UDC 549.621.4

### KALSILITE IN THE ROCKS OF KHIBINY MASSIF: MORPHOLOGY, PARAGENESIS, GENETIC CONDITIONS

Olga A. Ageeva,

Institute of Ore Deposit Geology, Petrography, Mineralogy and Geochemistry RAS, Moscow, ageeva@igem.ru Boris Ye. Borutzky

Institute of Ore Deposit Geology, Petrography, Mineralogy and Geochemistry RAS, Moscow, ageeva@igem.ru

Kalsilite in Khibiny massif is typical for poikilitic nepheline syenites (ristschorrites) where it occurs in close intergrowth with nepheline and orthoclase. This mineral is observed in the nepheline grains as veinlets, segregations of irregular shape or rims at the boundaries of nepheline and orthoclase grains. Also it occurs in the composition of radiate-fibrous kalsilite-orthoclase intergrowths, as a rule, framing nepheline grains.

Formation of kalsilite is determined to concern to most early stage of K-Si-metasomatosis, influencing on massive coarse-grained urtites. It is caused by strong increasing activity of potassium relatively to sodium. Nepheline of initial rocks was the matrix for kalsilite formation, which was accompanied and changed by formation of other potassium minerals, including the main rock-forming mineral of ristschorrites — potassium feldspar.

Different chemical activity of potassium and silica, which has determined kalsilite presence, degree of its development, and other peculiarities of ristschorrites mineralogy, is caused by both the character of replaced rocks, and the chemical composition of influencing solutions (the potassium concentration in them). 4 tables, 3 figures, and 24 references.

The problem of kalsilite formation in ristschorrites of Khibiny massif (Kola peninsula) as a problem of genesis of ristschorrites themselves is a discussion subject till now. We shall note that ristschorrites (poikilitic nepheline syenites) in Khibiny massif are spatially connected to massive coarse-grained urtites and form together with them the gradual transitions across the rocks of intermediate composition (juvites, feldspar urtites etc.). Together with rocks of ijolite-urtite complex they compose the Central Arc of Khibiny massif, which is located between nepheline syenites: khibinites (outside) and foyaites (inside). On quantitative-mineral composition ristschorrites corresponds to «common» nepheline syenites of this massif (khibinites, foyaites etc.), having, as it is known, primary magmatic genesis, but on a number of mineralogical and petrological features are distinguished from them. First of all they are characterized by strongly pronounced poikilitic structure, very inconsistent mineral composition and irregular granularity (the size of feldspar poikilocrystals fluctuates from 1 up to 15 cm, and its content -- from 50% to 80%). Their high-potassium chemical composition is their second peculiarity: ristschorrites are strongly stood out against all rocks of Khibiny massif by its increased content of potassium (Table 1). That is caused, first of all, by feldspars in them do not have potassium-sodium chemical composition as in common nepheline syenites, but significantly potassium one (in ristschorrites the adularia-like orthoclase is most widespread).

From the beginning of research of geological structure of Khibiny massif till now the alternative hypotheses of magmatic (N.A. Eliseev, S.I. Zak, A.V. Galakhov, T.N. Ivanova, A.A. Arzamastsev *et al.*) and metasomatic (L.L. Solodovnikova, I.P. Tikhonenkov, B.Ye. Borutzky *et al.*) genesis of ristschorrites are developed. The discovery of potassium analogue of nepheline, kalsilite, in ristschorrites (Borutzky etc., 1973, 1976) was unexpected, raised a number of new problems before mineralogists, and resulted in appearance of new views on the ristschorrites genesis, and, in particular, on source of potassium, which is necessary to formation of such high-potassium rocks within the bounds of significantly sodium agpaitic nepheline syenites massif.

In ristschorrites kalsilite plays, as a rule, the role of accessory mineral and yields to nepheline on its content in the rock, but in some areas its amount is strongly increased. The optical properties of these two feldspathoids are very close to each other, which make some difficulties in diagnostics and study of kalsilite segregation forms. But just the occurrence form of kalsilite and the character of its relations with nepheline and feldspar are the most important indicator features, allowing to detect the mechanism of its formation in the rocks, and, consequently, to reconstruct the history of formation of these rocks. In this article there are the new results of detail study of chemical composition, segregation forms of kalsilite and its relations with other minerals in the rocks of Khibiny massif, which was performed by high-permission scanning microscope JSM-5300 with X-ray energy-dispersive spectrometer Link ISIS.

40

# Kalsilite occurrences in the rocks of different genesis

Kalsilite is widespread only in the alkaline rocks of ultrapotassium series. As a rock-forming mineral it is noted in the rocks of different genesis: volcanites, intrusive and metasomatic rocks. In ultrapotassium ultrabasic volcanites from Uganda (Holmes, 1942), Nyragongo (Zaire), Saint Venanzo (Italy) kalsilite is associated with diopside, olivine, pyroxene, biotite, perovskite, glass etc. From leucocratic minerals, besides kalsilite, the leucite, melilite, and nepheline can be present in these rocks. Kalsilite is mainly observed in small-grained matrix in assemblage with other feldspathoids and feldspar or without them, rarely it occurs in the compound macro- and micropertite intergrowths in nepheline phenocrysts, which is considered as the structures of disintegration of solid kalsilite-nepheline solution (Sahama, 1960; Aurissicchio, Federico, 1985).

