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DELHAYELITE CRYSTALS FROM RISTSCHORRITES OF THE RASVUMCHORR PLATEAU (KHIBINY MASSIF)

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The small (to 0.2x0.3x2 mm) well-shaped delhayelite crystals, sometimes double-terminated, were found in the Khibiny massif in the macrocrystalline fenaksite aggregations in ristschorrites of the Rasvumchorr plateau. The crystals are prismatic, elongated on c axis, in different degree flattened on b axis; 10 simple forms are determined (measured for the first time). Parameters of the rhombic unit cell are as follows: a=6.52(1); b=24.83(6); c=7.07(1) Å; V=1144.95 Å^3. The studied delhayelite is characterized by the highest content of the alkaline elements known for delhayelites; the content of H_2O is low (by the IR spectroscopy data and chemical analyses), especially in the grey, darkest crystals, representing unaltered delhayelite. The X-ray powder pattern (the most intensive lines are as follows (d, A (I)): 3.10 (10), 3.03 (9), 2.87 (9), 1.910 (10), 1.630(10)) and the IR spectrum are given.
3 tables, 2 figures, 14 references.

The well-shaped small (to 0.2x0.3x2 mm in size) delhayelite crystals, sometimes double-terminated, were found in the crystalline aggregations of ultraagpaitic minerals coarse ristschorrites of the Rasvumchorr plateau (the Central mine). Delhayelite, Cl- and F-bearing alumosilicate of Ca and alkaline elements, was found for the first time by M.D. Dorfman in 1952, in pegmatites among the massive urtites of the Material'naya adit (Mt. Yukspor), and described under the name «mineral No. 3» (Dorfman, 1958). In 1959, a new mineral, delhayelite, was described (Sahama, Hytцnen, 1959) from kalsilite-bearing melilite-nepheline lavas of the Shaheru volcano (DR Congo). Since that time, for the Khibinian «mineral No. 3», similar, but not identical to delhayelite from Congo, the name «delhayelite» was accepted (Dorfman, 1962). The mineral is quite widely spread in massive urtites and ristschorrites containing the beds of apatite-nepheline ores (Kostyleva-Labuntsova *et al.*, 1978). The lamellar mica-like delhayelite grains reach 10 cm in length and sometimes form large (up to 30 cm in size) monomineral aggregations.

The delhayelite crystals found by us are confined to the branching veinlet-like (up to 4 cm in size) and nest-shaped (up to 7 cm in diameter) macrocrystalline aggregations with irregular and unclear borders. They are composed by fenaksite, in which lomonosovite, villiaumite, djerfisherite, and rasvumite are noted. The grey, light grey and colourless delhayelite crystals form inclusions in fenaksite (Sokolova *et al.*, 1993). Moreover, in cavities among crystalline aggregates of fenaksite, the smaller (up to 0.1x0.2x1 mm) delhayelite crystals occur; their lagest face overgrows on the fenaksite prismatic crystals (4x5x8 mm in size).

Five colourless and grey translucent crystals were measured with the Goldschmidt two-circle goniometer (Tabl. 1). The symbols of faces were detected by a method of double ratios of cosines (the Wul method) and verified by the trigonometric formulae. In the accepted orientation, the axes ratio is as follows: *a:b:c*=0.8101:1:0.866. They are more close to the structural orientation by Chiragov and Mamedov (1974) (*a:b:c*=0.266:1:0.288), distinguishing by the segments on axis *a* and *c*, which are three times larger.

According to the measurements, the prismatic crystals of delhayelite are elongated on

Table 1. **Faces coordinates of delhayelite crystals**

Symbols of faces	Data of measurements (average values)		Calculated coordinates	
	φ	ρ	φ	ρ
010	0°00′	90°00′	0°00′	90°00′
160	11 36	90 00	11 50	90 00
340	42 42	90 00	42 10	90 00
110	50 59	90 00	51 00	90 00
025*	0 00	20 30	0 00	19 06
011*	0 00	40 30	0 00	40 54
223*	50 54	41 10	51 00	42 30
111	50 59	53 59	51 00	54 00
443*	50 54	62 00	51 00	61 24
322*	60 40	58 56	61 42	61 18

* *Found only on one crystal*

c axis and flattened on *b* axis in different degree (Fig. 1). In prismatic zone, the face (010) is the best developed, the cleavage is distinctly pronounced by this face; other faces are very narrow.

