The formation and differentiation of magmas

Rusak A.A.[1], Shchekina T.I.[2], Zinovieva N.G.[2], Khvostikov V.A.[3] Features of subliquidus crystallization in a high-fluoride model granite system (experimental study)

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Abstract. In the model high-fluoride lithium-containing granite system Si-Al-Na-K-Li-F-O-H, when the temperature decreases from 1250 °C to 400 °C at 1 kbar, a certain order of crystallization of mineral phases from coexisting aluminosilicate (L) and salt alkali-aluminofluoride (LF) melts is observed. At 1250 °C and C_{H2O} = 0-50 wt. % silicate melt is homogeneous. In experiments at 1000°C at a water content of ~ 10 wt. % there are signs of silicate-salt immiscibility in the form of spherical secretions of aluminofluoride composition. Starting from 800 °C and C_{H2O} = 2-15 wt. % liquid immiscibility is stably presented in the system, and at 700 °C and C_{H2O} = 2-50 wt. % partial crystallization of the salt melt begins with the formation of K-Na cryolite (Crl). In the silicate melt, quartz is the first to crystallize in the temperature range from 700 to 600 °C. With a further decrease in temperature, the crystallization of Li-mica of the polylithionite type occurs (at C_{H2O} = 15 wt. % in the system) at the boundary of the silicate and salt melt. The cryolite continues to crystallize in the salt melt, but there is also a melt saturated with REE, Y, and Sc, which were introduced into the system. In the range between 600 and 500 °C, orthoclase and Na - and Na-K cryolite crystallize in the system along with quartz in the form of separate phases. The silicate melt remains in the system up to 400 °C, being in a metastable, supercooled state. In salt globules, the residual melt is presented at 500 °C, and at 400°C it completely crystallizes. The observed Na - and Na-K cryolite secretions inside large quartz grains (~200 microns) are similar to those found in cryolite-containing granites (for example, the Madeira deposit). The simultaneous crystallization of two compositions of Na-and Na-K-cryolite indicates the decomposition of a homogeneous solid solution of cryolite and the coexistence of two phases – cryolite and elpasolite, starting from 600-500 °C.

Keywords: *aluminosilicate melt; aluminofluoride melt; lithium-containing granite system; cryolite-containing granites; lithium; fluorine; crystallization; cryolite; orthoclase; quartz; rare-earth elements.*

The aim of this work was to study the order of crystallization of phases from two equilibrium melts (aluminosilicate (L) and aluminofluoride salt (LF)); to compare the phase relations obtained in our experiment with those obtained earlier and to compare the data with natural objects.

The task of the study was to conduct experiments from high liquidus temperatures to crystallization temperatures of granite melt. The experimental parameters were selected are temperature from 1250 °C to 400 °C, pressure from 1 to 2 kbar and water concentration for some experiments ranged from 0 to 50 wt. %. It was important to understand at what water content in the fluorid system the melt is saturated with an aqueous fluid and its separation from the melt occurs. Previously, in the conducted experiments, the water content did not exceed 4-7 wt. % (Gramenitskiy et al., 2005; Alferyeva, 2012).

Methods of experiments. For the study, a model granite system with the addition of lithium (II) oxide was selected, in which the specified composition of the aluminosilicate melt corresponded to the composition of the quartz-albite-orthoclase granite eutectic at T = 690 °C and P_{H_2O} = 1 kbar at a content of 1 wt. % F (Manning, 1981) and 1.5 wt. % Li. As the salt component of the system, a composition similar in stoichiometry to the cryolite was used-Crl ($(Li,Na,K)_3AlF_6$), which was added in an amount sufficient to saturate the aluminosilicate melt with it. Previously, the natrium region of the system was mainly studied, then the lithium-natrium region (Alferyeva, 2012). In this paper, we consider the phase relations in lithium-natrium-potassium region, which is closed to the natural composition of granites. The initial composition of the silicate-salt mixture is shown in Table 1.

The following reagents were used as the initial charge are dried gel SiO_2, LiF, K_2SiF_6, NaF, AlF_3, Al_2SiO_5, Al_2O_3 and distilled water.

Table 1. The initial composition of the silicate-salt mixture (100%) – the reference composition A-40/11 for all series of experiments (at. %).

Si	Al	Na	K	Li	F	O	Sum
17.24	6.92	5.07	3.84	4.46	21.82	40.65	100

In a series of experiments, the entire range of rare-earth elements (REE) from La to Lu, including Sc, Y, was added in the form of oxides of 0.5-2 wt. % of the element. For experiments conducted at temperatures of 600-400 °C, REE was introduced in the following pairs ((1) Y_2O_3, La_2O_3; (2) Sm_2O_3, Gd_2O_3, Tb_2O_3; (3) CeO_2, Eu_2O_3 and Ho_2O_3; (4) Dy_2O_3; (5) Pr_2O_3, Lu_2O_3, Sc_2O_3; (6) Er_2O_3, Yb_2O_3; (7) Nd_2O_3, Tm_2O_3; (8) Sc_2O_3, Gd_2O_3), so that there is no overlap of X-ray lines during electron-probe microanalysis. The experiments were added from 0 to 50 wt. % of distilled water by weight of the sample. The reagent ratios were selected in such a way that the expected aluminosilicate melt in the experimental products was close to the compositions of highly evolved Li-F and cryolite-containing granites. Thoroughly mixed in a jasper mortar, the starting materials were placed in platinum ampoules (outer diameter-3 mm, wall thickness-0.2 mm, length-25 mm), into which distilled water was injected by a dispenser.

