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Chapter 14
Experimental Study of Amphibolization of the Basic Rocks of the Tiksheozersky Massif

Northern Karelia, Russia

T. N. Kovalskaya, D. A. Varlamov, Y. B. Shapovalov, G. M. Kalinin, and A. R. Kotelnikov

Abstract The work is devoted to experimental study of postmagmatic transformation of basic rocks (gabbroids) of the Tiksheozersky massif (North Karelia Russia). During the petrological study of gabbroids the formation of edges of alkaline amphiboles around the clinopyroxene grains (diopside-hedenbergite series), and then—low-temperature minerals containing Na, K, Cl. In order to recreate the conditions for the formation of amphibole rims a number of experiments were carried out at a temperature of 850 °C and a pressure of 3 kbar with solutions of KCl and KF concentrations of 0.5 M, 1 M and 2 M, respectively. In the course of experiments, amphiboles corresponding to natural amphiboles from rims around clinopyroxenes, Tiksheozersky massif were obtained and also phlogopites present in the basic rocks of the Tiksheozersky massif were obtained.

Keywords Alkaline magmatism · Gabbro · Carbonatite · Amphibole · Amphibolization · Postmagmatic processes · Experiment

14.1 Introduction

Amphibolite development on the basic rocks within the Fenno-Scandinavian shield is quite common (Khodorevskaya and Varlamov 2018; Safonov et al. 2014), however, the alkaline nature of postmagmatic changes in the basic rocks of the Tickshozersky massif is the most interesting.

The Tickshozersky massif, located in the circumpolar part of Northern Karelia, is a part of the Eletizersko-Tiksheozersky intrusive complex (Fig. 14.1a, b) and lies among the highly dislocated granitoids, migmatites and gneisses of the Archean

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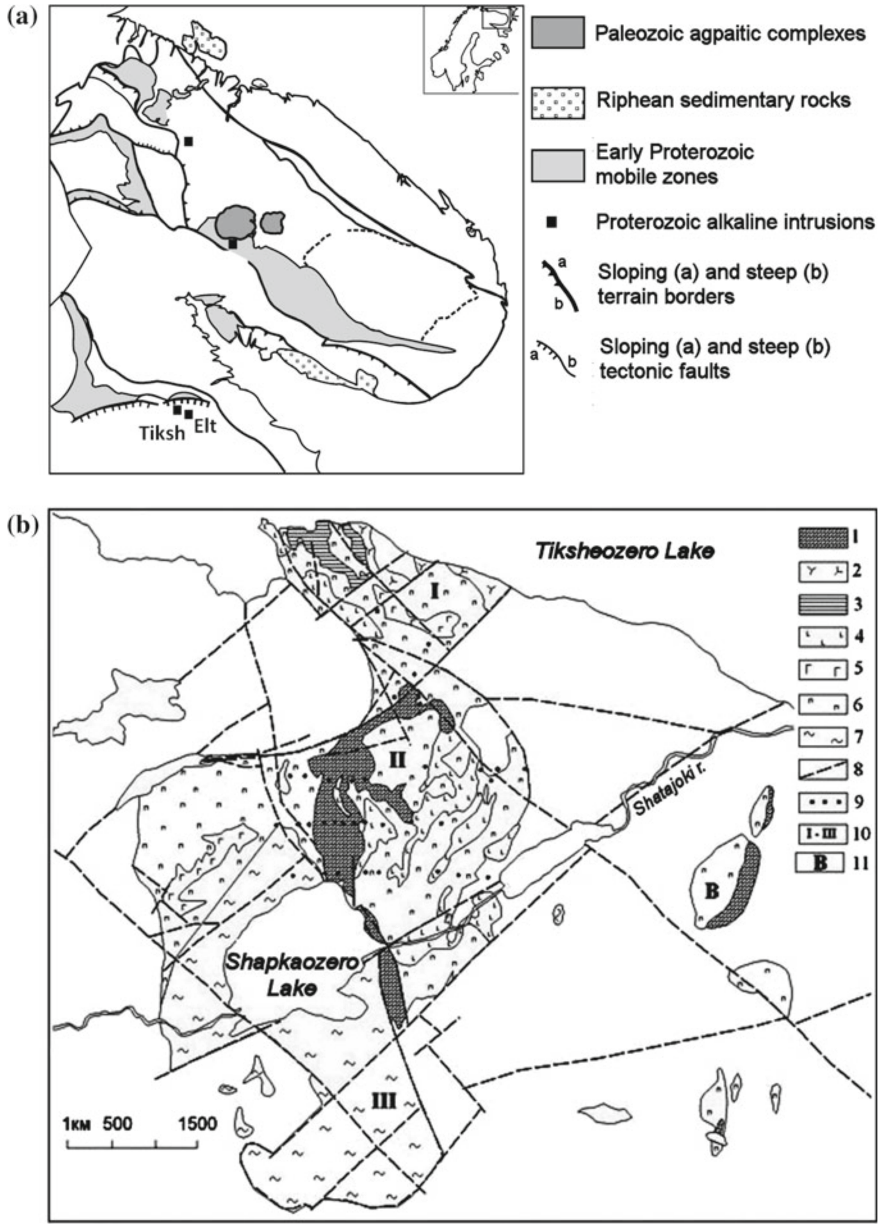

