.22
26	Nepheline mela-phonolites (3 an.)	$\text{K}_{1.35}\text{Na}_{5.51}\text{Ca}_{0.59}\text{Sr}_{0.00}\text{Ba}_{0.03}\text{Mg}_{0.54}\text{Mn}_{0.07}\text{Fe}_{0.74}^{2+}\text{Fe}_{0.53}^{3+}\text{Ti}_{0.33}\text{Zr}_{0.04}\text{Al}_{7.60}\text{Si}_{15.51}\text{P}_{0.10}\text{C}_{0.15}\text{O}_{49.76}\text{F}_{0.24}$	3.21
27	Rhomb-porphyr (4 an.)	$\text{K}_{2.81}\text{Na}_{3.82}\text{Ca}_{0.46}\text{Sr}_{0.02}\text{Ba}_{0.01}\text{Mg}_{0.46}\text{Mn}_{0.08}\text{Fe}_{0.39}^{2+}\text{Fe}_{0.57}^{3+}\text{Ti}_{0.32}\text{Zr}_{0.05}\text{Al}_{6.55}\text{Si}_{16.60}\text{P}_{0.11}\text{C}_{0.09}\text{O}_{49.81}\text{F}_{0.19}$	2.96

Notes: Petrochemical formulae are calculated for 50 atoms of oxygen (O + F).

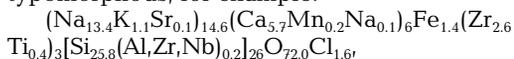
\* – calculated for the data by A.A. Arzamastsev et al. (1987); \*\* – calculated for our data

1988; 1997). Now it turned out that Alexander P. Khomyakov *et al.* determined metasomatic genesis of potassium eudialyte in ristschorrites, "disguised" as *rastsvetaevite*.

In as much as the text cited seemed well-known to us, although it has been "paraphrased", we decided to turn to the article on *rastsvetaevite* (Khomyakov *et al.*, 2006). There we found references to the publications of Olga A. Ageeva (Ageeva, 1999; Ageeva *et al.*, 2002<sub>1</sub>) where these ideas were borrowed. Would it be more correct to refer to Olga A. Ageeva Ph.D. thesis (2002) directly, which is totally devoted to the problem of mineral-forming process and typomorphism of the minerals in ristschorrites, as well as to refer to other publications discussing genetic features and typomorphism of the Khibiny eudialyte within "the central arch" rocks (Ageeva *et al.*, 2002<sub>2</sub>; Azarova, 2005), rather than "attribute" this conclusion to Alexander P. Khomyakov?

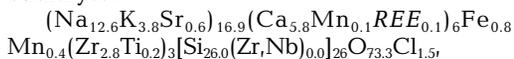
It was mentioned above in the previous chapter that according to our concept, ristschorrites were formed during the last stage of fenitisation, in the following succession: giant-grained urtite → feldspar urtite → juvite → ristschorrite. Mineralogy of accessory minerals in these metasomatic rocks, including eudialyte was studied by Olga A. Ageeva (1999; 2002) in detail. There are two morphological types of the minerals: metasomatically replaced relics of the altered substrate and new formations, i.e. the product of their re-crystallisation. The relict remnants show the non-equilibrium character of the infiltration metasomatism process, and the speed of advance of the flowing solutions is left behind the equilibrium of the chemical reactions progress. This enables one to trace the development of transformations in eudialyte, to find out its typomorphic features and to explain their character (Ageeva, 1999; 2002; Ageeva *et al.*, 2002<sub>1</sub>).

For the initial giant-grained urtites the *sodium* (sodium-ferri-ferrous) eudialyte<sup>2</sup>, is typomorphic, for example:



$$K_{\text{alk}} = 0.56, \Delta Z_{298}^{\text{H}_2\text{O}} = 4.933.$$

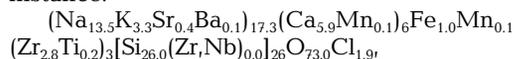
In ristschorrites it is replaced by eudialyte enriched in potassium – the *potassium-sodium* eudialyte:



$$K_{\text{alk}} = 0.63, \Delta Z_{298}^{\text{H}_2\text{O}} = 5.737.$$

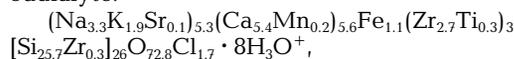
Having no access to structural analysis facilities we therefore group the components logically. However, it is clear that the potassium eudialyte is characterized by the higher alkali content (potassium, above all), the higher manganese (due to iron) content, the lower content of titanium and the higher content of strontium and silicon.