Installation. The experiments were carried out on a high-pressure gas installation with internal heating ("gas bomb») in the IEM RAS at temperatures from 1250 to 400 °C and a pressure of 1 kbar (at T = 700-800 °C, pressure parameters from 1 to 2 kbar were set in experiments). The duration of the experiments was up to 7 days. Experiments from 400 to 600 °C were carried out in two stages, using the method of the "top-down" approach to equilibrium. The ampoules with the substance were heated to T = 800 °C at P = 1 kbar, kept for 3 days, and slowly cooled to the set temperatures for 8 hours. Then they were kept for 3 days at 400-600 °C and hardened. The quenching rate on the "gas bomb" was 150-200 degrees per minute. Experiments were also carried out at 500 and 600 °C with a "bottom-up" approach to equilibrium, so without overheating.

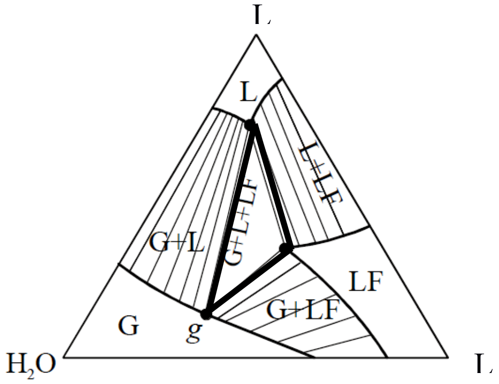
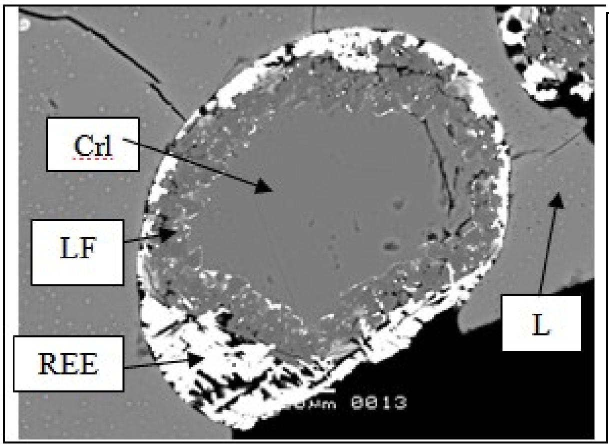


Fig. 1. Diagram of the isobaric-isothermal cross-section of the «silicate-salt-volatile component» diagram at the experimental parameters. The water content is shown on an enlarged scale (Rusak, 2019).

Equipment for research of products of experiments. The substance was studied using electron microscopy (Jeol JSM-6480LV (Japan) with energy-dispersive INCA Energy-350 and crystal-diffraction INCA Wave-500 (Oxford Instrument Ltd., UK)) and electron probe microanalysis (Superprobe JXA-8230 (Japan)) in the Laboratory of Local Methods of Substance Research of the Department of Petrology and Volcanology, Faculty of Geology, Moscow State University; laser ablation (quadrupole mass spectrometer with inductively coupled plasma X Series II (Thermo Scientific, USA) with a laser ablation prefix UP266 MACRO (New Wave Research, USA)) at the Analytical Certification Testing Center of the Institute of Problems of Microelectronics Technology and High-Purity Materials of the Russian Academy of Sciences (ASIC IPTM RAS). The fluid phase was analyzed by the ICP-MS method (from solution) in the Laboratory of Experimental Geochemistry of the Department of Geochemistry of the Faculty of Geology of Moscow State University.

The results of the experiments. The order of phase crystallization in a model Li-containing system with limiting concentrations of fluorine at a temperature drop from 1250 to 400 °C and with different amounts of water (when saturated with an aqueous fluid from 10 wt. %) is experimentally obtained. The phase relations can be characterized using a schematic diagram of the system "silicate–salt–volatile (aqueous fluid)" (fig. 1). The central part of the diagram is the working area of the study. In experiments conducted at 1250 °C and C_{H_2O} = 0-50 wt. %, the aluminosilicate melt (L) is homogeneous. It contains small globules (<10 microns) of alkaline-aluminofluoride composition, which the authors treat as quenching phases (FP). When analyzing the quenching aluminofluoride melt (LF) over an area without quenching phases and with their capture, the changes in the main rock-forming elements did not exceed more than 0.01-0.1 at. %. All quenching phases were evenly distributed over the sample. In experiments at 1000 °C at a water content of ~ 10 wt. % there are signs of silicate-salt immiscibility (liquation) in the form of spherical and elongated oval secretions of aluminofluoride composition, the size of which ranged from 20 to 80 microns in diameter. Starting from 800 °C and C_{H_2O} = 2-15 wt. % liquid immiscibility is stably present in the system. It is represented by a hardened silicate melt, in the matrix of which there are large rounded globules of aluminofluoride melt, saturated with lithium fluorides (grisite), natrium and potassium (cryolite, cryolithionite), as well as REE (analogues of fluocerite and gagarinite, etc. (Shchekina et al., 2021)). In experiments at 700 °C and water concentrations from 2 to 50 wt. % partial crystallization of the salt melt begins with the formation of large crystals of K-Na cryolite up to 120 microns in diameter. Cryolite does not concentrate REE fluorides, and since it occupies more than half the volume of the entire globule, the residual salt melt saturated with rare-earths is pushed into the marginal part of the globules. Rare-earth elements in the form of fluorides often form their own phases at the globule boundary (fig. 2). Quartz crystallizes in the silicate melt in the temperature range from 700 to 600 °C. At these parameters of the experiment according to the diagram (Hemley et al., 1994), β-quartz crystallizes in the system. At 500 °C, large quartz crystals crystallize from the aluminosilicate melt, which can be considered analogs of pea-shaped quartz in rare-metal granites.