Fig. 14.1 Schematic position of the Tiksheozero massif **a** (**Tiksh**—Tiksheozersky massif, **Elt**—Elet'ozero massif) and **b** geological structure of Tiksheozersky massif (according to Kholodilov 1988): 1—carbonatites, 2—nepheline syenites, 3—teralites, 4—melteigites, ijolite-urtites, 5—gabbros, 6—pyroxenites, 7—olivinites, serpentinized olivinites, 8—fractures, 9—drill holes. Geological blocks: **I**—Tiksheozero, **II**—Central, **III**—Shapkozersky, **B**—Eastern

and Proterozoic (Sharkov et al. 2015). It is represented by a body of a rounded-elliptic shape with a diameter of about 20 km and is composed of olivinites, gabbro, pyroxenites (sometimes with nepheline), ijolites, carbonatites, and amphibole-calcite-cancrinite rocks. The age of the Tikshoozero massif is estimated at about 1.8–1.9 Ga (Shchiptsov et al. 2007). Petrological study of rocks of the massif was carried out by the authors during the field seasons of 2010–2016, in which the rocks composing the massif were described in detail (Kovalskaya et al. 2018a, b), after which the study of the mineral relations and composition in the thin rock sections and polished sections using optic polarization microscope and scanning electron microscope Tescan Vega II XMU was carried out. The change of mineral composition and mineral associations in different types of rocks was traced.

The central part of the massif is composed of olivinites, in some places strongly serpentinized and chloritized, with inclusions of aluminochromites, relics of olivine and clinopyroxene. The X_{Mg} of olivines is 0.83–0.88. The basic rocks are pyroxenites and gabbroids, which are also quite altered. Pyroxenites are composed of clinopyroxene (diopside-hedenbergite and avgite), phlogopite, titanomagnetite. In the gabbroids there is also pyroxene composition of diopside-hedenbergite, plagioclase with a proportion of anortite component of 70–75%, amphibole of two generations, corresponding to the composition of pargasite and richterite-cataphorite. The first amphibole forms independent grains, the second one is found in the rims around the grains of clinopyroxene diopside-hedenbergite composition, which is probably a result of postmagmatic high-temperature changes in the rocks of the massif. An example of the relationship between clinopyroxene and amphibole is shown in Fig. 14.2. In addition, there are strong secondary changes in the gabbroids—carbonatization of rocks, formation of low-temperature zeolites. Amphibole of different composition can be

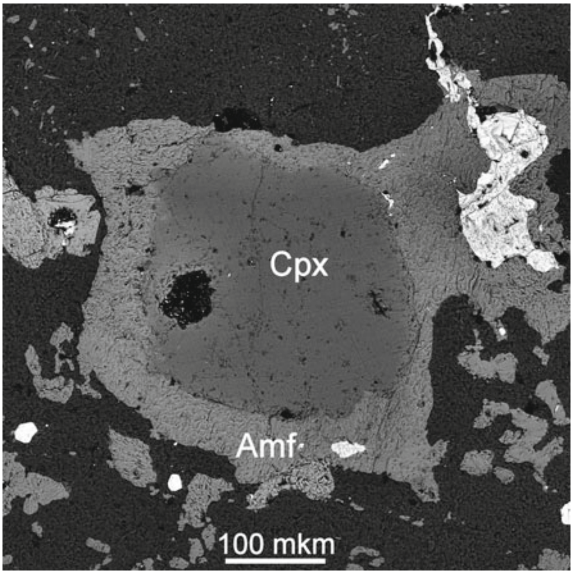

Fig. 14.2 Natural amphibole rims around clinopyroxene. The abbreviations of minerals are similar to Table 14.1

found within the same rock, which is a consequence of the change in physical and chemical conditions of rock formation and the potential of alkaline components.