During the following hypogenic leaching (obviously due to increasing aqua content in the fluid), the *potassium-sodium* eudialyte, for instance:



$$K_{\text{alk}} = 0.65, \Delta Z_{298}^{\text{H}_2\text{O}} = 5.761,$$

is replaced by the *potassium-oxonium* eudialyte:



$$K_{\text{alk}} = 0.21, \Delta Z_{298}^{\text{H}_2\text{O}} = 1.970.$$

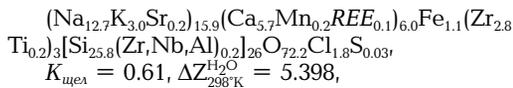
It is obvious that the alkali, calcium and strontium are intensively carried away from the structure, while manganese, titanium and zirconium are less mobile and get relatively accumulated. Potassium is carried away less intensive than sodium (apparently, activity of K in the system is still high), which is replaced by oxonium groupings. The following transformation of the potassium-oxonium eudialyte result in its decomposition and formation of individual grains of the water-containing potassium and potassium-sodium zirconium silicates: paraumbite, potassium gaidonayite, georgechaoite etc. These processes of the eudialyte transformation within ristschorrites are the principal and fundamental; corresponding to the character of the host rocks transformation – ristschorritization.

However, there are exceptions: in the contact zone of ristschorrites with unaltered urtites (with the intense "soda" mineralisation) and in the so-called *soda horizons* amongst urtites. The titanium-enriched eudialyte and alluaivite are formed under those conditions.

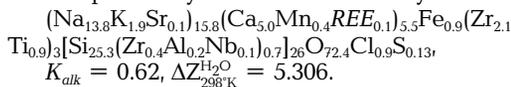
Unlike alluaivite described by Alexander P. Khomyakov in the Lovozero massif (Khomyakov *et al.*, 1990; Rastsvetaeva *et al.*, 1990<sub>2</sub>) – individual crystals on eudialyte, the Khibiny alluaivite occurs not only as separate formations but also it forms gradual conversion from the potassium-sodium eudialyte replaced, to the titanium eudialyte (Ageeva *et al.*, 2002<sub>1</sub>).

In ristschorrites from Rasvumschorr mountain the *potassium-sodium* eudialyte:

<sup>2</sup> – The analyses of eudialyte were calculated on the basis of (Si + Al + Zr + Ti + Nb + W) = 29 cations, which form the "rigid" frame of the structure containing SiO<sub>4</sub>-tetrahedra rings connecting with (Zr,Ti)-octahedra.  $K_{\text{alk}} = (\text{Na} + \text{K})/\text{Si}$  (in atomic %) – the relative coefficient of alkalinity.  $\Delta Z_{298}^{\text{H}_2\text{O}}$  (kcal) – index of the total basicity of the mineral, after Alexey A. Marakushev (1979).

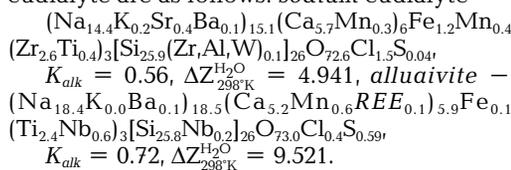


is replaced by the *titanium eudialyte*:



In this case in the same summary alkalinity, ferriferrous and basicity, potassium is replaced by sodium, strontium is leached, calcium is replaced by manganese, zirconium – by titanium, the number of additional octahedra substituting silicon increases, chlorine content decreases, sulphur content increases. The mineral-forming medium becomes enriched in titanium and we see it in the paragenesis of titanium eudialyte with Ti-bearing aegirine.

