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# EXPERIMENT

IN Mineralogy Crystallography  
Petrology Geophysics  
Geochemistry Isotopy

# GeoSciences

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Mineralogy  
Petrology  
Geochemistry

Crystallography  
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# GeoSciences

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**Rusak A.A., Lukanin O.A. Experimental study of silicate melts of basalt composition and the SiO<sub>2</sub>-MgO-FeO-C model system in equilibrium with a liquid iron alloy at high pressures. UDC: 550.4, 552**

Vernadsky Institute of Geochemistry and analytical chemistry RAS (GEOKHI RAS), Russia, 119991, Moscow, st. Kosygina, 19. (aleks7975@yandex.ru; lukanin@geokhi.ru)

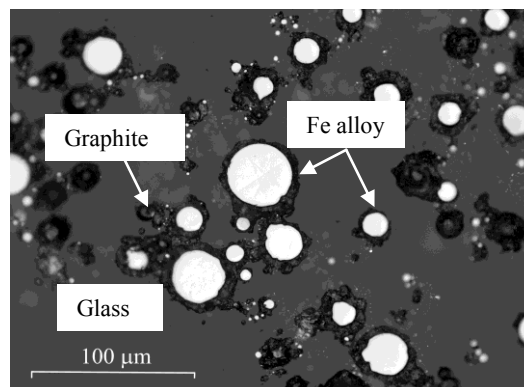
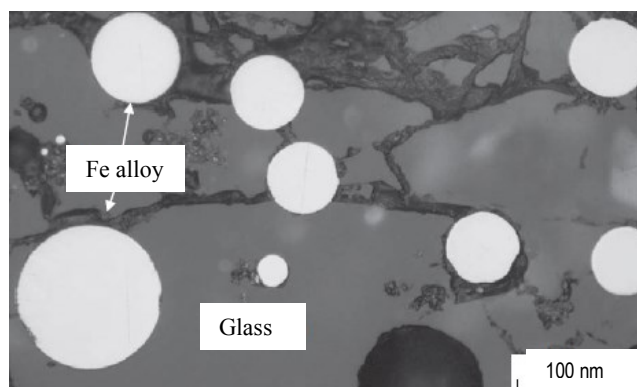
**Abstract.** The processes of formation in systems of ultrabasite, basite composition of the metallic phase of iron, which in natural conditions are realized in some basaltic magmas (for example, basalts of the Disco island), and can also occur during the melting of the restored mantle of the Earth and other planetary bodies, were modeled. The formation of liquid metal globules, mainly of Fe-(Ni) composition, was observed in experiments conducted with basite melts at T = 1400 and 1550°C, P = 1,5 and 4 GPa and oxygen volatiles at 1,4 – 1,9 and 0,5 – 2,9 log. units below the Fe-FeO buffer in the presence of graphite. In addition, experiments were carried out in the SiO<sub>2</sub>-MgO-FeO-C system at 1500 – 1600°C and 2.5-3 GPa on a high-pressure installation with a toroidal seal of the "anvil with a hole" type. According to the results of the study of quenching samples, no iron droplets were found in the experimental products. At T = 1600°C and P = 2,5 and 3 GPa, the products of the experiments were glass of the basic composition, quartz crystals and pyroxene. At T = 1500°C and P = 3 GPa, glass with graphite inclusions was formed. The volatility of oxygen in the experiments was controlled by a graphite CCO buffer. A three-component fusibility diagram is constructed for the SiO<sub>2</sub>-MgO-FeO

system, which outlines the area of possible separation of metallic iron droplets under ultra-reducing conditions.

**Keywords:** silicate melt; metallic phase of iron; melting; crystallization; reduced mantle; high pressures; oxygen volatility; CCO buffer; reducing conditions.

**Introduction.** Magma is a multicomponent system containing petrogenic, rare and volatile components. The main factors controlling the transport and composition of volatile components from the subsurface to the Earth's surface are the solubility of volatile components in magma and the redox conditions of their mantle source (Kadik et al., 2006). In modern theories of the formation of the early Earth, the composition of gases of the planet's outer shells is associated with the degassing of magmas formed during the global melting of the mantle ("magmatic ocean") in the presence of the metallic phase of iron (Wetherill, 1990; Walter et al., 2000) at low oxygen fugacity values. The source and composition of the early mantle volatiles remains a debatable issue. According to homogeneous accretion, volatiles could have accumulated from the introduced material of carbonaceous chondrites, which are enriched with water, since CI chondrites mainly consist of water-containing silicates (Wanke et al., 1984). According to the views (Javoy, 1995), carbon and hydrogen were in the silicate mantle of the Earth during the entire process of segregation of iron into the core. The presence of volatile components affects the PT conditions, the composition of the formed mantle magmas (early melting products of the Earth) and their differentiation.

The purpose of this study was to analyze the processes of crystallization and differentiation of magmatic melts under reducing conditions, when a metallic phase of iron is formed in equilibrium with the silicate melt and crystals.



**Fig.1.** Metal drops of iron alloy in glass of basalt composition (images in BSE) (Kadik et al., 2017). Experimental conditions: T = 1400°C, P = 1.5 GPa, ΔlgfO<sub>2</sub>(IW) = -1.8; with the addition of Si<sub>3</sub>N<sub>4</sub> from 0.4 to 2.8 wt. %.