The carbonatites of the massif are composed intrusive stocks of tens of meters in size, eruptive formations of the breccian texture, veins and veinlets (Safronova 1990). The largest body of carbonatites of the Tiksheozersky massif is traced by drilling to a depth of 450 m. Apatite-calcite ores of complex type were found in carbonatite of the massif (Metallogeny…2001). The mineral composition of the studied rocks is shown in Table 14.1. Paragenetic analysis carried out earlier and geothermometers applied on its basis (Perchuk 1970) allowed to estimate the formation temperatures of amphibole paragenesis. The formation temperatures of amphibole-pyroxene paragenesis of the Tickshozersky massif using clinopyroxene-amphibole, biotite-amphibole and pyroxene-biotite geothermometers (Perchuk and Ryabchikov 1976) were estimated in the range of 710–980 °C. An assessment of the pressure of the formation of amphibole rims using an amphibole geothermometer (Simakin and Shaposhnikova 2017) was not possible due to the alkaline nature of the amphibole. Values of pressure at formation of the Tiksheozersky massif, proceeding from the literature data (Metallogeny… 2001), are estimated as 3–4 kbar. Therefore, for the reconstruction of the mechanism and conditions of the process of amphibolization of the Ticksheozersky massif, an attempt was made to model it experimentally with parameters similar to the calculated ones. This method is described in detail in the paper (Suk et al. 2007). The study of the sodalite-containing paragenesis in the rocks of later phases of formation of the Tiksheozersky massif and carried out on the basis of the obtained thermometry data showed that these associations were formed at a temperature of about 450 °C (Ustinov et al. 2006). The anionic group in sodalite is represented only by Cl^- ion. These data make it possible to use KCl solution of various concentrations as a fluid for modeling the amphibolization process.

14.2 Experimental Technique

Source materials For the experiments, the crushed gabbro of the Lukkulaisvaara massif (Karelia) was used as a starting material, since the composition of the basic rocks of the Lukkulaisvaara massifs is similar in chemical composition to that of the Tikshozersky massif (Table 14.2), and they were subjected much less to secondary changes than that of the Tikshozersky massif. Small differences in composition are observed in the content of titanium, aluminum, sodium and potassium. The increased titanium content (relative to the gabbroids of the Lukkulaisvaara massif) is associated with the presence of ilmenite and titanomagnetite in the rocks of the Tiksheozersky massif, and sodium and potassium—with intensive postmagmatic changes observed in the Tiksheozersky massif. KCl and KF solutions with concentrations of 0.5, 1 M and 2 M, respectively, were used as fluids. The ratio "rock/fluid" was 10/1 by weight (Kovalskaya et al. 2018a).

Table 14.1 Mineral composition studied samples from Tiksheozero massif

Rock	Mineral composition	Alteration degree	Structure
Carbonatite	Cal + Bi + Pyr	Weak	Fine-grained
Carbonatite	Cal + Dol + Bi + Ab + Ilm	Weak	Fine-grained
Pyroxenite	Cal + Cpx 1 + CPx 2 + Bi + Am + Ilm + Ap + Ort + Sph	Strong	Medium-grained, traces of cumulative
Gabbro	Pl + Cpx + Amf1 + Amf2 + Ilm +Cal	Average	Medium-grained
Pyroxenite	Cpx 1 + Cpx 2 + Amf + Sph + Ilm + Pyr + Cal	Strong	Medium- and compact-grained (altered areas)
Gabbro	Amf1 + Amf2 + Cpx + Pl + Ilm + Sph +Pyr	Average	Medium- and compact-grained
Altered pyroxenite	Cpx + Amf + Bi +Cal + Ilm + Mt + сульфиды	Very strong	Compact-grained
Syenite	Ab + Ksp + Natr + Cal + Str (мало) + Bi + Mt + Mu	Very strong	Compact-grained
Pyroxenite	Bi + Cpx + Amf1 + Amf2 + Sod + Natr + Cal + Ilm + Mt + Sph	Very strong	Medium- and compact-grained
Ijolite	Sod + Amf + Cpx + Cal +Ap + Sph + Ilm	Average	Compact-grained
Carbonate-amphibolic rock	Cal + Amf1 + Amf2 + Bi + Sod + сульфиды	Not clear	Not defined
Pyroxenite	Cpx + Bi + Cal + Sod + Mt	Average	Medium-grained
Olivinite	Ol + Cpx + Serp + Chrt + Chlt	Serpentinization, average	Medium- and coarse-grained, cumulative