For the "soda" horizons among urtites of Rasvumschorr mountain the compositions of the newly-formed alluaivite and associated eudialyte are as follows: *sodium eudialyte* –



The primary *sodium eudialyte* here, as with the majority of eudialyte from urtites or their relicts, was sodium-ferriferrous, almost non-potassium and was not affected by ristschorritisation process. As a result of transformation we observe the same trend: the total substitution of potassium by sodium (with enrichment in the latter), calcium by manganese, zirconium by titanium and niobium; leaching of strontium, iron, chlorine and increasing sulphur concentration. It is interesting that in these ultra-alkaline sodium conditions, the sodium-ferriferrous eudialyte and alluaivite move outside the limits of their stability fields and are replaced by zirsinalite  $\text{Na}_6\text{CaZr}[\text{Si}_6\text{O}_{18}]$  and koashvite  $\text{Na}_6(\text{Ca,Mn})(\text{Ti,Fe})[\text{Si}_6\text{O}_{18}]$  respectively, and later transformed into lovozerite  $\text{Na}_3\text{H}_3\text{CaZr}[\text{Si}_6\text{O}_{18}]$  or into tinsalite  $\text{Na}_3\text{H}_3(\text{Ca,Mn})(\text{Ti,Fe})[\text{Si}_6\text{O}_{18}]$ .

Let us have a look at all these varied substitutions in the eudialyte structure in terms of the principle of acidic-basic interaction by Dmitry S. Korzhinsky (1955; 1993).

### The structural-chemical typtomorphism of eudialyte and the principle of acidic-basic interaction of the components by Dmitry S. Korzhinsky

Trying to explain the multiple variations in the Khibiny eudialyte from the chemical and

thermodynamic points of view, we engage the principle of acidic-basic interaction of the components by Dmitry S. Korzhinsky (1955; 1993). In alkali-basic magmatic melts, according to this principle, the *activity* of the most basic components is increasing while the activity of the acidic components is decreasing. This leads to: (1) the expansion of the crystallisation fields of the alkali leucocratic minerals (nepheline, alkali feldspar) due to contraction of the melanocratic minerals (pyroxene, amphibole) and, therefore, leads to the agpaite sequence of crystallisation; (2) the dissociation of amphoteric components according to the acidic type, after which they function as anions in the crystallising minerals, and which explains the wide diversity of alkaline titanium- and zirconium silicates; (3) the intense absorption of Cs, Rb, K, Na, Li, Ba, Sr, Ca, REE, Y, Mn, Nb, Ta, Zr, Hf, Ti, Ga, Th, U as micro-impurities in crystallising minerals; (4) the dissolution of fugitive components: aqua, Cl, F, S, CO<sub>2</sub> in a melt of decreasing temperature that prevents their dissociation. By virtue of alkali mobility in the magmatic process (Korzhinsky, 1946) any local enrichment in them is possible within separate parts of the magma chamber, accumulation within the periphery and dissociation of the alkaline fluids from the magma. Thus, the conditions of acidity-basicity is a considerable factor in the mineral-forming process, and obviously has to be reflected in the components abundance and hence on the structural-chemical isomorphism in the minerals.