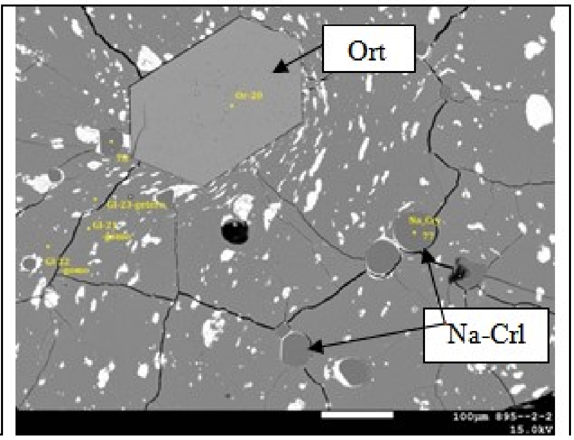


Fig. 2. A salt globule (d~150 microns), in the center of which a cryolite was crystallized, surrounded by a hardened salt melt with REE fluorides located in the marginal part of the globule on the border with the aluminosilicate melt.

Fig. 3. Crystallization of orthoclase from an aluminosilicate melt and rounded Na-Crl crystals from a salt melt. Image in BSE.

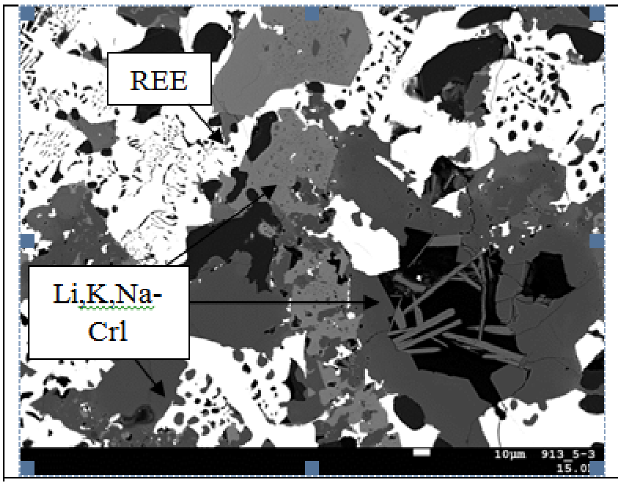


Fig. 4. Large crystals of alkali- and REE fluorides. Image in BSE.

A new phase in the experiment was Li-mica ($KLi_2(Al,Sc)(Al,Si)_4O_{10}(F,OH)_2$) type of polylithionite (at C_{H2O} = 15 wt. % in the system), which crystallizes at the boundary of the silicate and salt melts. In mica, scandium partially replaces aluminum in the octahedral position. The cryolite continues to crystallize in the salt melt, but there is also a melt saturated with REE, Li, Y and Sc. When studied by the method of the "bottom-up" approach to the equilibrium of the system, in the temperature range from 600 to 500 °C, orthoclase and Na- and Na-K cryolite (the latter up to 400 °C) crystallize in the system along with quartz in the form of separate phases (fig. 3). Also in these experiments, the release of natrium and natrium-potassium cryolite inside large quartz grains (up to 200 microns across) is observed. Similar crystallization are found in cryolite-containing granites of the Madeira pluton (Shchekina, 2013). This fact confirms the magmatic nature of the cryolite. The silicate melt remains in the system up to 400 °C, being in a metastable, supercooled state. In salt globules, the residual melt is presented at 500 °C, and at 400 °C it completely crystallizes. Large idiomorphic crystals of alkali fluorides and REE are formed (fig. 4).

Discussion of the results and conclusions. It is shown that the equilibrium of the aluminosilicate and aluminofluoride salt melts is reproduced and preserved from a temperature of 800°C and up to 500°C at 1 and 2 kbar. When the temperature decreases in the model granite system, a certain order of crystallization of the phases is observed. Silicate melt exists up to 500 °C, from it crystallizes, cryolite, quartz, from the salt melt – cryolite, REE fluorides and Sc, Y, Li fluorides. The residual aluminofluoride melt (hardened) is preserved up to 500 °C. At 400 °C, the silicate melt is in a metastable, quenched state, and REE, Sc, Y, Li fluorides and alkali-aluminofluorides form large crystals, filling all interstitials (idiomorphic structure). The equilibrium crystallization of two cryolite compositions, Na- and Na-K, was found, which indicates the impossibility of crystallization of a homogeneous solid solution of Na-K cryolite, starting from ~ 600 °C, like natural ongonites, in which not Na-K feldspar is crystallized, but albite and potassium feldspar separately. And also, the simultaneous crystallization of two compositions of Na- and Na-K-cryolite indicates the decomposition of a homogeneous solid solution of cryolite and the coexistence of two phases-cryolite and elpasolite, starting from 600-500 °C.