Note Mineral abbreviations: *Ab* albite; *Amf* amphibole, амфибол; *Bi* biotite; *Cal* calcite; *Can* cancrinite; *Chlt* chlorite; *Chrt* chromite; *Dol* dolomite; *Ilm* ilmenite; *Ksp* potassic feldspar; *Mt* magnetite; *Natr* natrolite; *Ort* ortite (allanite); *Cpx* clinopyroxene; *Pyr* pyrrhotite, *Sod* sodalite; *Str* strontianite; *Sph* sphene (titanite); *Zeol* zeolite. The numbers next to the mineral abbreviation indicate the generation of its formation

Table 14.2 The average chemical composition (wt%) of gabbroids from the Lukkulaisvaara and Tiksheozersky massifs

Oxides	Lukkulaisvaara	Tiksheozersky
SiO_2	49.27	47.13
TiO_2	1.03	3.16
Al_2O_3	13.43	11.46
Cr_2O_3	0.13	0.18
FeO*	14.94	13.98
MnO	0.14	0.67
MgO	5.21	5.98
CaO	6.24	7.02
Na_2O	4.35	6.16
K_2O	1.81	3.86
Total	99.56	99.60

Note FeO*—all iron measured in form FeO

The equipment All experiments were conducted in high gas pressure units with internal heating of UVGD-10000 design of IEM RAS. Temperature control accuracy was ±2 °C; pressure ±50 bar.

Methodology of experiments Source materials were loaded into Ø5 × 0.2 × 50 mm or Ø4 × 0.1 × 50 mm platinum ampoules, the necessary amount of fluid solution was added, weighed and welded. The equipped ampoules were loaded into the reactors of the plants, put into operation and maintained at the parameters of experiments for 10 days. First, the reaction mixture was heated to 1100 °C and set the pressure of 3 kbar, the ampoules were maintained at these parameters for 3 h, then there was isobaric cooling to 850 °C, and the subsequent holding at these parameters for 10 days. Quenching was done in isobaric conditions. After the experience, the ampoules were also weighed to ensure that they were not depressurized.

Methods of analysis To determine the compositions of experimental and natural samples by the method of electron-probe X-ray analysis, the scanning electron microscope Tescan Vega II XMU (Tescan, Czech Republic) was used, equipped with INCA Energy 450 X-ray microanalysis system with energy dispersive (INCA X-sight) and crystal diffraction (INCA Wave 700) X-ray spectrometers (Oxford Instruments, England) and INCA Energy + software platform. The analysis conditions when using only the energy dispersive spectrometer were as follows: accelerating the voltage of 20 kV, the current of absorbed electrons from 150 to 400 pico-amperes, the analysis time at the point of 100 s, beam size 157–180 nm. When using the crystal diffraction spectrometer together with the energy dispersive conditions of the analysis were different: accelerating the voltage of 20 kV, the current of absorbed electrons at Co 20 nA, the total time of analysis at 170 s. Accuracy of analyses (by main elements, using EDS) was 2–3 relative %.

14.3 Experimental Results

In the course of two series of experiments (with KF and KCl solutions with concentration of 0.5, 1, 2 M) the following results were obtained. Products of experiments represented a fine crystalline mass (Figs. 14.3 and 14.4) of greenish-grey color. Separate crystallites were clearly identified during microscopic observation.