According to Alexey A. Marakushev (1979), indexes of basicity  $\Delta Z_{298\text{K}}^{\text{H}_2\text{O}}$ , kcal, (affinity with proton) of the components, calculated as oxides, decrease in the following order: Cs<sub>2</sub>O (64.248) > Rb<sub>2</sub>O (61.114) > K<sub>2</sub>O (56.388) > Na<sub>2</sub>O (44.910) > Li<sub>2</sub>O (30.094) > BaO (28.321) > SrO (26.966) > EuO (24.330) > CaO (21.192) > La<sub>2</sub>O<sub>3</sub> (13.715) > MgO (13.680) > Ce<sub>2</sub>O<sub>3</sub> (13.025) > Pr<sub>2</sub>O<sub>3</sub> (12.817) > Pm<sub>2</sub>O<sub>3</sub> (12.651) > Nd<sub>2</sub>O<sub>3</sub> (12.145) > MnO (11.558) > Sm<sub>2</sub>O<sub>3</sub> (10.953) > Eu<sub>2</sub>O<sub>3</sub> (10.881) > Gd<sub>2</sub>O<sub>3</sub> (10.813) > Ho<sub>2</sub>O<sub>3</sub> (10.593) > Yb<sub>2</sub>O<sub>3</sub> (9.869) > Y<sub>2</sub>O<sub>3</sub> (9.833) > Tb<sub>2</sub>O<sub>3</sub> (9.468) > Dy<sub>2</sub>O<sub>3</sub> (9.440) > Tm<sub>2</sub>O<sub>3</sub> (9.220) > Er<sub>2</sub>O<sub>3</sub> (8.726) > PbO (7.713) > ZnO (6.800) > FeO (6.698) > GeO (6.368) > BeO (4.808) > Sc<sub>2</sub>O<sub>3</sub> (4.232) > Al<sub>2</sub>O<sub>3</sub> (3.326) > ThO<sub>2</sub> (0.455) > Ga<sub>2</sub>O<sub>3</sub> (0.454) > H<sub>2</sub>O (0.000) > Cr<sub>2</sub>O<sub>3</sub> (-0.008) > Mn<sub>2</sub>O<sub>3</sub> (-1.298) > SiO<sub>2</sub> (-1.886) > Fe<sub>2</sub>O<sub>3</sub> (-1.958) > B<sub>2</sub>O<sub>3</sub> (-2.026) > GeO<sub>2</sub> (-2.197) > Ta<sub>2</sub>O<sub>5</sub> (-2.291) > Nb<sub>2</sub>O<sub>5</sub> (-2.460) > HfO<sub>2</sub> (-2.674) > H<sub>2</sub>S (-2.770) > UO<sub>2</sub> (-2.807) > CO<sub>2</sub> (-2.936) > UO<sub>3</sub> (-3.3) > ZrO<sub>2</sub> (-3.633) > CeO<sub>2</sub> (-3.740) > WO<sub>2</sub> (-4.467) > P<sub>2</sub>O<sub>5</sub> (-4.536) > TiO<sub>2</sub> (-4.659) > WO<sub>3</sub> (-5.1) > HF (-18.700) > HCl (-20.410).

Thus, in the following isomorphous pairs numerators contain more basic components and denominators more acidic components: Rb/K, K/Na, Li/Mg, Ba/Sr, Sr/Ca, Ca/REE, Ca/Mg, Ca/Mn,  $Mn^{2+}/Fe^{2+}$ ,  $Fe^{2+}/Fe^{3+}$ , Ca/Th, REE/Th, Al/Ga, Al/B, Al/Fe<sup>3+</sup>, Si/Ge<sup>4+</sup>, Ta/Nb, Hf/Zr, Nb/Ti, Zr/Ti, Fe/Ta, Fe/Nb, Fe/Zr, Fe/Ti, Al/Si, Si/Nb, Si/Zr, Si/Ti, Si/W,  $S^{2-}/C^{4+}$ ,  $S^{2-}/Cl$ , F/Cl. In the line of REE of The Mendeleev's Periodic Table of the chemical elements the monotonous succession of decreasing basicity is broken:  $La^{3+} > Ce^{3+} > Pr^{3+} > Pm^{3+} > Nd^{3+} > Sm^{3+} > Eu^{3+} > Gd^{3+} > Ho^{3+} > Yb^{3+} > (Y^{3+}) > Tb^{3+} > Dy^{3+} > Tm^{3+} > Er^{3+}$  (excluding  $Eu^{2+}$  and  $Ce^{4+}$ ).

