

The formation and differentiation of magmas

Gnuchev Y.Y., Bychkov D.A., Koptev-Dvornikov E.V. A single plagioclase liquidus compositometer for water-containing and anhydrous systems. UDC 552.111

Moscow State University named after. M.V. Lomonosov. Geological Faculty, Moscow. gnuchevyakov@mail.ru;

Abstract. Based on literary sources, a selection of water-saturated experiments with known and unknown water content in the melt, as well as water-containing and water-free experiments reproducing the plagioclase-melt equilibrium, was compiled, containing the results of 841 quenching experiments characterizing silicate systems in a wide range of intensive parameters. For water-saturated experiments with unspecified water content, its content was calculated based on the equation we previously proposed (Gnuchev, 2023).

As a result of optimization, a plagioclase compositometer was obtained (system of equations) reproducing the content of the main endpoints with an accuracy no worse than ± 2.3 mol. % at 95% confidence level in both dry and wet systems;

The compositometer was verified by comparing calculated and experimental liquidus temperatures of plagioclase. The width of the confidence interval for the temperature estimate with a 95% probability does not exceed ± 4.5 °C. Average deviations of calculated concentrations of terminals from experimental ones in mol. % do not exceed 0.224, which indicates unbiasedness.

Keywords: *Plagioclase compositometer (thermos-barometer); sampling of experiments; silicate melt*

At the moment, our scientific group has developed a complex of compositometers that allows us to predict the crystallization of olivine, plagioclase, augite, orthopyroxene and ore minerals (sulfides, chrome spinels, magnetite and ilmenite) coexisting with the melt, however, these equations were obtained by processing the results of anhydrous experiments, while the vast majority of natural magmas and lavas are more or less hydrous.

The presence of volatile components in the melt leads to a significant, but not equal, decrease in the crystallization temperature of minerals, as a result of which the crystallization sequence of hydrous melts can differ significantly from the crystallization order of anhydrous systems and affect the release of ore minerals from the magma.

An analysis of the literature showed that the most pronounced decrease in temperature is observed in the main rock-forming mineral - plagioclase, so the goal of the study was to develop a plagioclase liquidus compositometer general for anhydrous and hydrous systems.

To achieve this goal, it was necessary to solve several problems:

1) collect a sample of experimental data

characterizing the compositions of melts (anhydrous, water-containing and water-saturated) and plagioclase, temperature, pressure and oxygen fugacity during the experiments;

2) optimize the coefficients for variables in the system of compositometer equations for calculating the contents of endpoints in plagioclases by minimizing the difference between the experimental and calculated contents of endpoints;

3) verify the plagioclase compositometer by calculating liquidus temperatures from the sample and comparing them with experimental data.

Formation of a sample of experimental data.

The main source of data for sampling was the INFOREX database (Ariskin, 1996). From the INFOREX database, only those experiments were selected in which the measured melt composition, temperature, pressure were presented and oxygen fugacity was controlled (necessary for calculating activity according to the Nielsen and Dungan model (Nielsen, 1983)), and for water-containing systems there were no other volatile components other than water.

Based on the proposed D.A. Bychkov protocol for preliminary analysis of the quality of experimental data (Bychkov, 2022), a sample of increased reliability was formed, characterizing the equilibrium of plagioclase with the melt. After completing all selection procedures, the sample included 841 experiments.

For saturated experiments with unknown water content, the water content was obtained using a new version of the equation for calculating saturated water content (Gnuchev, 2023). Thanks to this, the sample of water-saturated experiments was expanded from 35 to 202. For the first time, this approach to expanding the sample was used by A.A. Ariskin and R.R. Almeev (Almeev, 1996).

The polyhedron 841 of experimental melt compositions in the coordinates of oxide concentrations for the final sample is characterized by the following values (wt %): SiO₂ from 40.0 to 78.2, TiO₂ from 0 to 7.76, Al₂O₃ from 9.97 to 22.9, FeO* from 0 to 20.9 (FeO* - all iron, converted to FeO), MgO from 0.1 to 13.0, CaO from 0.2 to 19.2, Na₂O from 0 to 7.6, K₂O from 0 to 7.88, P₂O₅ from 0 to 3.1, H₂O from 0 to 22.95. The final sample represents a range of melt compositions from basalt to rhyolite.

The range of intensive sampling parameters is characterized by temperature 750 – 1350°C, pressure from 1 bar to 20.0 kbar, oxygen fugacity $\lg f_{O_2}$ from -13.5 to -5.6.