The obtained data substantiate the idea of the formation of large cryolite bodies in the rare-metal ore deposits of Ivigtut, Piting, Zashikha, Ulug-Tanzek, etc. from salt, fluorine-saturated melts (Shchekina et al., 2013), which separate from fluorine- and lithium-rich aluminosilicate magmas at the late stages of differentiation.

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Rusak A.A., Lukanin O.A., Kononkova N. N., Kargaltsev A.A. Experimental study of the melting of the SiO_2-MgO-FeO model composition, in the presence of graphite and calcium carbonate, at high thermodynamic parameters UDC 550.4, 552

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Abstract. The first experiments were carried out in the SiO_2-MgO-FeO system in the presence of calcium carbonate and graphite phases at a temperature of 1500 – 1600 °C and pressures of 2.5 – 3.5 GPa. The experiments were carried out on a high-pressure unit NL-13T with a toroidal seal of the "anvil with a hole" type with an exposure time of 40 minutes. The zonal structure of the samples was found in the experimental products. The central zone is composed of basic glass and small quartz crystals, and the marginal zone is composed of calcium pyroxene crystals and rounded graphite crystals. At a higher pressure, the central part is depleted of quartz crystals. There is a direct dependence of the SiO_2 –FeO concentrations at T = 1600 °C and P = 3 GPa. In glass without quartz, the FeO content is less than in glass with small quartz crystals. No separate metallic iron droplets were formed in the system, since the oxygen volatility was higher than the iron-wustite buffer (fO_2 > IW).This result is a case of crystallization in the region of instability of the metal phase.

Keywords: *basic composition glass, quartz, pyroxene, graphite, reducing system, iron, redox conditions, oxygen volatility; buffer, graphite buffer, iron-wustite buffer.*

Introduction. In many hypotheses of the origin of the Earth, it is assumed that the formation of the Earth occurred as a result of the accretion of a mixture of silicate and metallic particles similar to chondrite meteorites (Vinogradov, 1961; Birch, 1965; Elsasser, 1963; Urey, 1962, etc.). There are two hypotheses of the formation of the early Earth are homogeneous and heterogeneous. According to the homogeneous hypothesis, the formed Earth in the process of accretion was composed of a homogeneous substance, which was a mixture of metallic and silicate phases. The accretion of the Earth lasted for quite a long time (10^7-10^8 years) (Ringwood, 1982). There was a gradual heating inside the Earth, due to the decay energy of long-lived radioactive isotopes, which gradually led to the melting of the metallic phase of iron and its gradual segregation into the core. According to the heterogeneous hypothesis, it is assumed that the metal core was formed first during accretion, then a silicate shell began to form when the temperature decreased.

A. E. Ringwood (1978) believed that some of the volatile components were dissipated during the accretion process, then at a later stage the volatile components were released from rocks similar to carbonaceous chondrites. One of the assumptions is a slow accretion in "cold" conditions, during which the volatiles were preserved in the Earth. Volatile compounds (H_2O, CO_2, N_2, etc.) accumulated and gradually formed the hydrosphere and the Earth's atmosphere.

Regardless of the homogeneous or heterogeneous scenario of the Earth's accretion, impact events played an important role in the formation of planetary matter at the final stages. Under the impact bombardment, the mantle material melted, which led to the formation of a magmatic ocean.

The problems associated with the differentiation of the initial planetary matter in the conditions of the early Earth during the formation of the magmatic ocean, its subsequent crystallization, currently remain the subject of active discussion. One of the ways to solve them is the experimental study of the processes of melting and crystallization of model silicate systems in a wide range of RT parameters under various redox conditions.

The study of the influence of volatile components (volatile components) remains a very relevant issue for experimental research. Recently, many experiments have been made in the oxidative region at the oxygen volatility of the "modern mantle" (fO_2 > IW). There are few studies concerning the processes of magma differentiation under the reducing conditions characteristic of the early stages of the Earth's formation, with the formation of a metallic phase (fO_2<IW-1).

In this work, data on the effect of carbon on phase equilibria during melting and crystallization of the composition corresponding to the composition of the early Earth before the separation of the core (McDonough, 2017) with a simplified composition of SiO_2-MgO-FeO, in the oxidative region at oxygen volatility fO_2 > IW are obtained.

The following *aims* were set in the work are to study melting and crystallization in a SiO_2-MgO-FeO system of composition in the presence of a graphite phase (graphite capsule) and a calcium carbonate phase («toroid») at high temperatures and pressures. To achieve the aims, the following *tasks* were set are to conduct a series of experiments at temperatures of 1600 °C and 1500 °C and a pressure of 2.5 GPa and at a temperature of 1600 °C and a pressure of 3 and 3.5 GPa.