In alkaline rocks of ultrapotassium intrusive complexes the morphology of kalsilite segregations and the character of its intergrowths with other minerals are very diverse that in a number of cases complicates their interpretation. Often it is observed the thin

dactyloscopic and subgraphic intergrowths of kalsilite with potassium feldspar, which have the distinct eight-angle and ovoid contours and are interpreted as pseudoleucite, the product of postcrystalization disintegration of leucite. The most important criteria for such explanation are the preservation of crystallographic contours of tetragonthreeoctahedron and equal molecular ratio of kalsilite and potassium feldspar (1:1) in the bounds of «intergrowth». That sort of intergrowths is observed in kalsilite-orthoclase syenites (synnyrites) of Synnyr, Yakshin (Pribaikalia), Murun, Sakun (East Transbaikalia) and other massifs. The content of kalsilite in synnyrites of Synnyr massif reaches 20 - 35% at 60 - 75% of orthoclase. The phenocrysts of pseudoleucite up to 20 cm in size compose from 10 to 60% of the rock volume and occur in small-grained matrix, consisting of potassium feldspar, nepheline, and pyroxene (Kurepin, 1973).

However, in the rocks of these massifs there are the other types of intergrowths: micrographic kalsilite-(nepheline)-feldspar intergrowths without distinct shape and fixed mineral ratios, irregular poikilitic ingrowths of kalsilite and nepheline in feldspar, kalsilite

Table 1 Chemical composition (wt %) of poikilitic nepheline syenites and contacting with them rocks of Khibiny massif

|                                    | urtite | nepheline syenite |       | ristschorrite-I | ristschorrite-II |       |        | ristschorrite-III |       |
|------------------------------------|--------|-------------------|-------|-----------------|------------------|-------|--------|-------------------|-------|
| <u>№ of sample</u><br>Constituents | 1      | 2                 | 3     | 4               | 5                | 6     | 7      | 8                 | 9     |
| SiO <sub>2</sub>                   | 43,19  | 54,45             | 58,95 | 57,93           | 54,56            | 55,98 | 52,86  | 56,06             | 54,02 |
| TiO <sub>2</sub>                   | 0,79   | 1,43              | 0,44  | 0,19            | 0,98             | 0,57  | 1,57   | 0,07              | 0,16  |
| ZrO <sub>2</sub>                   | 0,04   | 0,051             | 0,018 | 0,033           | 0,016            | 0,03  | 0,03   | 0,002             | 0,002 |
| Nb <sub>2</sub> O <sub>5</sub>     | 0,01   | 0,032             | 0,013 | 0,002           | 0,018            | 0,01  | 0,08   | 0,001             | 0,001 |
| $P_2O_5$                           | 3,81   | 0,224             | 0,123 | 0,038           | 0,051            | 0,58  | 0,41   | 0,059             | 0,015 |
| $Al_2O_3$                          | 23,32  | 24,13             | 20,65 | 23,90           | 21,38            | 18,26 | 18,96  | 22,66             | 20,82 |
| Fe <sub>2</sub> O <sub>3</sub>     | 3,53   | 4,50*             | 3,62* | 1,43*           | 3,78*            | 2,20  | 2,96   | 1,14*             | 2,51* |
| FeO                                | 1,47   | _                 | -     | -               | _                | 0,56  | 2,71   | _                 | -     |
| MgO                                | 0,10   | 0,53              | 0,61  | 0,17            | 0,30             | 0,19  | 0,15   | 0,09              | 0,14  |
| MnO                                | 0,07   | 0,146             | 0,151 | 0,044           | 0,078            | 0,07  | 0,72   | 0,017             | 0,033 |
| CaO                                | 5,94   | 1,35              | 0,61  | 0,18            | 1,23             | 0,95  | 1,41   | 0,628             | 0,21  |
| SrO                                | 0,42   | 0,158             | 0,024 | 0,017           | 0,131            | 0,13  | 0,10   | 0,066             | 0,025 |
| BaO                                | 0,12   | 0,311             | 0,044 | 0,065           | 0,316            | 0,24  | 0,10   | 0,060             | 0,092 |
| Na <sub>2</sub> O                  | 10,46  | 6,47              | 7,07  | 8,41            | 5,58             | 3,22  | 4,85   | 5,22              | 1,45  |
| K <sub>2</sub> O                   | 5,33   | 6,68              | 6,21  | 6,97            | 10,33            | 12,38 | 12,44  | 13,11             | 19,66 |
| Rb <sub>2</sub> O                  | 0,009  | 0,014             | 0,023 | 0,026           | 0,029            | 0,035 | 0,085  | 0,096             | 0,132 |
| Cl                                 | 0,03   | 0,047             | 0,021 | 0,018           | 0,034            | 0,17  | 0,39   | 0,018             | 0,056 |
| S                                  | 0,25   | 0,02              | 0,01  | 0,02            | 0,03             | 0,17  | 0,16   | 0,12              | 0,07  |
| Loss                               | 1,4    | _                 | -     | _               | -                | 0,41  | 0,43   | _                 | _     |
| Total                              | 100,47 | 100,54            | 98,59 | 99,44           | 98,84            | 96,26 | 100,38 | 99,41             | 99,96 |
| Note.                              |        |                   |       |                 |                  |       |        |                   |       |

Analyst A.I. Yakushev, Philips Analytical (PW2400) IGEM RAS. The distribution of  $Fe^{+2}/Fe^{+3}$  was performed by method of wet chemistry, analyst O.G. Unanova.