Development of a plagioclase composimeter general for anhydrous and hydrous systems. After preparing a representative experimental sample, it was necessary to select coefficients that optimally reproduce the experimental compositions. This was done by using the “Solver” add-in in Excel. The calculation was carried out using the method “GRG nonlinear solving method.”

The comparison of experimental and calculated contents of endmembers in plagioclase (anorthite, albite, orthoclase) shown in Figure 1 shows their good agreement, as evidenced by the proximity of the slope coefficients to 1, and the free terms to zero in the regression equations, the values of the

coefficients of determination are close to one and a very small width of confidence corridors. For albite, the maximum width of the confidence corridor at the 95% confidence level does not exceed ± 2.3 mol. %. For anorthite, the maximum width of the confidence corridor is ± 1.1 mol. %, and for orthoclase does not exceed ± 0.15 mol. %. The nature of the histograms of residuals in Figure 1 demonstrates the closeness of the distributions to normal. Calculated average deviations of calculated concentrations from experimental ones in mol. % are 0.053, 0.224 and 0.011, standard deviations are 5.43, 7.05 and 0.37, respectively.

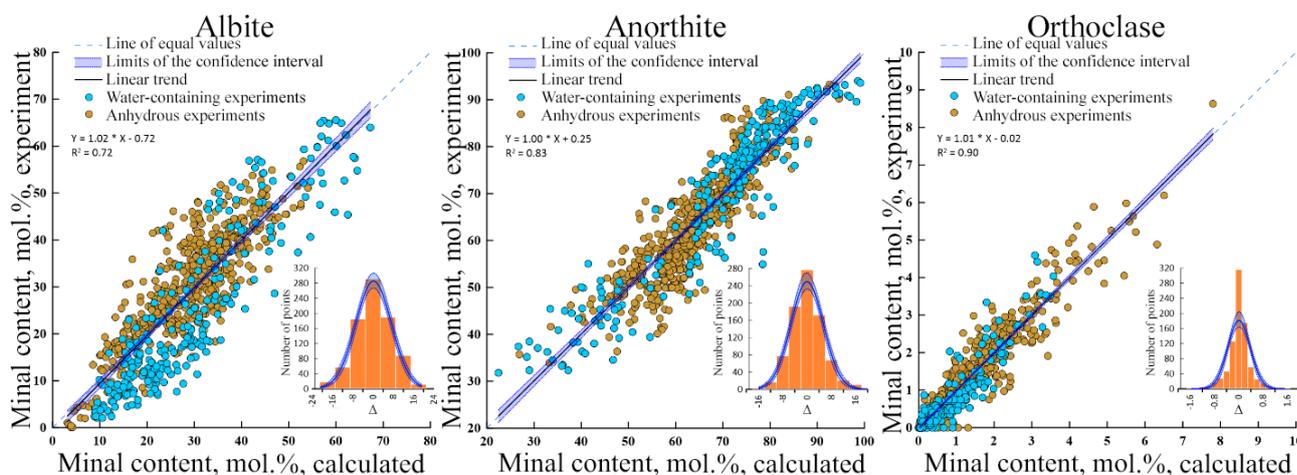


Fig. 1 Comparison of the results of calculating the contents of Albite, Anorthite and Orthoclase with experimental data in silicate melts (for dry, water-containing and water-saturated experiments). The black line is a linear trend, the blue dotted line is a line of equal values. The blue semi-transparent area is the confidence area at the 95% confidence level, 841 experiments in the sample.

It is worth noting that in Figure 2, the clouds of points (dry and water experiments) consistently lie along lines of equal values (with the exception of magnanorthite), however, since all experiments with water were carried out at elevated pressures, we can observe the dependence - the predominance of high mole fractions of anorthite and on the contrary, low albite and orthoclase. This circumstance was noted earlier in the reviewed literature (Housh, Luhr, 1991).

Composimeter verification. As a verification of the obtained plagioclase composimeter, the reproduction of experimental mineral liquidus temperatures in the Composimeter program developed by D.A. Bychkov was checked. Given the composition, pressure and volatility of oxygen, the iterative method finds a temperature at which the sum of the molar fractions of the minerals is equal to 1. It is this temperature that is taken as the liquidus temperature of the corresponding mineral. Thus, the calculated liquidus temperature was obtained not by optimizing experimental data, but as a result of a joint solution of the system of equations of the composimeter and

the mass balance equation.