Parameters of the rhombic unit cell of the studied delhayelite are close to the parameters determined earlier for other samples: $a=6.52(1)$; $b=24.83(6)$; $c=7.07(1)$Å; $V=1144.95$Å^3. The X-ray powder pattern contains more than 50 lines (Tabl. 2).

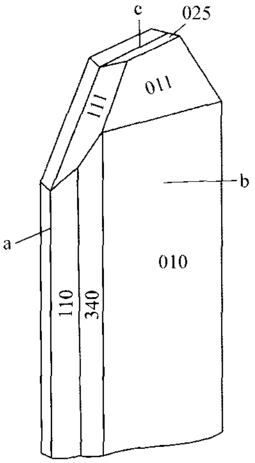
Chemical analyses of four delhayelite crystals (Cameca MS-46 electron microprobe instrument) are given in Table 3, where also analyses of the Khibinian lamellar delhayelite, the mineral from Congo and hydrodelhayelite are presented.

It is well-known, that delhayelite is easily hydrated. In all known analyses is H_2O (to 2 wt %), which is an evidence of the late hydrothermal or hypergene alteration of mineral that results in formation of hydrodelhayelite (Chiragov, 1978; Dorfman, Chiragov, 1979). The carrying-out of Na, F, Cl, and partly K takes place (Chiragov, Mamedov, 1974; Ragimov *et al.*, 1980; Canillo *et al.*, 1970).

Water was not determined in the delhayelite crystals because of lack of material. Therefore the IR-spectra of the studied crystals with those of lamellar delhayelite specimens with the known H_2O content (an. 6 in Table 3) and with IR-spectra of the hydrodelhayelite with the highest content of H_2O (an. 8 in Table 3), were compared.

The IR spectra (Fig. 2) were obtained with a Specord 75 IR spectrophotometer in the range 400-4000 cm^{-1}. The standards were gaseous ammonia and polystyrene. Samples were prepared by a standard method, as pellets with KBr. The spectrum of KBr was subtracted automatically. In the range 500-800 cm^{-1} (the most sensible to fine structural peculiarities of silicates), all samples of delhayelite give the same set of narrow bands with the absorption maximums at 590, 607-608, 635-636, 662-665, and 701-703 cm^{-1}. In the range of water molecules vibrations, the IR spectra of coarse-lamellar delhayelite and of the studied crystals are identical (Fig. 2, spectrum 1): they contain a weak broad band of stretching vibrations in a range of 3300-3700 cm^{-1} and two weak bands of H-O-H bending vibrations in the frequency ranges 1560-1585 and 1625-1640 cm^{-1}. Presence of two types of the stretching H-O-H angles is an evidence of polytypic state of water molecules in delhayelite. The comparing samples insignificantly differ only by position of the maximum in a range of 1070-1090 cm^{-1} (1077 and 1086 cm^{-1} respectively). In this interval, the stretching vibrations of the Si-O-Si bridge, as well as stretching vibrations of the SO_4-groups are shown. Possibly, these samples differ by content of the sulphate anions (in these samples sulphur was not determined).

The IR spectrum of hydrodelhayelite is strongly distinguished from the spectrum of delhayelite in all range 400-4000 cm^{-1}, that is an evidence of significant changes of del-