Analyses: 1 — massive coarse-grained urtite (hole 1456, Mt. Rasvumchorr); 2-3 — nepheline syenites: 2 — khibinite (from indigenous outcrop, Mt. Takhtarvumchorr), 3 — foyaite (Northern Ristschorr ravine); 4 — micaceous ristschorrite of I group, analyses 3—4 was made from one sample, representing the zone of sharp contact of ristschorrite and foyaite; 5 — micaceous ristschorrite of II group (Mt. Kukisvumchorr); 6—7 — pyroxene ristschorrite of II group (Mt. Rasvumchorr); 8—9 — ultrapotassium ristschorrites of III group (hole 1292, Mt. Poachvumchorr). The dash is the absence of data. \* — The sum of iron, detected as Fe<sub>2</sub>O<sub>3</sub>.

| № of                           |                |        | Nepheline  |       |               | Alkaline feldspar |       |       |       |         |  |
|--------------------------------|----------------|--------|------------|-------|---------------|-------------------|-------|-------|-------|---------|--|
| sample<br>Constit.             | 1              | 2      | 3          | 4     | 5             | 6                 | 7     | 8     | 9     | 10      |  |
| SiO <sub>2</sub>               | 44,30          | 44,79  | 42,50      | 40.77 | 43,33         | 64,98             | 61,64 | 63,36 | 64,13 | 64,95   |  |
| Al2O <sub>3</sub>              | 44,50<br>31,94 |        | 42,30      | 32,67 | 43,33         | 19,44             | 18,05 | 17,64 |       |         |  |
|                                |                | 32,11  |            |       |               |                   |       |       | 18,24 | 17,48   |  |
| Fe <sub>2</sub> O <sub>3</sub> | 0,91           | 0,65   | 0,83       | 1,30  | 1,68          | 0,31              | 0,19  | 0,95  | 0,46  | 1,23    |  |
| CaO                            | 0,00           | 0,02   | 0,00       | 0     | 0,14          | 0,36              | 0,21  | 0     | 0,01  | 0,26    |  |
| BaO                            | 0              | 0      | 0          | 0     | 0             | 0                 | 3,36  | 0,48  | 0,04  |         |  |
| Na <sub>2</sub> O              | 16,67          | 17,15  | 17,29      | 16,33 | 14,37         | 5,02              | 2,81  | 0,74  | 0,45  | 0,62    |  |
| K <sub>2</sub> O               | 5,81           | 6,15   | 8,08       | 8,79  | 8,82          | 9,20              | 12,36 | 15,72 | 15,54 | 16,17   |  |
| Rb <sub>2</sub> O              | 0              | 0      | 0          | 0     | 0             | 0                 | 0     | 0,030 | 0,110 | no data |  |
| Total                          | 99,63          | 100,87 | 100,13     | 99,86 | 99,39         | 99,31             | 98,62 | 98,92 | 98,98 | 100,70  |  |
|                                |                |        |            | Numbe | rs of ions on | the basis of      |       |       |       |         |  |
|                                |                | cat    | ions sum = | : 12  |               | cations sum = $5$ |       |       |       |         |  |
| Si                             | 1,09           | 1,09   | 1,03       | 1,00  | 1,09          | 2,95              | 2,91  | 2,97  | 3,00  | 2,99    |  |
| Al                             | 0,93           | 0,92   | 0,90       | 0,95  | 0,92          | 1,04              | 1,00  | 0,98  | 1,01  | 0,95    |  |
| Fe                             | 0              | 0      | 0          | 0     | 0             | 0,01              | 0,01  | 0,03  | 0,02  | 0,04    |  |
| Ca                             | 0              | 0      | 0          | 0     | 0             | 0,02              | 0,01  | 0     | o     | 0.01    |  |
| Ba                             | 0              | 0      | 0          | 0     | 0             | 0                 | 0,06  | 0,01  | 0     | 0       |  |
| Na                             | 0.80           | 0.81   | 0,82       | 0,78  | 0,70          | 0,44              | 0,26  | 0,07  | 0,04  | 0,06    |  |
| K                              | 0,18           | 0,19   | 0,25       | 0,28  | 0,28          | 0,53              | 0,74  | 0,94  | 0.93  | 0,95    |  |
| Rb                             | 0              | 0      | 0          | 0     | 0             | 0                 | 0     | 0     | 0,002 | 0,00    |  |
| 0                              | 16,27          | 16,19  | 15,80      | 15,79 | 16,24         | 7,99              | 7,92  | 7,97  | 8,03  | 7,98    |  |

Table 2. Chemical composition (wt %) of nepheline and alkaline feldspar from the rocks of Khibiny massif

Note.

Analyses: 1-5 — nepheline: 1-2 — from the zone of contact of ristschorrite and nepheline syenite (foyaite), Northern Ristschorr ravine, an. 1 — from foyaite; an. 2 — from ristschorrite of I group; an. 3 — from massive coarse-grained urtite (Mt. Rasvumchorr); an. 4 — from pyroxene ristschorrite of II group (Mt. Rasvumchorr); an. 5 — from ultrapotassium ristschorrite of II group (Mt. Poachvumchorr); 6-10 — feldspars: an. 6 — from nepheline syenite — foyaite (Mt. Partamchorr), an. 7 — from pyroxene ristschorrite of I group; an. 8 — from massive coarse-grained urtite (Mt. Yukspor); an. 9 — from pyroxene ristschorrite of II group (Mt. Rasvumchorr); an. 10 — from ultrapotassium ristschorrite of III group (Mt. Poachvumchorr); an. 10 — from ultrapotassium ristschorrite of III group (Mt. Poachvumchorr); an. 10 — from ultrapotassium ristschorrite of 8, 8-9 (Borutzky, 1988); an. 10 — analyst N.V. Trubkin (JSM-5300 + Link ISIS, IGEM RAS).

poikilocrystals with inclusions of dark-coloured minerals etc. An appearance of these forms can be caused by different reasons. Formation of the ones is explained by direct eutectic or cotectic magmatic crystallization from the melt (Smyslov, 1986, and others), for others - by «feldspathization» of nepheline (Arkhangel'skaya, 1965) or reactionary replacement of earlier feldspar by kalsilite (Bagdasarov, Luk'yanova, 1969; Samsonova et al., 1968). In Murun massif the new type of kalsilite-bearing rocks is detected. It is the analogue of feldspar-free rocks of urtite-jacupirangite series, which kalsilite instead nepheline is developed in (Konev, 1985; Konev et al., 1996). According to (Konev, 1985), these rocks have the primary magmatic origin, but in a number of alkaline complexes, Ozerskii, Tazheran (Priolkhonye), Murun, the typical metasomatic kalsilite-bearing rocks, kalsilitized skarns, are noted (Konev, Samoilov, 1974).