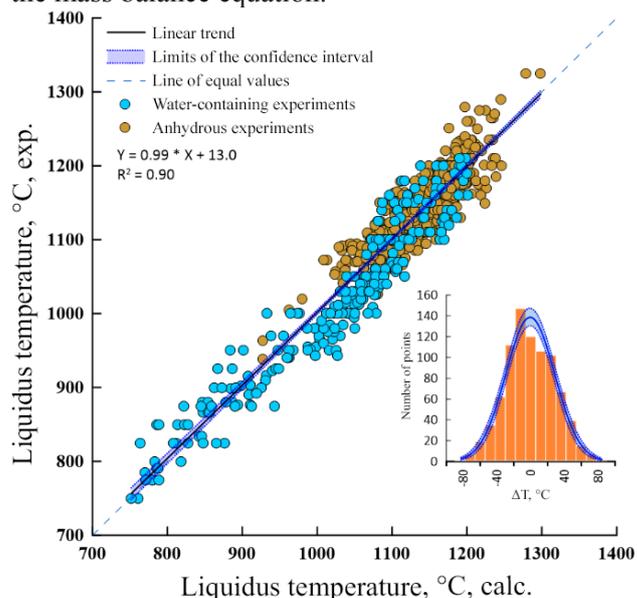


Fig. 2. Graph of correspondence between calculated and experimental values of liquidus temperature (for dry, water-containing and water-saturated experiments). The blue semi-transparent area is the confidence area at the 95% confidence level, 841 experiments in the sample.

Thus, from Figure 2 it is clear that aqueous and anhydrous, atmospheric and high-pressure experiments form a single cloud of points, which indicates that the goal set in this work has been achieved, namely, obtaining a compositometer for simulating the equilibrium of plagioclase with a melt common to anhydrous and hydrous systems.

Conclusion. Since the initial plagioclase sample was insufficiently characterized in the field of water-saturated experiments, the approach described in (Gnuchev, 2023) was used. Thus, the sample was expanded in the area of water-saturated experiments (from 35 to 202 experiments), and the final sample, including dry, water-containing and water-saturated experiments, amounted to 841 experiments from 78 works.

On its basis, the coefficients of the compositometer system of equations were optimized and its further verification was carried out by comparing the results of calculating the liquidus temperature with experimental data.

The resulting plagioclase compositometer is capable of calculating with high accuracy the crystallization temperature and composition of plagioclase for both anhydrous and hydrous systems, as evidenced by the quality of reproduction of both the contents of the main endpoints and liquidus temperatures (confidence region ± 4.5 °C).

Quantitative characterization of the influence of water on the liquidus temperature of plagioclase and its composition is the task of further research.

References

- Al'meev, R. R., & Ariskin, A. A. (1996). Mineral-melt equilibria in a hydrous basaltic system: computer modeling. *Geochemistry International*, 34(7), 563-573.
- Bychkov D. A., Koptev-Dvornikov E. V. The problem of equilibrium of quenching experiments in melt-solid phase systems and approaches to its solution. *Proceedings of VESEMG-2022. GEOKHI M*, 2022. pp. 88–91.
- Gnuchev, Y. Y., Bychkov, D. A., & Koptev-Dvornikov, E. V. (2023). An Equation for the Calculation of Saturated Water Contents in Silicate Melts: A New Version. *Geochemistry International*, 61(9), 937-947.
- Frenkel M.Ya., Yaroshevsky A.A., Ariskin A.A., Barmina G.S., Koptev-Dvornikov E.V., Kireev B.S. Dynamics of intrachamber differentiation of basic magmas M.: Nauka, 1988. - 216 p.
- Ariskin A. A., Barmina G. S., Meshalkin S. S., Nikolaev G. S., Almeev R.R. (1996) INFOREX-3.0: A database on experimental studies of phase equilibria in igneous rocks and synthetic systems: II. Data description and petrological applications. *Comput. Geosci.* 22 (10) 1073–1082.
- Housh, T. B., Luhr, J. F. (1991). Plagioclase-melt equilibria in hydrous systems. *American Mineralogist*, 76(3-4), 477-492.
- Lange, R. A., Frey, H. M., Hector, J. (2009). A thermodynamic model for the plagioclase-liquid hygrometer/thermometer. *American Mineralogist*, 94(4), 494-506.
- Nielsen, R. L., Dungan, M. A. (1983). Low pressure mineral-melt equilibria in natural anhydrous mafic systems. *Contributions to Mineralogy and Petrology*, 84, 310-326.
- Waters, L. E., Lange, R. A. (2015). An updated calibration of the plagioclase-liquid hygrometer-thermometer applicable to basalts through rhyolites. *American mineralogist*, 100(10), 2172-2184.