Experiments with 0.5 M KCl solution The analysis of products of experiments with 0.5 M KCl fluid concentration did not reveal formation of alkaline amphiboles. In interstitium between newly formed clinopyroxenes there are small grains of potassium feldspar.

Experiments with 1 M KCl solution In experiments with such salt concentration in the fluid clinopyroxenes of diopside-hedenbergite series and amphibole with compositions corresponding to the richterite-cataphorite were obtained, analogues to observed in the Tiksheozersky massif's gabbroids (Tables 14.3 and 14.4, Figs. 14.3 and 14.4). The size of the individual grains reaches 100 μm. Potassium feldspar and titanomagnetite have been diagnosed in some experiments.

Experiments with 2 M KCl solution Among the products of this series of experiments there are alkaline amphibole, which differ greatly from each other in composition, and single grains of clinopyroxene; titanomagnetite was found as an accessory mineral.

Experiments with 0.5 M KF solution As in the experiment with 0.5 M KCl as a fluid, no alkaline amphibole was observed in this experiment. Clinopyroxene and

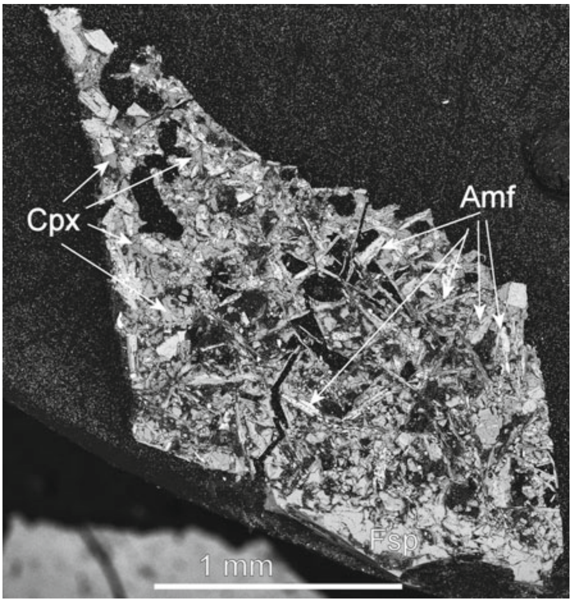

Fig. 14.3 Results of runs with 1 M KCl solution at a temperature of 850 °C and a pressure of 3 kbar

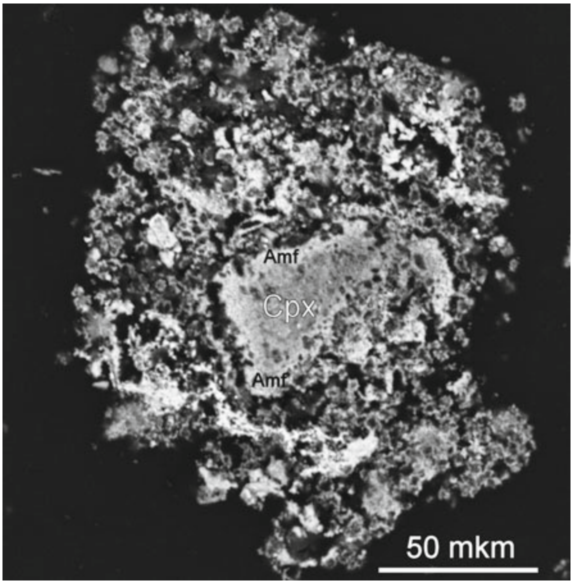

Fig. 14.4 Results of runs with 1 M KF solution at a temperature of 850 °C and a pressure of 3 kbar

phlogopite individuals were diagnosed in the experimental products. The size of crystallites in experimental products does not exceed 50 μm.

Experiments with 1 M KF solution As well as in the experiments with 1 M concentration of KCl, clinopyroxenes of diopside-hedenbergite series (Fig. 14.5, Table 14.3) and alkaline amphiboles of riherite-cataphorites series were diagnosed in the products of these experiments (Fig. 14.6, Table 14.4). However, we recorded amphiboles of this composition in the ijolite-urtites of the Tiksheozersky massif. Possibly, the differences in the composition of amphiboles were influenced by the subsequent postmagmatic carbonatization of the massif.

Experiments with 2 M solution of KF In the products of these experiments, the formation of a significant amount of fluorite was observed, which is apparently associated with a high concentration of F^- ions in the fluid, as well as needles of fluoride-containing phlogopite.