It is necessary to record that in above-mentioned intergrowths with orthoclase in most of enumerated massifs the nepheline can be present instead kalsilite and together with it, forming the same segregation shapes as kalsilite. In Lugijn Gol massif (Mongolian People's Republic) «pseudoleucitic syenites» are widespread, which do not absolutely contain kalsilite (Kovalenko *et al.*, 1974). The leucocratic part of these rocks has nepheline-feldspar composition. Nepheline and potassium feldspar form globular «pseudoleucite» intergrowths, which are considered as the product of disintegration of K,Naanalcime or reaction of primary potassium leucite with sodium melt (Kononova *et al.*, 1981).

#### Kalsilite in the rocks of Khibiny massif

In Khibiny massif kalsilite is widespread in the rocks of ristschorrites complex. For the first time it was detected in juvites at apatite deposit Yukspor (Borutzky *et al.*, 1973). Later the kalsilite-bearing rocks (ristschorrites and juvites) were noted in region of mountains Eveslogchorr, Poachvumchorr, Kukisvumchorr, Rasvumchorr, and others. Although within the bounds of studied massif in the most of cases kalsilite associates with nepheline, the ristschorrites strongly enriched by kalsilite (up to 15-20%) and practically without nepheline (Kozyreva *et al.*, 1990). The zones of ultrapotassium rocks are more characteristic for inner side of ijolite-urtite arc, i.e. for its upper (in geological section) parts. Also enrichment by kalsilite is noted for ristschorrites, joined to hanging wall of ore rock mass of apatite-nepheline deposits (Kozyreva *et al.*, 1990).

All ristschorrites of Khibiny massif can be divided into three groups by kalsilite presence and degree of its development:

#### I group — ristschorrites, non-containing kalsilite

These ristschorrites are noted near the contacts of considered rocks with nepheline syenites (khibinites, foyaites et al.), and sometimes at significant distance from those contacts. In near-contact zones they contain the areas, composed by relics of nepheline syenites. By content of main petrogenic elements these ristschorrites (Table 1, an. 4) are close to «common» nepheline syenites (Table 1, an. 2-3). On the diagram  $SiO_2$ -Na<sub>2</sub>O-K<sub>2</sub>O the points, corresponding to compositions of both rocks, fall into the same field and approach to the point, conforming the chemical composition of potassium-sodium feldspar (Fig. 1). In comparison with other groups of ristschorrites these rocks are less potassium and more silicic.

The peculiarity of this rocks group, contrary to tendency established for ristschorrites, is the slightly increased content of sodium in feldspar (Table 2, an. 7) and presence in this feldspar the corroded and redistributed albite pertite intergrowths, i.e. relic potassium-sodium feldspars (Tikhonenkov, 1963; Borutzky, 1988; Borutzky *et al.*, 1975, 1986). Among accessories the potassium-free and low-potassium alkaline minerals prevail: lamprophyllite Na<sub>2</sub>Sr<sub>2</sub>(Ti,Fe,Mn)<sub>3</sub>(SiO<sub>4</sub>)<sub>4</sub>(OH,F)<sub>2</sub>, sodium eudialyte Na<sub>15</sub>Ca<sub>6</sub>Fe<sub>3</sub>Zr<sub>3</sub>Si<sub>26</sub>O<sub>73</sub>(OH,Cl)<sub>5</sub>, aenigmatite NaFe<sub>5</sub>TiSi<sub>6</sub>O<sub>20</sub>.

#### *Il group — ristschorrites and juvites with low content of kalsilite (from 0.1 to 5%)*

In Khibiny massif this group is most widespread. On the diagram  $SiO_2$ - $Na_2O$ - $K_2O$  the position of points, corresponding to most potassium compositions of rocks of this group, is close to orthoclase (Fig. 1).

Kalsilite (Table 3, an. 1-7) by its content in rock significantly yields to nepheline, which in its turn is characterized by increased content of potassium (Table 2, an. 4). Feldspar has considerably potassium composition (Table 2, an. 9). The increased content of rubidium (Table 2, an. 8-9) is noted in it that can be connected to high-alkali conditions of these rocks formation (Borutzky, 1988). Among accessories there are potassium and potassium-containing minerals: astrophyllite, magnesioastrophyllite, wadeite, delhayelite, fenaksite, scherbakovite (Table 4, an. 1, 3-5) *etc.*, and potassium-enriched varieties of sodium minerals: potassium eudialyte, potassium barytolamprophyllite (Table 4, an. 6-7) *et al.* From dark-coloured rock-forming minerals there are aegirine, alkali amphibole, and biotite. The minerals, determined in this group of ristschorrites, as a rule replace the primary minerals of initial urtites (nepheline, aegirine-diopside, titanite, Sr-lamprophyllite, Naeudialyte *etc.*), which relics are constantly discovered in these rocks.

