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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 SiO₂-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 SiO₂-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 SiO₂-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 (fO₂ > 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 (10⁷-10⁸ 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 (H₂O, CO₂, N₂, 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.

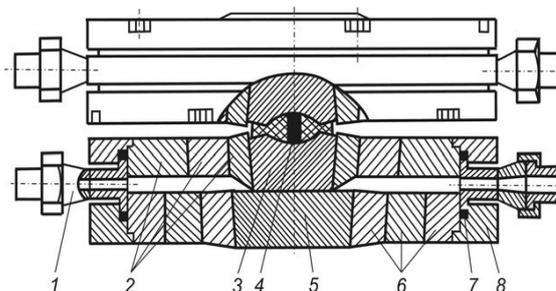


Fig. 1. A solid-phase device of the "anvil with a hole" type is a toroid. 1 – cooling system fitting; 2 – rings supporting the anvil; 3 – anvil; 4 – reaction volume; 5 – stand; 6 – stand support system; 7 – seal; 8 – housing.

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).

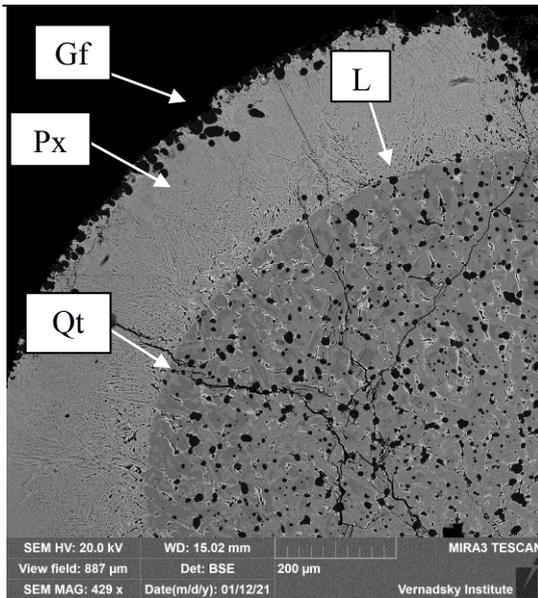


Fig. 2a. Contact of the marginal and central zones of the sample ($T=1600\text{ }^{\circ}\text{C}$, $P=2.5\text{ GPa}$). The central zone: L - glass of the basic composition, Qtz - quartz; the marginal zone: Px - pyroxene, Gf - graphite.

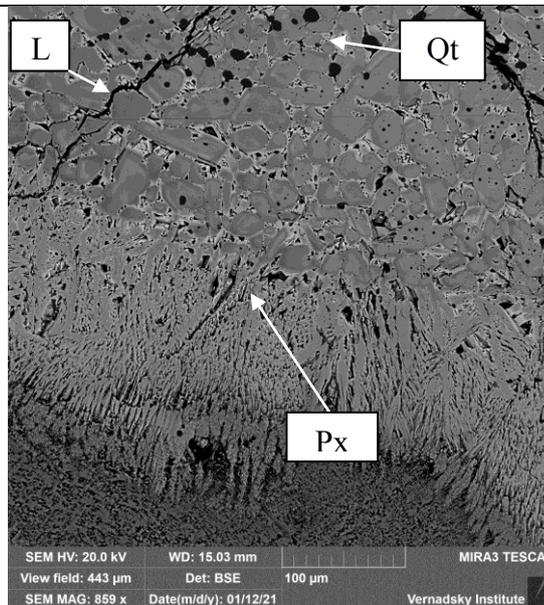


Fig. 2b. The edge zone of the sample ($T=1600\text{ }^{\circ}\text{C}$, $P=2.5\text{ GPa}$). Elongated pyroxene crystals (Px).

In experiments at $1600\text{ }^{\circ}\text{C}$ 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 ($T = 1600\text{ }^{\circ}\text{C}$ and $P = 3\text{ GPa}$), 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 ($T = 1600\text{ }^{\circ}\text{C}$ and $P = 3\text{ GPa}$). 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 $T = 1600\text{ }^{\circ}\text{C}$ 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). $T_{\text{exp}}=1600\text{ }^{\circ}\text{C}$, $P = 2.5$ 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 $T = 1600\text{ }^{\circ}\text{C}$ and $P = 3\text{ GPa}$.

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 SiO₂-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-CO₂-CO₃²⁻ 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 lherzolites 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 fO_2 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