Kotelnikov A.R.¹, Ananiev V.V.², Suk N.I.¹, Krinochkina O.K.³, Krinochkin L.A.⁴
Experimental and theoretical modeling of crystallization of gabbro-dolerite of Kosmosero (Zaonezhie, Karelia). UDC 553.21+550.42: 550.89

¹IEM RAS, Chernogolovka, Moscow region; ²IVS FEB RAS, Petropavlosk-Kamchatskii; ³MSCU, Moscow; ⁴IMGRE, Moscow (kotelnik1950@vandex.ru)

Abstract. Samples of gabbro-dolerites from coastal outcrops of Kosmosero Lake, Zaonezhie, Karelia were studied., as well as samples from the Maksovskoye deposit. These rocks are located within the Onega Paleoproterozoic structure, which is part of the Karelian structural-facies zone and belong to the Ludykovian intrusive complex, gabbro-dolerite subcomplex (age 1.96 billion years). Samples of gabbro-dolerites were studied by optical, microprobe and X-ray methods. The composition of the samples was determined by ICP-ES-MS. PTX conditions for the crystallization of gabbro-dolerites have been determined by calculation methods based on available mineral geothermobarometers and a set of programs. To verify the calculated data, experiments were carried out on their melting and subsequent crystallization. The experiments were carried out at a temperature of 1230→1140°C and a pressure of 5.5→5.0 kbar. The composition of the phases after the experiments was studied by microprobe analysis. The composition of the phases in the experimental products is in good agreement with the calculation data.

Keywords: gabbro-dolerites, crystallization, melting, mineral geothermobarometers, experiment

The studied gabbro-dolerites are located within the Onega Paleoproterozoic structure, which is part of the Karelian structural-facies zone (SFZ) (Filippov, Deines, 2018). The Karelian epoch belongs to the early Proterozoic time and is separated from the previous epoch by a long (~100 million years) period of tectonic and endogenous rest. Since that time, the territory of the Karelian SFZ has been developing as a cratonized region. In Ludicovian times, along with the intensive accumulation of mafic and ultramafic volcanics, thick strata of carbonaceous shales are formed. This is a time of tectonic and endogenous activation of the territory. At the same time, the processes of sedimentation and magmatism gravitate towards the periphery of the Karelian craton. During the Svecofennian period (2.0

– 1.75 billion years), there was a significant change in the conditions of sedimentation and endogenous processes, as well as a restructuring of the structural plan of the territory. New specialized geological complexes are being formed, including the Zaonezhsky black shale and new types of associated deposits - shungites, uranium-vanadium, etc.

In recent years, a number of new deposits of various raw materials have been discovered, the analogues of which are not yet known in world practice. These “non-traditional” types of mineral raw materials (Pt-U-V in cosmoserites) have the greatest prospects in the Precambrian metallogeny of this region. The general composition of the ores is determined primarily by vanadium, which is concentrated mainly in micas - roscoelite and phlogopite (about 95%), as well as in hematite, nolanite and a number of other minerals (5% of vanadium). The ores are characterized by a very high V₂O₅ content – up to 2-5%. Uranium is present in ores of all deposits. Uranium minerals are represented by pitchblende, coffinite, uraninite and, less commonly, brannerite. The described gabbro-dolerites apparently belong to the Ludicovian intrusive complex, a gabbro-dolerite subcomplex. They occur in the form of sills. Their specialization is predominantly siderophilic (Co -12.1; Cu-2.9; V-2.8; Be-2.4; Th-2.2; Sc-2.0; (Fe, Ti) -1.7 ; (Y,Pb,Ni,Mn)-1.5 – relative to the clarks of the earth’s crust according to Vinogradov).