Kalsilite occurs both independently (Fig. 2a) and in intergrowth with nepheline, forming poikilitic ingrowths in feldspar. It is observed as veinlets, cutting the nepheline crystals (Fig. 2b, 2c), which in longitudinal (rectangular) sections of nepheline crystals are parallel, and in cross (hexagonal) ones are subparallel and situated fan-shaped to each other. In longitudinal sections the kalsilite veinlets parallel each other cuts the nepheline crystal parallel axis [001] or diagonally. Often the intergrowths of kalsilite and nepheline in orthoclase poikilocrystals of ristschorrites have irregular intricate shape (Fig. 2d). In a number of cases the intersection of several close to each other nepheline grains by the same veinlet of kalsilite was documented. The veinlets as a rule have very insignificant thickness ( $n \times 0.01$  mm) and are broken in the contacts of nepheline with feldspar (Fig. 2e).

We consider the described segregation forms of kalsilite are caused by its metasomatic genesis: kalsilite replace nepheline (and is observed in the grains of latter), and in the case of follo-



FIG. 1. The ration of silica and alkali metals (SiO<sub>2</sub> + Na<sub>2</sub>O +  $K_2O = 100\%$ ) in minerals (1): nepheline (Ne), leucite (Lc), orthoclase (Or), K-Na-feldspar (K-Na-Fsp) and in the main types of the rocks of Khibiny massif: 2 — massive coarse-grained urities; 3 — juvites; 4 — ristschorrites of II group; 5 — ristschorrites of II group; 6 — ristschorrites of I group; 7 — nepheline syenites



FIG. 2. The segregation forms of kalsilite (Ks) in ristschorrites of II group (Ne — nepheline, Or — orthoclase, Px — pyroxene, Ap — apatite), in reflected electrons (JSM-5300, Link ISIS):
a) the dislocation of kalsilite segregations groups (with similar orientation) in orthoclase poikilocrystal (dash line divides the parts with different 2V values, the explanation is in text);
b-c) the dislocation of kalsilite veinlets in cross (b) and longitudinal sections of nepheline crystal (c);
d) irregular intergrowths of kalsilite and nepheline in orthoclase poikilocrystals;
e) intersection of several close to each other nepheline grains by the same kalsilite veinlet;
f) nepheline-orthoclase inclusions in pyroxene poikilocrystal

| <u>№ of san</u><br>Constitue   |       | 2     | 3     | 4           | 5            | 6              | 7       | 8      | 9      | 10     |
|--------------------------------|-------|-------|-------|-------------|--------------|----------------|---------|--------|--------|--------|
| SiO <sub>2</sub>               | 39,83 | 40,17 | 37,14 | 37,16       | 37,98        | 37,42          | 37,51   | 38,78  | 39,32  | 39,32  |
| Al <sub>2</sub> O <sub>3</sub> | 27,32 | 27,88 | 28,51 | 30,34       | 29,27        | 30,34          | 30,92   | 28,82  | 30,06  | 30,05  |
| Fe <sub>2</sub> O <sub>3</sub> | 5,12  | 1,51  | 3,56  | 0,79        | 1,03         | 0,79           | 0,62    | 3,10   | 1,41   | 1,41   |
| CaO                            | 0,34  | 0,36  | 0,55  | 0,38        | 0,29         | 0,00           | 0,17    | 0,40   | 0,44   | 0,44   |
| Na <sub>2</sub> O              | 0,09  | 0     | 0,20  | 0,35        | 0,77         | 0,70           | 0,20    | 0      | 0      | 0      |
| K <sub>2</sub> Ō               | 27,40 | 29,69 | 29,77 | 30,52       | 29,71        | 30,34          | 30,57   | 29,70  | 29,13  | 29,13  |
| Total                          | 100,1 | 99,61 | 99,73 | 99,54       | 99,05        | 99,59          | 99,99   | 100,80 | 100,36 | 100,40 |
|                                |       |       | Num   | ber of ions | on the basis | s of cations s | sum = 3 |        |        |        |
| Si                             | 1,07  | 1,07  | 0,99  | 0,98        | 1,01         | 0,99           | 0,99    | 1,03   | 1,04   | 1,04   |
| Al                             | 0,87  | 0,88  | 0,90  | 0,94        | 0,92         | 0,94           | 0,96    | 0,90   | 0,94   | 0,94   |
| Fe                             | 0,10  | 0,03  | 0,07  | 0,02        | 0,02         | 0,02           | 0,01    | 0,06   | 0,03   | 0,03   |
| Ca                             | 0,01  | 0,01  | 0,02  | 0,01        | 0,01         | 0,00           | 0,00    | 0,01   | 0,01   | 0,01   |
| Na                             | 0,00  | 0,00  | 0,01  | 0,02        | 0,04         | 0,04           | 0,01    | 0,00   | 0,00   | 0,00   |
| K                              | 0,94  | 1,01  | 1,01  | 1,03        | 1,01         | 1,02           | 1,03    | 1,00   | 0,98   | 0,98   |
| 0                              | 4,09  | 4,02  | 3,94  | 3,95        | 3,95         | 3,94           | 3,95    | 4,01   | 4,03   | 4,03   |

Table 3. Chemical composition (wt %) of kalsilite from the rocks of Khibiny massif

Analyses 1, 2 — from micaceous ristschorrite of II group (Mt. Yukspor); 3-7 — from pyroxene ristschorrites of II group, 4-7- from one sample (Mt. Rasvumchorr); an. 8-10- from ultrapotassium ristschorrites of III group (Mt. Poachvumchorr); an. 9-10- from one sample. Analyst - N.V. Trubkin (JSM-5300 + Link ISIS, IGEM RAS)

wing replacement of nepheline by potassium feldspar it will remain as relic.