14.4 Discussion of Results

The conducted series of experiments on modeling the process of amphibolization in the Tickshozersky massif gabbrides and their comparison with the results of the study of natural samples showed the following results:

1. The process took place at the high-temperature postmagmatic stage at a temperature of about 850 °C.

Table 14.3 Composition (wt%) and formula units of clinopyroxenes from Tiksheozero massif and synthesized clinopyroxenes

Oxide	Clinopyroxenes from natural samples of Tiksheozero massif										Synthesized clinopyroxenes		
	Olivinite	оливинит	Pyroxenite	Pyroxenite	Pyroxenite	Gabbro	Gabbro	Syenite	Syenite	Amphibole-cancrinite rock	1 M KF	1M KCl	2 M KCl
SiO_2	48.09	48.00	53.65	52.68	54.03	52.09	52.69	53.31	53.70	52.96	51.83	50.72	51.94
TiO_2	1.95	2.13	–	0.61	1.98	0.42	0.38	–	–	–	–	–	–
Al_2O_3	4.99	6.04	0.11	2.29	–	0.81	1.59	3.07	2.09	0.20	2.43	3.02	2.12
FeO	9.68	7.22	7.97	3.97	10.06	8.07	6.40	8.82	8.67	7.84	8.01	7.45	8.15
MnO	0.16	–	0.16	0.12	–	0.10	0.03	–	–	0.11	–	–	–
MgO	10.98	12.34	14.16	18.66	17.80	14.68	15.04	13.56	14.89	13.22	14.72	17.03	16.01
CaO	22.36	23.67	22.93	21.03	16.13	23.83	24.10	20.79	19.72	25.40	22.12	21.17	21.78
Na_2O	1.55	0.60	1.02	–	–	–	0.08	0.46	0.94	0.23	0.89	0.61	–
K_2O	0.26												
Total	100.00	100.00	100.00	99.94	100.00	100.00	100.02	100.00	100.00	99.99	100.00	100.00	100.00
Formula units (to 6 oxygens)													
Si	1.79	1.78	1.98	1.91	2.08	1.94	1.94	2.02	2.02	1.98	1.94	1.882	1.928
Ti	0.05	0.06	0.00	0.02	0.06	0.01	0.01	0.00	0.00	0.00	–		
Al_{tot}	0.22	0.26	0.00	0.10	0.00	0.04	0.07	0.13	0.09	0.01	0.107	0.132	0.093
Fe_{tot}	0.30	0.22	0.25	0.12	0.31	0.25	0.20	0.27	0.26	0.24	0.251	0.231	0.253
Mn	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00			
Mg	0.61	0.68	0.78	1.01	0.99	0.81	0.83	1.01	1.02	0.74	0.821	0.942	0.88
Ca	0.89	0.94	0.91	0.82	0.56	0.95	0.95	0.54	0.53	1.02	0.887	0.842	0.86
Na	0.11	0.04	0.07	0.00	0.00	0.00	0.01	0.03	0.07	0.02	0.064	0.044	
K	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–		

Table 14.4 Composition (wt%) of natural amphiboles from Tiksheozero massif and synthesized amphiboles

Oxide	Natural samples						Synthesized samples (fluid)	
	Pyroxenite	Gabbro	Gabbro	Ijoliteurtite	Syenite	Carbonatite	Synthesized amphibole (1 M KF)	Synthesized amphibole (1 M KCl)
SiO_2	44.08	41.33	43.27	49.10	40.21	51.91	47.18	46.12
TiO_2	0.48	0.06	1.41	0.91	1.07	0.94	1.32	0.86
Al_2O_3	11.20	17.28	10.91	6.53	14.30	4.06	12.78	10.42
Cr_2O_3	–	–	–	–	–	–	–	–
FeO^*	16.43	20.44	18.57	13.23	19.38	13.75	14.94	15.91
MnO	0.00	0.13	0.05	0.00	0.19	0.09	0.25	0.03
MgO	11.81	6.36	10.81	15.60	9.06	14.70	12.32	13.81
CaO	13.47	11.96	9.00	8.68	10.93	7.30	6.14	8.01
Na_2O	1.29	1.85	5.16	5.43	3.57	6.66	2.24	3.71
K_2O	1.24	0.58	0.81	0.52	1.30	0.59	1.83	1.13
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Note FeO*—all iron in microprobe analysis is calculated as FeO