Methods of experiments. The initial mixture, according to the content of the main petrogenic components, consisted of quartz (SiO_2), magnesium oxide (MgO) and iron oxalate (FeC_2O_4), which then released carbon dioxide when heated and left iron (II) oxide. This mixture was poured into quartz capsule in the form of a powder. At a temperature of 1505 °C and atmospheric pressure, it was melted in a high-temperature vertical tubular furnace Nabertherm RHTV 1700 at GEOKHI RAS. The selected glass (without adhering quartz) was ground in a jasper mortar to a homogeneous state in an atmosphere of ethyl alcohol. The finished mixture was poured into a graphite capsule (heater), compacted, covered with a graphite lid on top and inserted into a «toroid» made of calcium carbonate, which served as a pressure transmitting medium. The assembled ensemble was placed inside the anvils of the high-pressure installation "anvil with a hole" (NL-13T) with a toroidal seal (fig. 1), and an experiment was conducted for 40 minutes. To determine the chemical composition of the solid products of the experiments, the Cameca SX 100 microanalyzer with five wave spectrometers and the Broker Flash 6 energy-dispersion prefix was used at GEOKHI RAS. International standards of the Smithsonian Institution (Glass XF 2) corresponding to the glass of the main composition were used to configure the device and analyze the phases. Electronic images were obtained in the reflected electron mode (BSE): the accelerating voltage is 15 kV and the current is 30 nA. The analytical scanning electron microscope (SEM) Tescan MIRA 3 at GEOKHI RAS was used to study the phase relations and chemical composition. Bitmap images in BSE were obtained at an accelerating voltage of 20 kV, an operating distance of 15 kV (0.8 nm) and a beam intensity of 14 mA.

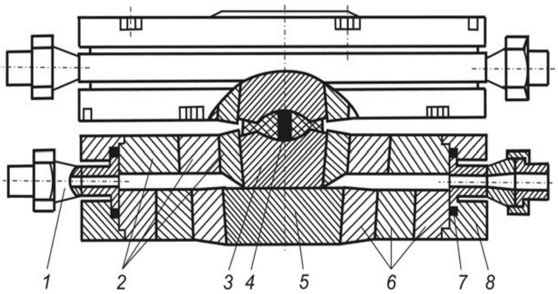

Fig. 1. A solid-phase device of the "anvil with a hole" type is a toroid. 1 – cooling system fitting; 2 – rings supporting the anvil; 3 – anvil; 4 – reaction volume; 5 – stand; 6 – stand support system; 7 – seal; 8 – housing.

The results of the experiments. The obtained phases in well-reproduced experiments were characterized by structural-textural and chemical homogeneity (T = 1600 °C and P = 2.5 and 3 GPa), which indicates the achievement of equilibrium in the experiments. The experimental products are represented by tempered glass of light gray color with cylindrical cavities (~1.5 x 1.5 mm) of dark gray color. Some series of experiments conducted at 1500 °C and 2.5 GPa and 1600 °C and 3.5 GPa did not form a proper cylinder, but crystallized as a white mineral aggregate inside a graphite capsule.

The experimental products are represented by a zonal structure. In the central zone of the sample at a temperature of 1600 °C and a pressure of 2.5 GPa, a tempered glass of the main composition is formed, inside which rounded quartz crystals (~15-20 microns) (fig. 2a). The marginal zone is represented by calcium silicate, pyroxene, which forms elongated needle-shaped and six-shaped crystals, and graphite of rounded and oval shape (~30 microns) crystallizes along the edges of the sample (fig. 2b).

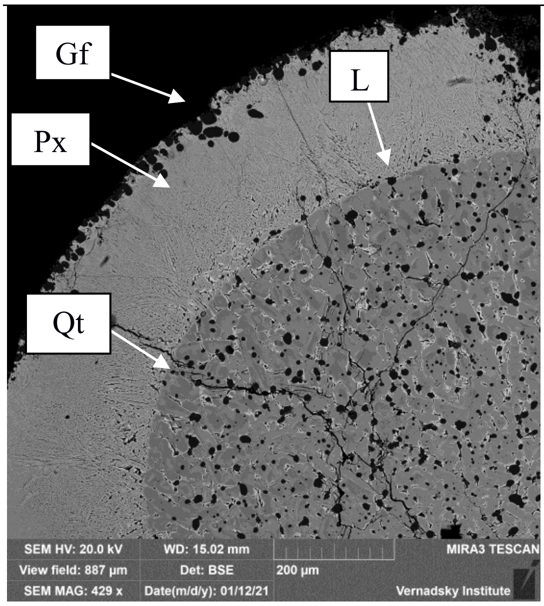

Fig. 2a. Contact of the marginal and central zones of the sample (T=1600 °C, P=2.5 GPa). The central zone: L - glass of the basic composition, Qtz - quartz; the marginal zone: Px - pyroxene, Gf - graphite.

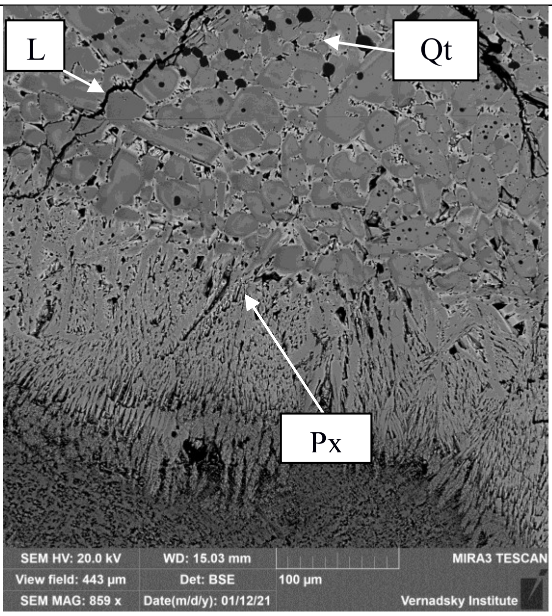

Fig. 2b. The edge zone of the sample (T=1600 °C, P=2.5 GPa). Elongated pyroxene crystals (Px).