#### III group — ristschorrites with high content of kalsilite (from 5-10 to 20%)

By appearance they are most resembled to «pseudoleucite» syenites, but in Khibiny massif have not wide spreading. By mineral composition these rocks are close to ristschorrites of II group. In the chemical composition of rockforming and accessory minerals (Table 2, an. 5, 10; Table 3, an. 8 - 10; Table 4, an. 2) the potassium content most possible for these minerals are detected. On the diagram SiO<sub>2</sub>-Na<sub>2</sub>O-K<sub>2</sub>O the position of points, corresponding to most potassium rocks of considered group, is approached to leucite (Fig. 1). The rubidium concentration is strongly increased and even in comparison with ristschorrites of II group (Table 1, an. 8-9).

In these rocks, as in ristschorrites of II group, the corroded or (rarely) idiomorphic nepheline grains, cut by above-mentioned kalsilite veinlets, occur (Fig. 3a), but more often they are located in the centre of kalsilite-(nepheline)orthoclase intergrowths, forming isolated inclusions in orthoclase poikilocrystal. Three types of these intergrowths are distinguished:

First type. The optical orientation of orthoclase in the plane of section is not changed and coincides with optical orientation of all poikilocrystal, and elongated kalsilite segregations, increasing on width and length from centre to periphery of «intergrowth», are oriented in the system close to radial.

The largest development is characteristic for one of the directions (Fig. 3b), which the optical orientation of single kalsilite segregations remains in constant for ingrowths elongated in reciprocally perpendicular directions. Usually kalsilite, forming the peripheral rims of central (relic) nepheline grains has the same optical orientation (Fig. 3b). In the same orthoclase poikilocrystal, preserving the single optical orientation at the significant area (up to  $10 \times 10$  cm), the several kalsilite-orthoclase intergrowths are found. As a rule, these parts are isometric, but do not have the distinct shape.

*The second type* is distinguished from the first one that the groups of equally oriented kalsilite segregations, located in poikilocrystal, do not show the radiate-fibrous structure and are characterized by development of irregular (Fig. 3a, 3c, 3d) or idiomorphic thin- and thicktabular, and sometimes dactyloscopic segregations. It is essential the nepheline forms the similar intergrowths with orthoclase. This type of intergrowths occurs in ristschorrites of II group. The measurements on Fedorov universal table show that in areas of feldspar poikilocrystals, which the accumulation of equally or regular oriented feldspathoid inclusions (presumably replaced by kalsilite or unaltered relics of primary nepheline, (Fig. 2a)) is observed in, the angle of optical axes is  $\sim 35^{\circ}$ , that corresponds to low sanidine (low-ordered modification of feldspar), and is distinguished from this value for other part of the poikilocrystal, non-containing such inclusions, in which the angle of optical axes is increased up to -56-58° and corresponds to high orthoclase (more ordered modification). It is essential that between these modifications there is gradual tran-



FIG. 3. Kalsilite (Ks) segregation forms in ristschorrites of III group (Ne — nepheline, Or — orthoclase, Vd — wadeite) in reflected electrons (JSM-5300, Link ISIS):

a) idiomorphic nepheline grain (to the right), crossed by kalsilite veinlet and isolated kalsilite segregations in orthoclase poikilocrystal (to the left);

b) nepheline grain, rounded by radiate-fibrous kalsilite-orthoclase intergrowth (of the first type); c-d) kalsilite segregations in rims, framing the relic nepheline grains, and in kalsilite-orthoclase intergrowths (of the second type); e) radiate-fibrous fine needle-shaped and symplektitic nepheline- and kalsilite-feldspar intergrowths (of the third type) in peripheral parts of nepheline grain;

f) kalsilite-feldspar intergrowth, forming poikilitic inclusion in pyroxene

sition (with gradual increasing of optical axes angle), besides that the spatial (and optical) orientation of poikilocrystal remains single at all its area. The central zones of nepheline grains were replaced by feldspar later than peripheral ones that can be the reason of observed heterogeneity. As a result of that in these parts the relics of replaced feldspathoid remained, and the process of Si/Al-ordering of feldspar was developed in smaller degree than in edge zones, where the solution action was longer.

The third type is represented by radiatefibrous fine needle-shaped and symplektitic intergrowths, which are characterized by synchronous wavy extinction both kalsilite and feldspar. That sort of intergrowths is observed in peripheral parts of nepheline grains and sometimes is separated from these grains by zones of nepheline-orthoclase intergrowths, analogous to them both on morphology and segregation sizes (Fig. 3e). The above-mentioned kalsilite veinlets are often characterized by the wavy extinction, and the kalsilite rims on the nepheline grains surface have the same extinction, and, by our opinion, can be the base for formation of considered type of kalsilite-feldspar intergrowths during the process of rock orthoclasization.

Kalsilite often composes the kalsilite-(nepheline)-feldspar intergrowths, forming poikilitic inclusions in pyroxene (rarely in other minerals: lamprophyllite, lomonosovite, titanite), composing the characteristic for ristschorrites (of II and III groups) melanocratic parts. These inclusions (0.2-2 mm in size) often have roundish contours (Fig. 2f, 3f), but along with them the monomineral idiomorphic inclusions of hexagonal nepheline grains are observed. The ingrowths of feldspathoid within the poikilitic inclusion are as a rule elongated, but sometimes they have isometric shape. Quite often the peripheral part of nepheline and kalsilite-(nepheline)-orthoclase poikilitic inclusions is formed by orthoclase (Fig. 2a). The optical orientation of feldspathoid in all (or in group) poikilitic inclusions, corresponding to single pyroxene poikilocrystal often proves to be similar. The optical orientation of orthoclase, growing together with it, is distinguished from the orientation of feldspathoid, but is single for all ingrowths and coincides with orientation of orthoclase poikilocrystal joining to this pyroxene crystal. In the areas of contact of aegirinediopside with kalsilite-(nepheline)-orthoclase intergrowths its replacement by aegirine, biotite, and potassium-bearing amphibole is noted.