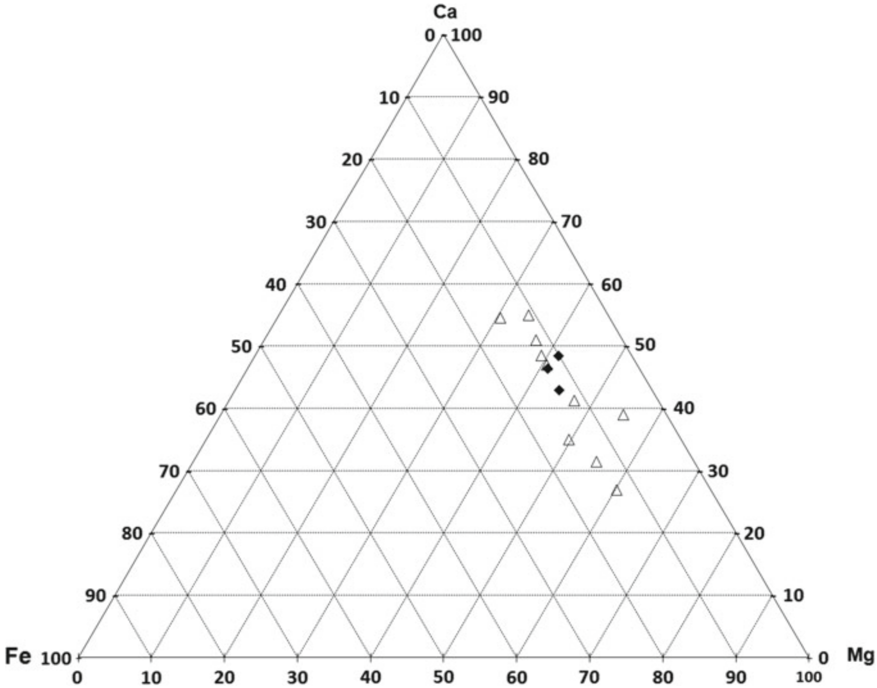

Fig. 14.5 The 'Aeg-Di-Hed' diagram for clinopyroxenes from various rocks of the Tiksheozero massif and experimental products: empty triangles—natural clinopyroxenes, filled rhombus—synthesized clinopyroxenes

2. The concentration of salt (KCl or KF) in the fluid at high-temperature postmagmatic changes of the Tickshozersky massif gabbroids fluctuated within 1 M. Amphiboles were not formed at lower concentrations, and fluorite and phlogopite were formed at higher concentrations.
3. One of the possible mechanisms for the amphibolization of gabbro in the Tickshozersky massif was the separation of volatiles during the subsequent introduction of alkaline rocks, i.e., ijolite-urtites, which is indicated by the similarity of later-generation amphibole compositions in the gabbroids, ijolite-urtites and samples obtained in the course of behavioural experiments.

Thus, the data obtained by us characterize the temperature and fluid regime of formation of amphibole rims around clinopyroxenes in the gabbroids of the Tiksheozersky massif, and also shows that the complex of differentiated rocks of the massif could be formed as a result of the complex evolution of heterogeneous fluid-magmatic system.