In experiments at 1600 °C and 3 GPa, the phase relations remained the same, but in the central zone quartz does not exceed 10 microns. Calcium pyroxene, apparently, could be formed in the process of diffusion between the «toroid» and the sample. Graphite rounded crystals (up to 30 microns in diameter) could be captured from a graphite heater.
The average values and standard deviations of SiO_2, MgO and FeO for the initial glass obtained in a vertical tube furnace and for the experimental products are shown in table 1. When studying the chemical composition of the samples (T = 1600 °C and P = 3 GPa), a direct dependence of the iron oxide content on silicon (II) oxide was found are the less SiO_2 in the glass of the main composition, the lower the FeO concentration (table 2).

Images were obtained using the Cameca SX 100 microanalyzer with five wave spectrometers and the Bruker XFlash 6 energy-dispersion prefix, which displayed the concentrations of the main rock-forming elements (Si, Mg, Fe and Ca) in the central and marginal parts of the sample (T = 1600 °C and P = 3 GPa). The depletion of iron at the contact of the marginal and central zones, and the enrichment of the central zone with magnesium, in contrast to the marginal zone, is shown. Silicon is evenly distributed in both zones of the sample, and calcium is mainly embedded in the pyroxene structure, i.e. it is mainly located in the marginal zone.

Table 1. Average compositions of glasses obtained at 1 atm in a tubular furnace and average compositions of glasses obtained in experiments at T = 1600 °C and P = 2.5 and 3 GPa.

№ exp.	Comp.	SiO_2	MgO	FeO	Total
Initial glass (a)	X (10)	51.36	15.48	33.17	100
	S (10)	2.50	0.91	1.59	
138 (b)	X (4)	52.08	20.40	27.47	100
	S (4)	0.60	1.58	2.14	
159 (c)	X (3)	54.24	16.12	29.64	100
	S (3)	0.14	0.15	0.01	

Symbols: a) Average compositions of the initial glasses; b) Average compositions of glass in the central zone of the sample (exp. 138); c) Average compositions of glass in the central zone of the sample (exp. 159). T_{exp}=1600 °C, P = 2.5 and 3 GPa. These values are indicated in wt. %. X – average values, S – standard deviations. The data shown in parentheses indicate the number of analyses.

Table 2. Dependence of SiO_2-FeO concentrations for the experiment performed at T = 1600 °C and P = 3 GPa.

Phases	Comp.	MgO	SiO_2	FeO	Total
From L to S	X (3)	16.12	54.24	29.64	100
	S (3)	0.14	0.15	0.01	
From L to S without Q	X (2)	21.22	52.85	25.93	100
	S (2)	0.26	0.90	0.63	

Symbols: The table shows the average contents of the main rock-forming elements for exp. 159 in glasses of the main composition with and without quartz. The data are given in wt. %. X – average values, S – standard deviations. The data shown in parentheses indicate the number of analyses.

Conclusions. The first experiments conducted in the SiO_2-MgO-FeO system in the presence of graphite and calcium carbonate showed that three phases which were detected at these experimental parameters are glass, quartz crystals <10-30 microns and calcium silicate similar to Ca-pyroxene in stoichiometry. There are no separate drops of the metallic phase of iron, the oxygen volatility was most likely controlled by a graphite buffer C-CO-CO_2-CO_3^{2-} so above the IW (Fe-FeO) buffer. This result is a case of crystallization in the region of instability of the metal phase.

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Zharkova E.V., Lukanin O.A. Intrinsic oxygen fugacity of minerals of spinel lerzolites from alkaline basalts of various regions

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Abstract. The data of electrochemical determinations of intrinsic oxygen fugacity (fO_2) of minerals (olivines, pyroxenes and spinels) from spinel lherzolites - xenoliths in alkaline basalt-basaltoids of Mongolia, the Baikal rift zone and the Middle Tien Shan are generalized. For all studied samples, the fO_2 values measured in the temperature range 800 - 1100 °C are located between the WM-IW buffer equilibria, varying within 1.5-2.5 log units. fO_2 depending on temperature, type of mineral, area of sampling. The difference in fO2 at a constant temperature close to the solidus of 1050 ° C between different samples is 2 log units. The highest fO_2 values were determined for the minerals of spinel lherzolites of the Baikal rift zone, and the lowest for the minerals of the Tien Shan. Assuming that the system is closed to oxygen as magmas rise from depth, the data obtained characterize possible variations in redox conditions within the spinel facies of ultrabasic rocks in the upper mantle. Oxythermobarometry measurements, indicate that the intrinsic oxygen fugacity recorded by spinel-bearing peridotite rocks, which originate at a depth of 30–50 km in the mantle, ranges from approximately 3 log units below to 2 log units above the fayalite–magnetite–quartz oxygen buffer.