According to (Plechov, Serebryakov, 2003) these parts are the relics of fergusites (the plutonic rocks, containing nearly 70% of pseudoleucite and 30% of pyroxene), grasped by ristschorrites. However, our researches have shown that the distribution of feldspathoid ingrowths in feldspar of ristschorrites is very irregular and along with kalsilite-feldspar intergrowths, which analyses are exactly recalculated on leucite formula (at ratio of kalsilite and feldspar 1:1), the areas with strong predominance of some or different phase are noted. Moreover, in these rocks we did not detect the intergrowths with distinct crystallographic contours, which could reflect the cubic habit of primary leucite. By our opinion, these mineral relations can be explained by metasomatic hypothesis of ristschorrites genesis. They are caused by particular inheritance the structure of massive coarse-grained urtites by ristschorrites, which replaces them. For these urtites the melanocratic parts, consisting of enlarged (up to 10-20 mm) pyroxene poikilocrystals and accessory minerals

Table 4. Chemical composition (wt %) of accessory minerals from ristschorrites

| № of<br>sample<br>Consti-<br>tuents | 1      | 2      | 3     | 4      | 5      | 6      | 7     |
|-------------------------------------|--------|--------|-------|--------|--------|--------|-------|
| SiO <sub>2</sub>                    | 45,98  | 47,46  | 44,54 | 61,80  | 42,44  | 51,87  | 30,17 |
| TiO <sub>2</sub>                    | 1,80   | 8,27   | 0     | 0      | 23,27  | 0,55   | 26,93 |
| ZrO2                                | 28,97  | 20,99  | 0     | 0      | 0      | 11,54  | 0     |
| Nb <sub>2</sub> O <sub>5</sub>      | 0      | 0      | 0     | 0      | 5,34   | 0      | 1,80  |
| $Al_2O_3$                           | 0      | 0,08   | 5,88  | 0      | 0,19   | 0      | 0     |
| $Fe_2O_3$                           | 0      | 0      | 0     | 0      | 0,99   | 0      | 3,43  |
| FeO                                 | 0,04   | 0      | 0,34  | 12,07  | 0      | 2,24   | 0     |
| MnO                                 | 0,02   | 0      | 0,09  | 5,09   | 0,06   | 1,26   | 1,02  |
| MgO                                 | 0,07   | 0      | 0,03  | 0,46   | 0      | 0      | 0,19  |
| CaO                                 | 0,20   | 0,20   | 13,17 | 0,35   | 0,21   | 10,70  | 0,67  |
| SrO                                 | 0      | 0      | 0     | 0      | 0      | 1,90   | 1,05  |
| BaO                                 | 0      | 0      | 0     | 0      | 9,44   | 0      | 20,67 |
| Na <sub>2</sub> O                   | 0      | 0,06   | 6,52  | 8,44   | 6,87   | 12,95  | 9,32  |
| $K_2O$                              | 24,01  | 23,91  | 18,39 | 12,40  | 11,52  | 5,92   | 4,05  |
| CÌ                                  | 0      | 0      | 3,57  | 0      | 0      | 1,78   | 0     |
| $-O = C_1$                          | 2 -    | -      | 0,81  | -      | ~      | 0,41   | -     |
| Total                               | 100,96 | 100,97 | 91,72 | 100,61 | 100,33 | 100,95 | 99,30 |

Formulae:

 $\begin{array}{l} 1. \ (K_{2,00}Ca_{0,01})_{2,01}(Zr_{0,02}Ti_{0,09})_{1,01}Si_3O_{9,03} \cdot \sum_{Si,Ai} = 3 \\ 2. \ (K_{1,92}Na_{0,01}Ca_{0,01})_{1,94}(Zr_{0,65}Ti_{0,39})_{1,04}(Si_{2,99}A_{10,01})_3O_{9,05} \cdot \sum_{Si,Ai} = 3 \\ 3. \ K_{3,65}Ca_{2,19}Na_{1,96}Fe_{0,04}Mn_{0,01}Mg_{0,01}Si_{6,92}AI_{1,06}CI_{0,96}O_{19,58} \cdot \end{array}$ 

 $\sum_{\text{Si,AI}} = 7$ 

 $\begin{array}{l} 4. \ \widetilde{Na}_{1,06}K_{1,02}Ca_{0,02}Fe_{0,65}Mn_{0,28}Mg_{0,04}Si_4O_{10,04} - \sum_{Si,Ai} = 4 \\ 5. \ \widetilde{Na}_{1,25}(K_{1,38}Ba_{0,35}Ca_{0,02})_{2,99}(Ti_{1,64}Nb_{0,23}Fe_{0,06})_{1,95}(Si_{3,98}Al_{0,02})_4 \end{array}$  $O_{13.60} - \sum_{Si,Al} = 4$ 

6.  $(Na_{12,57}K_{3,78}Sr_{0,55})_{16,90}(Ca_{5,74}TR_{0,12}Mn_{0,14})_6(Fe_{0,84}Mn_{0,39})_{1,24}$ 

 $\begin{array}{l} (zr_{2.79}T_{0.21})_{3.6} (z_{0.29}T_{0.00})_{3.6} (z_{0.29}T_{0.00})_{2.6} (z_{0.27}T_{0.13})_{3.6} (z_{0.29}T_{0.00})_{2.6} (z_{0.27}T_{0.13})_{3.6} (z_{0.27}T_{0.13})_{2.6} (z_{0.27}T_{0$  $(Ti_{0.69}Nb_{0.11})_{0.80}Si_4O_{16.92} - \sum_{Si,AI} = 4$ 

Note.