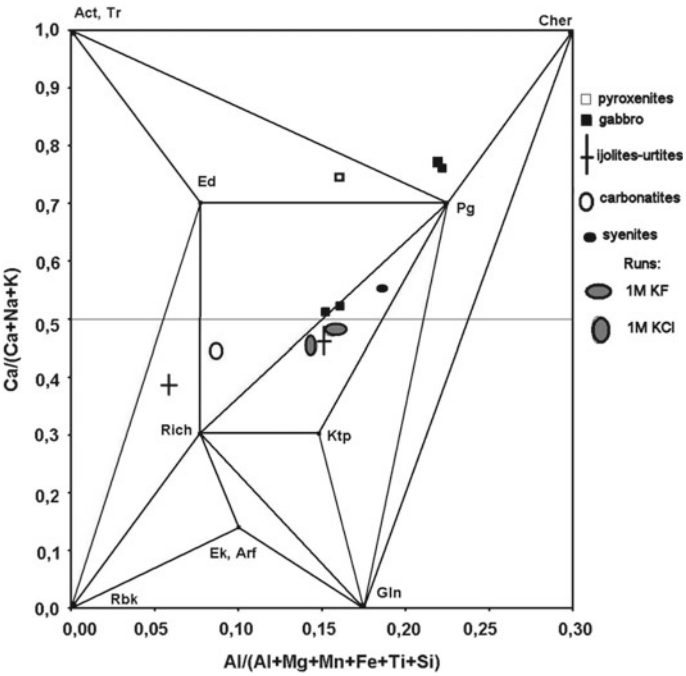

Fig. 14.6 Classification of amphiboles from the Tikshozero massif and synthetic amphiboles (Safonov et al. 2014)

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References

Khodorevskaya L, Varlamov DA (2018) High-temperature metasomatism of the layered mafic–ultramafic massif in Kiy island, Belomorian mobile belt. Geochem Int 56(6):535–553

Kholodilov NN, Karpatenkov VN (1988) Report on the results of prospecting for apatite and other minerals within the Tikshozero group of arrays of North Karelia for 1985–1988. In: Funds of Central Kola Geological Expedition (in Russian)

Kovalskaya TN, Varlamov DA, Shapovalov YuB, Kalinin GM, Kotelnikov AR (2018a) Experimental study of postmagmatic processes in Tiksheozerskiy massif. Exp Geosci 24(1):117–120

Kovalskaya TN, Varlamov DA, Shapovalov YuB, Kalinin GM, Kotelnikov AR (2018b) Experimental study of post-magmatic processes in the Tikshozero massif. In: Proceedings of the All-Russian annual seminar on experimental mineralogy, petrology and geochemistry, Moscow, GEOKHI, pp 207–210 (in Russian)

Metallogeny of igneous complexes of intraplate geodynamic environments (2001) Moscow, GEOS, p 640 (in Russian)

Perchuk LL (1970) Equilibrium of rock-forming minerals Moscow, Nauka, p 320 (in Russian)

Perchuk LL, Ryabchikov ID (1976) Phase matching in mineral systems. Moscow, Nedra, p 287 (in Russian)
Safonov OG, Kosova SA, Van Reenen DD (2014) Interaction of biotite–amphibole gneiss with H_2O–CO_2–(K, Na)Cl fluids at 550 MPa and 750 and 800 °C: experimental study and applications to dehydration and partial melting in the middle crust. J Petrol 55(12):2419–2456
Safronova GP (1990) Rock-forming carbonates and apatite of the Tiksheozersky massif. In: New in mineralogy of the Karelo-Kola region Petrozavodsk, pp 25–39 (in Russian)
Sharkov EV, Bogina MM, Chistyakov AV, Belyatsky BV, Antonov AV, Lepekhina EN, Shchiptsov VV (2015) Genesis and age of zircon from alkali and mafic rocks of the Elet'ozero complex, North Karelia. Petrology 23(3):259–280
Shchiptsov VV, Bubnova TP, Garanzha AV, Skamnitskaya LS, Shchiptsova NI (2007) Geological-technological and economic assessment of the resource potential of carbonatites of the Tikshozero massif (ultrabasic—alkaline rock formation and carbonatites). In: Proceedings of geology and ore deposit of Karelia, issue 10. Petrozavodsk: Karelian Scientific Center RAS, pp 159–170 (in Russian)
Simakin AG, Shaposhnikova OY (2017) Novel amphibole geobarometer for high-magnesium andesite and basalt magmas. Petrology 25(2):226–240
Suk NI, Kotel'nikov AR, Koval'skii AM (2007) Mineral thermometry and the composition of fluids of the sodalite syenites of the Lovozero alkaline massif. Petrology 15(5):441–458
Ustinov VI, Grinenko VA, Kotelnikov AR, Suk NI, Kovalskaya TN, Smirnova EP (2006) Thermometry of sodalite-containing associations of rocks of the Lovozersky and Tikshozero alkaline massifs. In: Materials of the All-Russian meeting "Geochemistry, Petrology, Mineralogy and Genesis of Alkaline Rocks" Miass, pp 267–272 (in Russian)