According to Alexey A. Marakushev (1979), the activity ( $\log \alpha_{M+}$ ) of potassium is always higher than the activity of sodium at any temperatures and pH. The values of  $\Delta Z_{298K}^{H_2O}$ ,  $\Delta Z_{1200K}^{H_2O}$ ,  $\Delta Z_{600K}^{H_2O}$  and  $\Delta Z_{298K}^{K_2O}$  and  $Na_2O$  — are 86.200, 66.332 and 56.388 kcal and 70.000, 53.025 and 44.910 kcal, respectively. In other words, during interaction of the fluids with materially sodium urtite substrate of a higher basicity, activity of potassium has to increase compared to that of sodium; although it will decrease later by cooling. In the process of ristschorritisation of urtites, the nepheline-aegirine-diopside paragenesis is replaced by the kalsilite — aegirine-diopside paragenesis (kalsilite has higher basicity than nepheline) and then — by the orthoclase — aegirine paragenesis (minerals of the lower basicity). Excess sodium is leached from the forming metasomatic rocks, but later "settles" as a "soda" mineralisation and albite veins.

To compare the basicity of the different eudialyte formed we need to compare the ratio of total basic and acidic components, as the more basic components in the structure (alkali, calcium) co-exist with acidic components (silicon, zirconium, titanium, niobium, chlorine). Such a comparison indicates that there is a general trend of enrichment of eudialyte in basic components during increasing alkalinity-basicity of the mineral-forming medium. However, essential deviations in certain structural positions can be observed in the case of pair substitutions. Apparently, the acidic-basic interaction can be shown in one and the same site within the structure.

In the Table 3 we give information on the structural positions in eudialyte with different symmetry and typical for them, isomorphous substitutions. Analysis of these data shows that even during *eucolitisation* of eudialyte the local substitution of the acidic components by the basic ones (for example, iron —

by manganese or chlorine — by fluorine) occurs as well as the substitution of the basic components by the acidic components (silicon — by niobium, zirconium, titanium or tin, and sodium — by calcium, strontium, REE and manganese) according to the general trend of decreasing alkalinity. As a result of such an inter-compensation of the components the equal site positions related through the centre of symmetry transform into the non-equal positions which leads to symmetry lowering and the "modular" structures appearance. Thus,  $N_1$  is split into  $N(1) = Na, Ca, REE$  and  $N(2) = Na, N4$  — for  $N(4) = Na, Ca, Sr, Mn, REE, H_3O^+$ , and also K, and  $N(3) = Na, Sr, Ba, REE$  and K, the "additional" silicon position — for  $M(4) = Si(7)$  and  $M(3) = Nb, Zr, Ti, W$ , and also Al, Mn or Na, calcium position — for  $M(1a)$  and  $M(1b)$ , that can be occupied also by Ca and Mn, Y, REE; and also Na and Sr, and iron position — for  $M(2,4)$  by  $Fe^{2+}$  and  $M(2,5)$  by  $Fe^{3+}$ , that can be occupied by Zr, Ti, Nb, Ta, and also Mn, REE and Y; and sodium substitutions  $N_5$  and  $N_6$ .

In *potassium* eudialyte the effect of the interaction is more definite: potassium (the component of the highest basicity) replaces sodium, iron is replaced by manganese, the content of silicon and strontium is increased, but part of the zirconium is replaced by acidic titanium. Potassium-sodium eudialyte is more basic than sodium eudialyte. The hydration of eudialyte leads to the abrupt decrease in total basicity and leaching of more basic components — sodium, potassium and calcium. In *titanium* eudialyte the basicity of the isomorphous components is decreased: potassium is replaced by sodium; calcium — by manganese and REE and zirconium — by titanium. Besides, the content of silicon is decreasing, although chlorine is partially replaced by the less acidic sulfur. The total basicity decreases. It can indicate that the "sodium" mineralisation in ristschorrites occurs as a result of leaching sodium, which has accumulated locally in separate zones within the rock. The same trend also lasts during the forming of alluaivite, however it is more contradictory: potassium is replaced by sodium, but strontium — by barium, calcium — by manganese and REE, zirconium — by titanium. Along with these iron is replaced by sodium, titanium — partially by niobium, chlorine — considerably by sulfur. The silicon content is the maximum possible in minerals with eudialyte structure. Therefore the genuine basicity of alluaivite is extremely high, it is determined by the maximum content of sodium. The acidic-basic interaction in