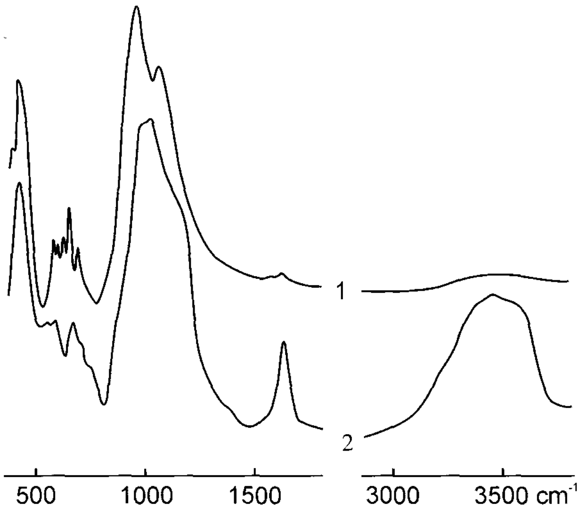


Fig. 1. *Delhayelite crystal from inclusions in fenaksite*

Fig. 2. *The IR spectra of delhayelite (1) and hydrodelhayelite (2)*

hayelite in the process of the hydrodelhayelite formation, which affects not only on large cations and water molecules but also on all covalent-bonded system (double layer). In particular, together with the series of the low-distinct strong bands of stretching vibrations of water molecules (3325-3520 cm^{-1}) and a band of bending vibrations of water molecules (1640 cm^{-1}) in the spectrum of hydrodelhayelite is the well-pronounced shoulder at 3210 cm^{-1} and also very bad-pronounced shoulders at 3040 and 1715 cm^{-1}, which can be the evidence of existence of the acidic-basic equilibrium of the following type: $(Si\text{-}O\text{-}H)^{+\delta}+H_2O \leftrightarrow Si\text{-}O+H_3O^+$. Together with delhayelite and hydrodelhayelite, in pegmatites of Khibiny there is a number of related minerals with the intermediate degree of hydration, which give the individual sets of narrow bands in a range 500-800 cm^{-1}.

As analyses showed, the studied delhayelite is characterized by the highest content of potassium ever analysed delhayelites (Dorfman, 1958; Kostyleva-Labuntsova *et al.*, 1978; Ageeva, 2002; Ageeva, Borutsky, 2004; Sharygin, 2002; Pekov, Podlesnyi, 2004). The potassium content in crystalsof delhayelite, forming inclusions in fenaksite, is higher that than in the accessory delhayelite from ristschorrites. In the latter, analysed by O.A. Ageeva (2002) for the first time, the content 17.32 – 18.87 wt % of K_2O or 3.35-3.65 K per formula was detected (electron microprobe analyses, 16 samples). The content of K_2O is inconstant and always exceeds the theoretical value by calculation on the following formulae: $K_7(Na_3Ca)Ca_4[AlS_{i7}O_{19}]_2F_4Cl_2$ (Canillo *et al.*, 1970) and $K_3Na_2Ca_2[(Al,Si)_8O_{19}](F,Cl)_2$ (Chiragov, Mamedov, 1974). This discrepancy was noted earlier (Ageeva, 2002; Ageeva, Borutsky, 2004; Sharygin, 2002), and for the studied delhayelite crystals it is more remarkable (to 3.94 K per formula). Apparently, the K site in the crystal structure requires refinement.

Table 2. **X-ray powder data of delhayelite from ristschorrites of the Rasvumchorr plateau (Fe-radiation, D=114.6 mm)**

hkl	*I*	*d* (Å)	*hkl*	*I*	*d* (Å)	*hkl*	*I*	*d* (Å)
200	5	12.94	322	4	2.303	233	2	1.585
110	1	6.71	802	4	2.258	314	3	1.565
400	1	6.24	003	6	2.176	433	4	1.547
–	2	6.04	303	7	2.103	342	5	1.527
301	1	5.07	431	0.5	2.089	533	5	1.522
401	2	4.43	11.1.1	4	2.045	442	7	1.503
311	2	4.10	912	5	2.003	633	0.5	1.492
411	1	3.79	722	2	1.975	124	2	1.479
601	1	3.49	032	10	1.910	804	6	1.444
511	7	3.44	731	2	1.880	14.2.2	1	1.429
220	6	3.36	023	7	1.851	814	5	1.414
102	6	3.24	223	3	1.833	624	2	1.395
710	3	3.19	930	6	1.792	724	5	1.369
800	10	3.10	14.0.0	2	1.778	11.4.1	2	1.362
121	9	3.03	040	7	1.757	942	7	1.354
112	7	2.94	632	7	1.732	824	2	1.339
402	9	2.87	903	3	1.710	651	3	1.309
801	7	2.815	440	3	1.701	052	3	1.297
421	7	2.753	623	2	1.687	252	2	1.291
502	3	2.712	10.3.1	1	1.655	332	2	1.282
412	5	2.660	104	10	1.630	452	3	1.271
621	7	2.458	033	2	1.598			