To assess the processes of petrogenesis of gabbro-dolerite sills, we selected samples from bedrock outcrops on the lake. Kosmozero and Maksovo deposits. Dolerite samples were studied by optical, microprobe and X-ray methods. The composition of the samples was determined by XRF and ICP-ES-MS methods. Based on analyzes of the geochemical spectra (spider diagrams) of gabbro-dolerites, their similarity to intracontinental plate formations is shown (Fig. 1). According to petrochemical characteristics, gabbro-dolerites belong to “normal” basalts. Gabbro-dolerite parageneses are represented by the following minerals: olivine (relics), orthopyroxene (rare), clinopyroxene, plagioclase, amphibole, biotite (rare), potassium feldspar, epidote, chlorite, ilmenite, zircon. The presence of hydrous (secondary) minerals indicates metamorphic changes in gabbro-dolerites. Table 1 presents the compositions of

minerals from a number of gabbro-dolerite samples studied. For a number of samples, X-ray studies of minerals were carried out, and the parameters of unit cells were determined (Table 2). Based on the compositions of coexisting minerals, the parameters of mineralogenesis of gabbro-dolerites were estimated (Fig. 2). For the magmatic stage, PT-parameters were estimated using thermometers and barometers (Nimis & Ulmer, 1998; Putirka, 2008); for the post-magmatic stage, parameters were estimated from Amph-Pl equilibria (Dale, e.a., 2000); according to Cpx-Opx compositions (Perchuk, Ryabchikov, 1976), according to the bifeldspar thermometer (Nekwasil, 1993). Chlorite (Kotelnikov et al., 2012) and the structural state of plagioclase (Kotelnikov et al., 2024) were also used to estimate temperature. It was shown that the first liquidus phases (olivine) were formed at T=1200±20°C (with a temperature range of 1220÷1170°C) and pressure P=7.4±1.1 kbar (with a range of 4.5÷8.8 kbar). Subsequently, with the rise and intrusion of the magmatic melt, the temperature dropped to 1140±30°C (range 1100÷1170°C), the pressure decreased to 3.4±1.1 kbar. The maximum values of the parameters of the post-magmatic stage were determined by the Amph-Pl equilibrium (Dale, e.a., 2000). These values are T=815 – 665°C; pressure 2.5 – 1.5 kbar. A further decrease in temperature led to the formation of minerals such as epidote and chlorite and the albitization of plagioclases. The temperatures of the final stages of hydrothermal processes are characterized by temperatures obtained from Pl-Ksp equilibria: 780 – 480°C; chlorite 270°C; and according to the values of the structural state of plagioclase (Kotelnikov et al. 2024): 235 – 180°C, at a pressure of 1.5 – 1.0 kbar.

To verify the calculated data, experiments were carried out on the melting and subsequent crystallization of dolerites. The experiments were carried out at a temperature of 1230→1140°C and a pressure of 5.5→5.0 kbar. The composition of the phases after the experiments was studied by microprobe analysis. The composition of mineral phases (Cpx, Pl) in the experimental products is in fairly good agreement with the calculation data (Table 3) using the Petrologist-3 software package ((Danyushevsky, Plechov, 2011).

Table 1. Compositions of minerals from gabbro-dolerites of Zaonezhye

Oxides	K23-4, Cosmozero					K23-8, Cosmozero				
	Cpx	Pl	Ksp	Ep	Chl	Cpx	Pl	Amph	Ilm	Chl
SiO ₂	53.13	66.96	64.56	38.90	25.80	51.88	68.72	48.310	0.24	26.04
TiO ₂	0.12	0.05	0.12	0.09	0.05	0.04	0.03	0.600	52.69	0.09

Oxides	K23-4, Cosmozero					K23-8, Cosmozero				
	Cpx	Pl	Ksp	Ep	Chl	Cpx	Pl	Amph	Ilm	Chl
Al ₂ O ₃	1.60	20.72	17.91	26.94	19.38	2.05	19.65	2.413	0.10	19.15
FeO	19.53	0.34	0.50	8.17	33.81	21.42	0.21	15.117	41.88	34.81
MnO	0.36	0.01	0.05	0.08	0.56	0.26	-	0.627	4.34	0.39
MgO	11.37	-	-	-	10.35	10.26	-	10.590	0.06	10.68
CaO	13.93	2.03	0.14	26.59	0.11	14.17	0.67	21.740	0.46	0.13
Na ₂ O	0.13	9.71	0.15	-	-	0.13	10.31	0.280	-	-
K ₂ O	0.02	0.13	16.48	-	-	0.03	0.17	0.000	-	-

Continuation of the table 1.