**Table 3. The character of isomorphous substitutions in different structural positions in eudialyte**

	Positions "splitting"			Typical component in the primary eudialyte	Isomorphous substitutions (components with the higher basicity comparing to the substituted position are marked with the <b>bold type</b> , more acidic components – with the regular type)
	Eudialyte <i>R3m</i>	Euclite <i>R3m</i>	Euclite <i>R3</i>		
$N_1$	<i>Na</i> (1a), <i>Na</i> (1b)	<i>Na</i> (1a), <i>Na</i> (1b)	<i>Na</i> (1a), <i>Na</i> (1b)	Na	Ca, <i>REE</i>
$N_2$		<i>Na</i> (2)	<i>Na</i> (2)	Na	–
$N_3$		<i>Na</i> (3a), <i>Na</i> (3b)	<i>Na</i> (3)	Na	<b>K</b> , <i>REE</i> , Sr, Ba
$N_4$	<i>Na</i> (4)	<i>Na</i> (4)	<i>Na</i> (4)	Na	<b>K</b> , $H_3O^+$ , Ca, Sr, Mn, <i>REE</i>
$N_5$	<i>Na</i> (5)	<i>Na</i> (5)	<i>Na</i> (5)	Na	–
$N_6^*$				Na	<b>K</b> , Sr
$N_7^*$				Na	<b>K</b> , Sr
$M_1$	$M_1$	$M_1$	$M$ (1a), $M$ (1b),	Ca	<b>Na</b> , Mn, <b>Sr</b> , Y, <i>REE</i> ,
$M_2$	$M$ (2,4) = ${}^4Fe^{2+}$	$M$ (2,4) = ${}^4Fe^{2+}$	$M$ (2,4) = ${}^4Fe^{2+}$	$Fe^{2+}$ , $Fe^{3+}$	$Fe^{3+}$ , <b>Mn</b> , <i>REE</i> , Y, <b>Na</b> , Ti, Nb, Ta, Zr
	$M$ (2,5) = ${}^5Fe^{3+}$	$M$ (2,5) = ${}^5Fe^{3+}$	$M$ (2,5) = ${}^5Fe^{3+}$		
Z	Z	Z	Z	Zr	<b>Nb</b> , Ti
$[Si_3O_9]$	<i>Si</i> (1)	<i>Si</i> (1), <i>Si</i> (2)	<i>Si</i> (1), <i>Si</i> (2)	Si	–
$[Si_9O_{27}]$	<i>Si</i> (3), <i>Si</i> (3s),	<i>Si</i> (3), <i>Si</i> (4),	<i>Si</i> (3), <i>Si</i> (4)	Si	–
	<i>Si</i> (5)	<i>Si</i> (5), <i>Si</i> (6)	<i>Si</i> (5a), <i>Si</i> (5b), <i>Si</i> (6a), <i>Si</i> (6b)		
$M_3$	$M$ (3a), $M$ (3b)	$M$ (3a), $M$ (3b)	M3	Si	<b>Al</b> , Nb, Zr, Ti, <b>Mn</b> , W, <b>Na</b>
$M_4$	<i>Si</i> (7), <i>Si</i> (7a)	<i>Si</i> (7), <i>Si</i> (7a)	<i>Si</i> (7), <i>Si</i> (7a)	Si	–
Oxygen positions	<i>O</i> (1-3), <i>O</i> (7-9),	<i>O</i> (1-18)	<i>O</i> (1-6),		
	<i>O</i> (13-15), <i>O</i> (19-20)		<i>O</i> (7a), <i>O</i> (7b), <i>O</i> (8-9), <i>O</i> (10a), <i>O</i> (10b), <i>O</i> (11-12), <i>O</i> (13a), <i>O</i> (13b), <i>O</i> (14a), <i>O</i> (14b), <i>O</i> (15), <i>O</i> (16a), <i>O</i> (16b), <i>O</i> (17a), <i>O</i> (17b), <i>O</i> (18-20)		
Anion positions X	<i>X</i> (1a), <i>X</i> (1b), <i>X</i> (1c), <i>X</i> (1d), <i>X</i> (1e), <i>X</i> (1f)	<i>X</i> (1a), <i>X</i> (1b), <i>X</i> (1c), <i>X</i> (1d), <i>X</i> (2a), <i>X</i> (2b), <i>X</i> (2c), <i>X</i> (2d)	<i>X</i> (1a), <i>X</i> (1b), <i>X</i> (1c), <i>X</i> (2a), <i>X</i> (2b), <i>X</i> (2c), <i>X</i> (2d)	Cl, <b>OH</b>	<b>F</b> , <b>C</b> , <b>S</b>