Keywords: *intrinsic oxygen fugacity (fO_2), olivine (Ol), orthopyroxene (Opx), clinopyroxene (Cpx), spinel (Spl), buffers equilibrium, spinel lherzolites.*

The chemical potential of oxygen is one of the most important characteristics of the thermodynamic state of the upper mantle, the value of which is associated with the behavior of volatile components and elements of variable valence in the process of differentiation of its substance. Estimation of the intrinsic oxygen fugacity (fO_2) inherent in deep redox reactions is an important task, the solution of which is carried out either by thermodynamic analysis of mineral equilibria of ultrabasic xenoliths of the upper mantle, or by direct experimental determination of fO_2 (intrinsic oxygen fugacity) of minerals of deep origin using solid electrochemical cells. Both assessment methods are complicated by the lack of data on the thermodynamic properties of mineral phases at high pressures, the uncertainty of solid solution models, and the degree of preservation of mineral equilibria during the transport of xenoliths of the upper mantle to the Earth's surface. In general, the estimate of the oxygen potential for the upper mantle nodules is very limited.

The paper presents the results of electrochemical determinations of the intrinsic oxygen fugacity of minerals from xenoliths of spinel lherzolites from various regions: Mongolia (Shavaryn-Tsaram volcano), the Baikal rift zone (BRZ, Udakan basalt plateau) and the Middle Tien Shan (Kuraminskaya zone, Kachik pipe). They were carried out experimentally on a high-temperature furnace with two solid electrolytes based on zirconium oxide stabilized with yttrium oxide in the temperature range from 800 to 1100˚C at normal atmospheric pressure. The use of two cells makes it possible to determine the fO_2 of minerals with a small buffer capacity in relation to oxygen (Sato, 1972). Samples of spinel lherzolites were selected for the experiments, which made it possible to measure the intrinsic oxygen fugacity of all mineral components of these rocks: olivine (Ol), orthopyroxene (Opx), clinopyroxene (Cpx), and spinel (Spl). This should help to increase the reliability of the data obtained and to establish the degree of preservation of the equilibrium between the minerals of spinel lherzolites in relation to the chemical potential of oxygen.

Brief description of the samples ShTs Z-1 is a spinel lherzolite xenolith from the Shavaryn-Tsaram volcano in the north of the Khangai highlands, relatively rich in pyroxenes, can be attributed to primitive lherzolites. It is a weakly cemented rock of light green color. There are no secondary changes in minerals.

L 121-2 - xenolith of spinel lherzolite from the Udakan basalt plateau of the Baikal Rift Zone (BRZ) - is characterized by a low degree of depletion and does not bear traces of metasomatic transformations, brought to the surface by Cenazoic basaltoids within the Baikal Rift Zone (BRZ).

Kch 9 - xenolith of spinel lherzolite from the Middle Tien Shan, Kuraminskaya zone, pipe Kachik - potassium-sodium titanium basalts. One of the features of the Tien Shan deep matter is the low degree of oxidation of the rocks.

The chemical and mineral composition of the samples is shown in Tables 1a and 1b.

Table 1a. Chemical and mineral composition of olivines and spinels

Oxide	ShTs Z-1 *Ol*	K 121-2 *Ol*	Kch 9 *Ol*	ShTs Z-1 *Spl*	K 121-2 *Spl*	Kch 9 *Spl*
SiO_2	41.01	40.25	41.73	0.05	-	-
MgO	49.00	48.09	50.76	21.01	20.73	20.63
Al_2O_3	-	-	0.01	60.71	57.17	56.3
Na_2O	-	-	0.01	-	-	-
K_2O	-	-	0.02	-	-	-
CaO	0.06	0.07	0.00	-	-	-
TiO_2	0.00	0.01	0.04	0.15	0.19	0.36
$FeO+Fe_2O_3$	11.00	10.05	6.95	10.88	11.82	11.33
MnO	0.16	0.09	0.10	0.15	0.10	0.11
Cr_2O_3	0.00	0.08	0.00	7.20	10.83	10.10
V_2O_5	0.00	0.00	0.10	0.15	0.05	0.11
NiO	0.28	0.34	0.35	0.40	0.32	0.45
CoO	-	-	0.03	-	-	-
Sum	101.51	98.98	100.10	100.70	101.21	99.37
FM	11.34	10.58	7.23	-	16.51	20.18
Fo	88.42	89.12	92.45	-	-	-
Fa	11.58	10.88	7.55	-	-	-

Table 1 b. Chemical and Mineral Composition of Ortho and Clinopyroxenes

Oxide	ShTs Z-1 *Opx*	K 121-2 *Opx*	Kch 9 *Opx*	ShTs Z-1 *Cpx*	K 121-2 *Cpx*	Kch 9 *Cpx*
Na_2O	0.11	0.19	0.09	2.06	1.65	0.41
SiO_2	55.33	54.71	55.85	52.12	52.00	52.76
MgO	31.72	31.37	30.47	14.02	15.21	16.99
Al_2O_3	4.81	5.51	5.55	7.73	6.90	3.05
TiO_2	0.17	0.14	0.97	0.73	0.60	0.16
CaO	0.56	1.04	0.13	20.49	18.96	22.14
$FeO+Fe_2O_3$	7.01	6.56	6.41	2.97	3.31	3.27
MnO	0.15	0.14	0.21	0.1	0.10	0.03
Cr_2O_3	0.17	0.45	0.39	-	0.75	0.96
V_2O_5	-	0.02	0.00	-	0.00	0.07
NiO	-	0.02	0.15	-	0.01	0.04
CoO	-	-	-	-	-	0.05
Sum	100.02	100.15	100.2	100.22	99.49	99.93
FM	11.24	10.7	10.86	10.92	11.16	9.85
Wo	1.11	2.09	1.99	48.35	44.32	45.79
En	87.77	87.44	87.37	46.02	49.46	48.87
Fs	11.12	14.47	10.64	5.64	6.22	5.34

The results of experimental determinations for minerals of spinel lherzolites are given in table. 2. All phases are characterized by a linear relationship between log fO_2 and 1/T (K), which has the form:
$\log fO_2 = A - (B/T(K))$.