Oxides	L-49, Maksovo						
	Ol	Opx	Cpx	Pl	Ksp	Amph	Bt
SiO ₂	30.38	47.49	50.44	58.66	65.05	44.27	34.35
TiO ₂	0.01	0.16	0.87	0.01	0.10	1.05	4.13
Al ₂ O ₃	-	0.37	2.63	24.78	18.61	6.37	12.95
FeO	66.77	42.48	18.73	0.36	0.13	27.50	30.69
MnO	0.89	1.09	0.27	-	-	0.30	0.08
MgO	3.46	7.53	12.40	-	-	6.27	5.20
CaO	-	1.38	14.26	7.35	0.30	10.06	-
Na ₂ O	-	0.07	0.56	7.08	2.66	1.54	-
K ₂ O	-	-	0.01	0.62	12.67	0.93	9.26

Table 2. Parameters of unit cells of plagioclase samples K23-4 and K23-8

№ samp.	Mineral	a, [Å]	b, [Å]	c, [Å]	α, [°]	β, [°]	γ, [°]	V, [Å ³]	n
K23-8	Ab	8.145	12.783	7.149	94.36	116.63	87.58	663.5	41
K23-8	Cpx	9.838	8.967	5.275	90.0	105.63	90.0	448.2	20
K23-8	Chl	5.571	9.152	14.261	90.0	90.21	90.0	727.2	29
K23-8	Ilm	5.084	5.084	14.087	90.0	90.0	120.0	315.3	8
K23-4	Ab	8.147	12.779	7.144	94.28	116.57	87.60	663.3	31

Table 3. Comparison of the compositions of products from experiments on melting gabbro-dolerites with calculated data

Oxides, wt. %	Calculation by Petrolog-3 (Danyushevsky, Plechov, 2011)			Experimental data		
	Melt	Cpx	Pl	Melt	Cpx	Pl
SiO ₂	50.90	50.41	52.61	54.82	50.42	54.80
TiO ₂	1.80	1.21	0.00	2.00	0.75	0.13
Al ₂ O ₃	13.31	4.08	29.69	16.09	4.41	27.52
FeO	15.78	12.62	0.88	10.51	12.39	0.68
MnO	0.34	0.27	0.00	0.23	0.33	0.00
MgO	4.81	15.53	0.2	4.27	18.20	0.0
CaO	8.82	15.62	12.14	7.95	13.21	11.50
Na ₂ O	2.41	0.32	4.40	3.85	0.25	5.03
K ₂ O	1.12	0.00	0.00	0.22	0.01	0.27
X _{Mg}	0.35	0.60	-	0.41	0.66÷0.71	-
X _{Ca}	0.61	-	0.60	0.52	-	0.41÷0.64

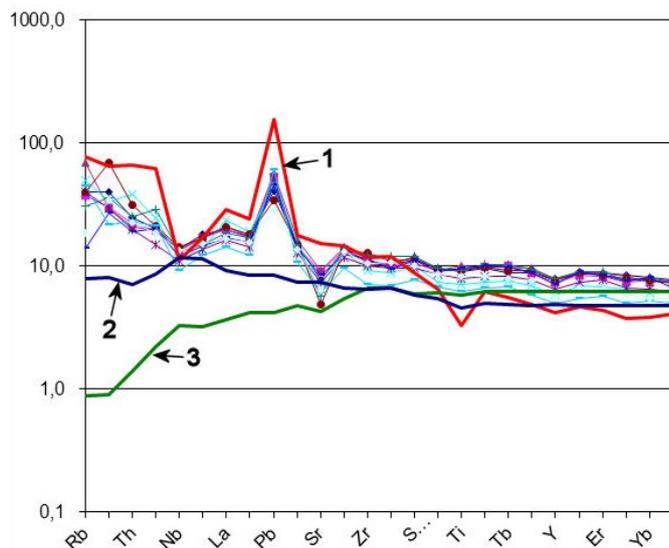


Fig. 1. Spider diagram of small elements of gabbro-dolerites of Kosmozero. 1 – composition of the earth's crust according to (Rudnick & Gao, 2003); 2, 3 – compositions of E-MORB and N-MORB according to (Sun & McDonough, 1989).