Notes: \* – in the "modular" structures by increasing cell parameter along c-axis up to 60 Å; besides, all the positions in the "modular" structures are getting redoubled:  $N_1$  and  $N_1^*$ ,  $N_6$  and  $N_6^*$ ,  $N_7$  and  $N_7^*$ ,  $M_1$  and  $M_1^*$ , Z and  $Z^*$ ,  $[Si_3O_9]^*$  and  $[Si_9O_{27}]^*$  etc.

eudialyte of different composition stabilize them within the limits of the stability field of the mineral, and allows us to consider them as varieties of the single mineral species.

### Conclusions

In the present paper the author tried to enlighten the current state of the mineral

typomorphism problem using eudialyte-euclite as an example, and to illustrate the possibility of applying typomorphism features data of this mineral as indicators of the mineral-forming processes in the Khibiny alkaline massif, Kola Peninsula. The structural typomorphism problem is not as simple as our opponents consider (Rastsvetaeva, Chukanov, 2006; Rastsvetaeva, 2007). In the previous

essay (Borutzky, 2008) we partially examined this problem. The intermediate members of the series eudialyte – alluaivite and potassium eudialyte in the Khibiny massif were formed during metasomatic replacement and later re-crystallization of normal sodium-ferri-ferrous eudialyte, which is typomorphic of the massive giant-grained urtites, being formed during the early stage of “the central arch” rocks fenitisation, and also their pegmatites and hydrothermal rocks. SEM and EMPA investigations of secondary eudialyte reveal replacement and transformation structures, i.e. relicts of the primary eudialyte. There are reasons to consider that these “relicts” can remain on a structural level. The same was determined by Giovanni Ferraris *et al.* (Ferraris *et al.*, 2001) in bornemanite formed during the replacement of lomonosovite; and Peter Nemeth (Nemeth *et al.*, 2005) in the structure compiled with epitaxial intergrowths of epistolite, murmanite and shkatulkaite.

Incidentally, in the structure of the zirconium alluaivite from the Khibiny massif (Ageeva *et al.*, 2002<sub>2</sub>), studied by Sergey V. Krivovichev (personal communication) no regular alternation of zirconium and titanium modules was detected, unlike *dualite* from the Lovozero massif (Rastsvetaeva *et al.*, 1999; Khomyakov *et al.*, 2007). The duplication of a c-parameter is determined by other reasons. Concerning potassium eudialyte, later named as *rastsvetaevite* (Rastsvetaeva, Khomyakov, 2001; Khomyakov *et al.*, 2006) and containing three modules: “eudialyte”, “alluaivite” (without titanium) and “barsanovite-kentbrooksite” is direct indication of the “eucolitisation” process beginning with conservation of primary eudialyte relicts in the newly-formed phase. That is why we consider that all diversity of potassium eudialyte in the Khibiny ristschorrites cannot be reduced to the formation of *rastsvetaevite* only. Moreover, our opponents know very well that after *potassium* eudialyte the *potassium-oxonium* variety is formed (Sokolova *et al.*, 1991; Rastsvetaeva *et al.*, 19901).

*Typomorphism* is a scientific issue, and it is not correct to reduce all the diversity of the relationships between the structure of eudialyte and geological conditions of their occurrence, i.e. *structural-chemical* isomorphism, only to the listing of the “new” mineral species. We believe that the structural analysis does not exhaust its potentialities, and we shall learn about the true reasons of the multiple structural-chemical typomorphic features of such a complex structures

as the *minerals of variable composition with variable structure*.

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