An. 1 — wadeite, an. 2 — titanium wadeite; an. 3 — delhayelite; an. 4 — fenaksite; an. an. 5 — scherbakovite; an. 6 potassium eudialyte; an. 7 — potassium barytolamprophyllite. An. 2 — from ristschorrite of III group, other analyses from ristschorrites of II group. An. 1, 5, 7 - analyst O.A. Ageeva (Cameca MS-46), an. 2-4 — analyst V.V. Khangulov (Camebax SX-50, IGEM RAS), an. 6 — analyst N.V. Trubkin (JSM-5300 + Link ISIS, IGEM RAS). The sum of an. 6 contains  $Ce_{2}O_{2} = 0.65$ 

(lamprophyllite, lomonosovite, titanite) with small ingrowths of nepheline (2-3 mm in size) are characteristic. Orthoclase and kalsilite mainly replaced the nepheline of initial rocks. Therefore, at replacement of nepheline in leucocratic parts of rock the feldspathoid-feldspar poikilitic intergrowths as if «sink» in large feldspar poikilocrystals, than at replacement of nepheline ingrowths in melanocratic parts they form roundish polymineral aggregates, distinctly rising above the background of dark-coloured mineral.

## Genesis of kalsilite-bearing rocks in Khibiny massif

Kalsilite morphology in the rocks of Khibiny massif is very diverse and does not allow giving simple explanation of its genesis way. The succession of formation (or transformation) of leucocratic minerals of kalsilite-bearing ristschorrites of the massif is clear determined: relic nepheline  $\rightarrow$  kalsilite (or kalsilite + orthoclase)  $\rightarrow$  orthoclase, and the evident features of metasomatic alteration of nepheline are discovered.

According to authors' hypothesis, ristschorrites in Khibiny alkaline complex was formed during K-Si-metasomatosis, influencing mainly on ijolite-urtites of Central Arc of the massif. The magma, which the metasomatic solutions separated from, apparently, had nephelinesyenite composition, that predetermined the migration first of all potassium and silica in ijolite-urtites, unsaturated by these elements, and the formation of metasotatites of nephelinesyenite composition.

Kalsilite formation is related to most early stage of considered process and caused by strong increasing of potassium activity relatively sodium one. Nepheline of initial rocks was the «matrix» for kalsilite genesis: 2Na<sub>2</sub>  $KAl_4Si_4O_{16} + 3K_2O \rightarrow 8KAlSiO_4 + 3Na_2O.$ Kalsilite formation was accompanied by genesis of the other significant potassium accessory and rock-forming minerals, replaced the minerals of initial rocks or crystallized independently. The strong increasing of potassium activity at this stage, which causes the anomalous enrichment of forming metasomatites by potassium and the appearance of specific potassium mineralization among significant sodium rocks, can be explained by development of acid-basic interaction during influence of alkaline solutions (separated from nepheline-syenite magma) on more basic matrix, ijolite-urtites (Zotov, 1989). The increasing of ratios of more basic components to less basic ones (K/Na, Mn/Fe, Ba/Sr, Sr/Ca, Ca/Mn, Zr/Ti), noted in accessory minerals (Ageeva et al., 2002), and the increased content of rubidium in feldspar of these rocks indicate the development of acidbasic interaction. The absence of kalsilite and distinctly revealed potassium mineralization in ristschorrites of I group, which are formed during replacement of nepheline syenites, is exlplained by less basicity in comparison with ijolite-urtites composition of these rocks, and its similarity to composition of influencing solutions. The differences in mineralogy and geochemistry of ristschorrites of II and III groups are probably caused by different potassium concentration in solutions.

In ristschorrites of II and III groups the crystallization of potassium feldspar took place simultaneously with kalsilite formation, and in the most part after that. Also the significant introduction not only potassium (exceeding its content in nepheline syenites), but silica (up to values in nepheline svenites), the carrying-out of other components (up to values in nepheline syenites), and the fall of rocks basicity index occur (Borutzky, 1988). Feldspar of ristschorrites, as it was mentioned, is distinguished by significantly potassium chemical composition. In ristschorrites rock-forming adularia with t.0 0,36-0,38 and  $2V 33-43^{\circ} (650-550^{\circ}C, ac$ cording to G. Hovis) coexists with more Si/Alordered orthoclase with  $t_100,39-0,43$  and 2V  $45-65^{\circ}$  (490-370°C, according to G. Hovis) and maximum-ordered nonlatticed microcline with 0.92 - 0.99,  $2V 80 - 83^\circ$ , which are forming the main volume of poikiloblast and were crystallized definitely below 500°№ (Borutzky, 1988). At the same time, determined feldspars in the bounds of single poikiloblast are subordinated to single optical orientation and there are no phase borders between them. The presence of feldspars of different structural modifications in ristschorrites is the evidence of unbalanced conditions of their formation and their cristallization in wide temperature range, that indicates the long history of ristschorrites formation.

The different development of the chemical activity of potassium and silica, which determined the peculiarities of mineralogy and geochemistry of distinguished ristschorrites groups, are caused by two major factors: the character of replaced rocks (in comparison of ristschorrites of I group with ristschorrites of II and III groups) and the composition of metasomatic solutions, the concentration of potassium in them (in comparison ristschorrites of II and III groups among each other). One of the main indicative signs of manifestation of either factor in given geological conditions are kalsilite presence and degree of its development. The work was supported by the grant of Russian Foundation for Basic Research (project  $N \ge 03 - 05 - 64139$ ).

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