Table 3. **Chemical composition of delhayelite and hydrodelhayelite (wt %)**

No. of sample. Constituent	1	2	3	4	5	6	7	8
Na_2O	7.29	7.04	7.20	7.45	6.88	6.52	3.20	0.22
K_2O	20.20	20.14	20.75	19.91	17.94	18.37	9.27	6.13
CaO	13.02	12.74	12.77	12.59	14.55	14.52	7.99	12.72
SrO	0.41	0.21	0.47	0.09	0.12	–	–	0.22
MgO	0.00	0.04	0.00	0.08	0.14	0.17	1.03	0.21
MnO	0.13	0.14	0.09	0.12	0.08	0.10	0.07	0.18
Fe_2O_3	0.69	0.55	0.53	0.57	0.67	0.54	2.72	0.65
Al_2O_3	5.76	5.52	5.99	6.26	6.48	6.59	9.22	8.46
TiO_2	0.00	0.00	0.00	0.00	0.07	Cʌ.	0.09	0.01
SiO_2	47.42	47.02	46.67	48.11	46.36	46.34	52.60	55.53
H_2O^+	n. d.	n. d.	n. d.	n. d.	1.23	1.49	5.93	5.58
H_2O^-	n. d.	n. d.	n. d.	n. d.	1.06	0.42	3.35	9.62
F	2.31	2.41	2.49	2.59	2.81	2.80	0.33	–
Cl	3.69	3.89	3.99	3.83	3.47	3.42	3.91	0.15
$-O=F_2,$ Cl_2,S	1.83	1.88	1.95	1.89	1.99	1.94	1.01	0.03
Total	99.09	97.85	99.20	99.71	100.21*	99.34	100.01**	99.65
Formula coefficients (calculation on Si + Al = 8)								
Na	2.09	2.04	2.08	2.08	1.98	1.87	0.78	0.05
K	3.80	3.84	3.94	3.66	3.39	3.46	1.49	0.96
Ca	2.06	2.04	2.04	1.94	2.31	2.30	1.08	1.66
Sr	0.04	0.02	0.04	0.01	0.01	0.00	–	0.02
Mg	0.00	0.01	0.00	0.02	0.03	0.04	0.19	0.04
Mn	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.02
Fe	0.08	0.06	0.06	0.06	0.06	0.07	0.26	0.06
Al	1.00	0.97	1.05	1.06	1.15	1.13	1.37	1.22
Ti	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00
Si	7.00	7.03	6.95	6.94	6.87	6.85	6.63	6.78
F	1.08	1.14	1.17	1.18	1.32	1.31	0.13	–
Cl	0.92	0.99	1.01	0.94	0.87	0.86	0.84	0.03

Note: ** – analysis total also contains (wt %): BeO – 0.17; REE_2O_3 – 0.11; S – 0.06. ** – analysis total contains SO_3 – 1.31 wt %. An. 1-4 – crystals of delhayelite from ristschorrites, the Rasvumchorr plateau; analyst T.I. Golovanova; 5, 6 – macrolamellar delhayelite: 5 – from pegmatite in massive urtite, Mt. Yukspor, analyst L.D. Nikitina (Dorfman, 1958); 6 – from pegmatite in ristschorrite, the Apatite circus of the Mt. Rasvumchorr, analyst G.M. Varshal (Kostyleva-Labuntsova et al., 1978); 7 – lamellar delhayelite from calcite-bearing melteigite-nepheline lavas of the Shaheru volcano, DR Congo (Sahama, Hytonen, 1959); 8 – hydrodelhayelite from pegmatite in ristschorrite, the Apatite circus of the Mt. Rasvumchorr, analyst G.M. Varshal (Kostyleva-Labuntsov a et al., 1978)*

For our delhayelite specimen, the surplus of Ca and deficiency of Na, which were noted for lamellar delhayelite (Sharygin, 2002), are not characteristic.

The original delhayelite from Congo (an. 7, Tabl. 3) is probably partly altered; it differs by lower content of the alkaline elements and high content of H_2O and occupy the intermediate position between proper delhayelite and hydrodelhayelite by chemical composition.

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