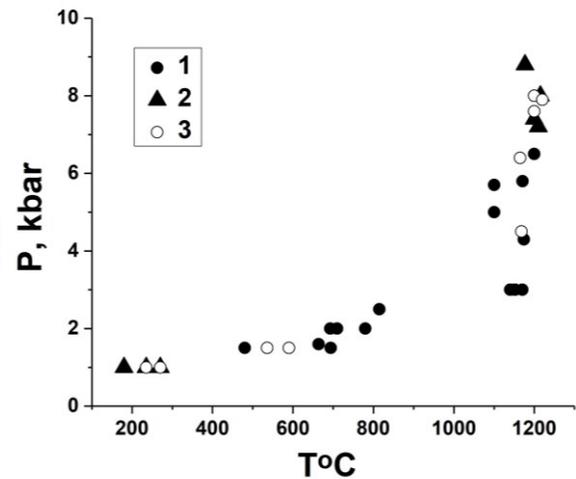


Fig. 2. Parameters of petrogenesis of gabbro-dolerites of Zaonezhye, calculated from mineral equilibria; 1 – sample L-49, Maksovo; 2 – K23-4, Kosmozero; 3 – K23-8, Kosmozero.

Conclusions

1. An analytical study of samples of gabbro-dolerite sills from Kosmozero, Zaonezhye, Karelia was carried out.

2. It is shown that, according to their petro- and geochemical characteristics, gabbro-dolerites belong to intracontinental plate formations.

3. Using the methods of mineral thermo- and barometry, the PTX parameters of the formation and evolution of gabbro-dolerites were assessed. Theoretical modeling of the crystallization process was carried out.

4. To verify the calculated data, gabbro-dolerites were melted at a temperature of 1230→1140°C and a pressure of 5.5→5.0 kbar. A comparison of experimental and calculated data was carried out.

The work was supported by the FMUF-2022-0004 program.

References

- Dale J., Holland T., Powell R. Hornblende-garnet-plagioclase thermobarometry: a natural assemblage calibration of the thermodynamics of hornblende // *Contrib. Mineral. Petrol.* 2000. V. 140. P. 353–362.
- Danyushevsky L.V., Plechov P. Petrolog 3: Integrated software for modeling crystallization processes // *Geochem. Geophys. Geosyst.* 2011. V. 12, Q07021, doi:10.1029/2011GC003516.
- Filippov M.M., Deines Yu.E. Substratal type of shungite deposits in Karelia. Federal Research Center "Karelian Scientific Center of the Russian Academy of Sciences". Petrozavodsk. 2018. 261 p.

- Kotelnikov A.R., Suk N.I., Z. Kotelnikova Z.A., Shchekina T.I., Kalinin G.M. Mineral geothermometers for low-temperature parageneses. *Bulletin of the ONZ RAS.* 2012. T. 4. NZ9001, doi:10.2205/2012NZ_ASEMPG.
- Kotelnikov A.R., Shchekina T.I., Suk N.I., Kotelnikova Z.A., Antonovskaya T.V. Structural Ordering of Feldspars as an Indicator of the Temperature of Mineral-Forming Processes. *Geochemistry International*, 2024. V. 62, N 5. P. 493–499.
- Nekvasil H. Ternary feldspar/melt equilibria: a review // In: *Feldspars and their reactions*. NATO ASI series. I. Parsons (ed.) 1994. V. 421. 650 p.
- Nimis P., Ulmer P. Clinopyroxene geobarometry of magmatic rocks. Part 1: An expanded structural geobarometer for anhydrous and hydrous, basic and ultrabasic systems // *Contrib. Mineral. Petrol.* 1998. V. 133. P. 122–135.
- Perchuk L.L., Ryabchikov I.D. Phase correspondence in mineral systems. M.: "Nedra". 1976. 287 p.
- Putirka K. Thermometers and Barometers for Volcanic Systems. In: Putirka, K., Tepley, F. (Eds.). *Minerals, Inclusions and Volcanic Processes, Reviews in Mineralogy and Geochemistry*. Mineralogical Soc. Am. 2008. V. 69. P. 61-120.
- Rudnick, R.L., Gao, S. (2003) 3.01 Composition of the continental crust. *Treatise On Geochemistry, Volume 3: The Crust*. Elsevier Ltd. 1st Edition, P. 1-64.
- Sun & McDonough 1989. Sun, S.S. and McDonough, W.F. (1989). Chemical and isotopic systematics of oceanic basalts; implications for mantle composition and processes. In: *Magmatism in the ocean basins*. Saunders, A.D. and Norry, M.J. (Editors), Geological Society of London, London. 42: 313-345.