It is retained both in the direct (increase in temperature) and in the reverse (decrease in temperature) course of the experiment, which indicates the equilibrium nature of the measured values of the intrinsic oxygen fugacity for each measured mineral.

Let us consider the obtained fO_2 values for each spinel lherzolite sample.

ShTs Z-1, the measured values of intrinsic oxygen fugacity Ol, Opx, Cpx, and Spl of each spinel lherzolite sample are close to each other in terms of log fO_2 - (1/T)(K) and are located between the buffer equilibria WM and IW. The fO_2 values of minerals indicate the equilibrium character of the spinel lherzolite phases in relation to the chemical potential of oxygen.

K 121-2 - the measured values of the intrinsic oxygen fugacity Ol, Opx, Cpx and Spl of each spinel lherzolite sample are located between the buffer equilibria WM and IW at low temperatures (800-850 °C) and almost completely fall on the buffer straight line WM at a temperature of 1050 °C and above.

Kch 9 - the measured values of the intrinsic oxygen fugacity Ol, Opx, Cpx and Spl of each spinel lherzolite sample are located between the buffer equilibria QFI and IW at low temperatures (800-850 °C) and approximately 1-1.5 orders of magnitude higher than IW at t ≥ 1100 °C.

Table 2. Coefficients "A" and "B" in the empirical dependence log fO_2 = A- (B/ T(K)) for measured minerals of spinel lherzolites from different regions

Sample	Mineral	A	B	r	n	lg fO_2 (1050˚C)	Δ(lg $fO_{2\text{form.}}$- lg $fO_{2\text{QFM}}$)
ShTs Z-1, Shavaryn-Tsaram volcano	Ol	10.804	30887	0.991	10	-12.54	-2.36
	Opx	13.421	33982	0.996	11	-12.26	-2.08
	Cpx	12.481	33190	0.992	10	-12.61	-2.43
	Spl	12.468	32913	0.998	11	-12.41	-2.23
K 121-2, Udakan basalt plateau (BRZ)	Ol	13.444	33232	0.991	9	-11.67	-1.49
	Opx	16.550	37277	0.996	9	-11.63	-1.45
	CrDi	16.495	37411	0.991	9	-11.78	-1.60
	Spl	18.230	39911	0.993	9	-11.94	-1.76
Kch 9, Kachik pipe, Kuraminskaya zone, middle Tien Shan	Ol	15.260	37832	0.994	7	-13.34	-3.16
	Opx	13.777	36050	0.990	9	-13.47	-3.29
	Cpx	11.045	32285	0.991	9	-13.36	-3.18
	CrSpl	11.226	33086	0.980	8	-13.78	-3.6

r - the correlation coefficient; n - number of experimental points

The dependence log fO_2 - (1/T(K)) for the studied minerals reflects the specificity of the chemical composition of each of them, the concentration of variable valence elements and defects in the structure. At the same time, at temperatures that correspond to the equilibrium coexistence of crystals, the equality of the chemical potential of oxygen in them must be observed. This is a necessary condition and can be used as one of the geothermometers, as was first proposed by Sato (Sato, 1972). Based on the necessity of equality of fO_2 of equilibrium coexisting phases, it can be shown that the maximum temperature of the mineral associations of the studied spinel lherzolites corresponds to 1100 °C, the minimum temperature is 900°C. The results of calculations based on experimental data are given in table 3. These temperature values are in good agreement with those obtained from pyroxene thermometers (Ryabchikov et al., 1983).

Table 3. Equilibrium temperature of minerals **(°C)**

	ShTs Z-1	K 121-2	Kch 9
Ol/Opx	910	1029	929
Ol/Cpx	1100	1096	1043
Ol/Spl	945	1123	904

As a result of the measurements of the intrinsic oxygen fugacity for minerals of spinel lherzolites, the lowest fO_2, when compared at a temperature of 1050 °C, has a sample of Kch 9 (Middle Tien Shan, Table 2) and lies in the region of buffer equilibrium IW, then from fO_2 to 1.5-2 lg units above is the sample ShTs Z-1 from the Shavaryn-Tsaram volcano. If we compare the redox state of the sample from the Middle Tien Shan with the spinel lherzolite of the Baikal rift zone, then the fO_2 values of the latter are characterized by higher values and lie in the region of the buffer equilibrium WM at a temperature of 1050 °C. The data obtained confirm the idea of the heterogeneity of the upper mantle, its lithospheric and asthenospheric layers in relation to the redox regime (Kadik, 1990; Balthaus et al., 1990; Frost, McCammon, 2008; Foley, 2011; Stagno et al., 2013). Oxythermobarometry measurements show that intrinsic oxygen fugacity recorded by spinel-bearing peridotite rocks that form at a depth of 30-50 km in the mantle (Woodland, Koch, 2003) ranges from about 3 log units. below and up to 2 log units. above FMQ is a silica oxygen buffer (that is, the log (fO_2) value determined relative to the buffer equilibrium; denote this value ΔQFM (O'Neill, Wall, 1987; Wood, 1991).

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