**Fig.2.** Glass with drops of metallic iron (Fe alloy) and graphite crystals (images in BSE) (Lukanin et al., 2020). Experimental conditions: T = 1550°C, P = 4 GPa, ΔlgfO<sub>2</sub>(IW) = -2.9, CSiC = 7 wt. %

## Redox conditions for the formation of the Fe metallic phase in a basalt system containing C-O-H-N volatile components

The formation of liquid metal globules, mainly of Fe-(Ni) composition, was observed in experiments conducted with basite melts at  $T = 1400^{\circ}\text{C}$ ,  $P = 1.5$  GPa and oxygen volatility by 1.4 – 1.9 log units below the iron-wustite (Fe-FeO) - IW buffer in the presence of an excess of graphite C and nitride silicon ( $\text{Si}_3\text{N}_4$ ) is the source of nitrogen in the system (fig.1) and at  $T = 1550^{\circ}\text{C}$ ,  $P = 4$  GPa and 0.5 – 2.9 log. units below the IW buffer in the presence of graphite and silicon carbide (SiC) are the carbon source in the system (fig. 2).

In the works (Kadik et al., 2017; Lukanin et al., 2020), the forms of dissolution of volatile components were studied and their ratios in basalt melts equilibrium with liquid iron alloy and graphite were estimated by IR and RAMAN spectroscopy of glasses. It is shown that during experiments at  $T = 1400, 1550^{\circ}\text{C}$  and  $P = 1.5; 4$  GPa, nitrogen, hydrogen and carbon are present in the melts in the form of complexes with N-H bonds ( $\text{NH}_3, \text{NH}_4^+$ , etc.), because silicon nitride, N-O (water in molecular form and OH group), C-H ( $\text{CH}_4$ ) and other hydrocarbon complexes, as well as hydrogen and nitrogen molecules. It is also shown that hydrogen dissolves in the melt of the main composition in the form of water and with a decrease in the volatility of oxygen, the concentration of water decreases by half, while the content of methane and other compounds with C-H bonds increases, which indicates the influence of carbon and hydrogen on the restoration of the system. A decrease in  $f\text{O}_2$  leads to the release of the metallic phase and, accordingly, a change in the composition of the melt in terms of silica content from basalt to andesite.

## Experiments on the $\text{SiO}_2\text{-MgO-FeO-C-H}$ system

Tasks of the work are conducting experiments in the  $\text{SiO}_2\text{-MgO-FeO-C-H}$  system at  $T = 1500$  and  $1600^{\circ}\text{C}$  and  $P = 2,5\text{-}3,5$  GPa; construction of a three-component fusibility diagram for the  $\text{SiO}_2\text{-MgO-FeO}$  system.

## Methodology

As an initial mixture, a simplified model gross composition of the Earth ("All Earth") was set according to the data (McDonough, 2017). The initial mixture in terms of the content of the main petrogenic components consisted of powdered quartz ( $\text{SiO}_2$ ) (puriss.spec.), magnesium oxide ( $\text{MgO}$ ) (puriss.spec.) and iron oxalate ( $\text{Fe}_2\text{O}_4$ ), from which  $\text{CO}_2$  was released by heating and FeO (II) remained. A mixture of reagents was melted in quartz ampoules at  $T = 1505^{\circ}\text{C}$  and  $P = 1$  atm in a high-temperature

vertical tubular furnace Nabertherm RHTV 1700 in GEOKHI RAS. The selected pure glass without quartz was placed in the ensemble of a high-pressure installation "anvil with a hole" (NL-13T) with a toroidal seal, and an experiment was conducted at GEOKHI RAS for 40 minutes.

To determine the elemental 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, samples of the Smithsonian Institution's main glass composition (Glass XF2) were used as standards. Micrographs in backscattered electrons (BSE) were obtained at an accelerating voltage of 15 kV and a current of 30 nA. The analytical scanning electron microscope Tescan MIRA 3 at GEOKHI RAS was used to study phase relations and chemical composition. Raster 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.

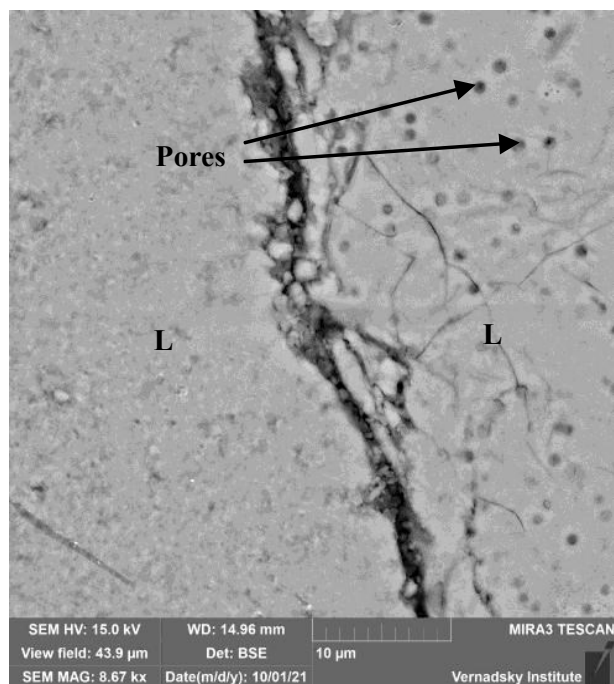
## Results of experiments and discussions

In experiments at a temperature of  $1600^{\circ}\text{C}$  a pressure of 2,5-3 GPa, metal iron droplets were absent, the experimental products were silicate glass of the main composition, quartz up to 25 microns in length and 5-10 microns in width, pyroxene and graphite. The structure of the samples is zonal, glass and quartz in the center, pyroxene on the periphery. Graphite partially penetrated into the edge zone. It occurs as rounded crystals up to 50 microns black in BSE. We work in an "open" system on the "anvil with a hole" installation, the samples are not in a platinum capsule, but in contact with graphite, it is impossible to estimate the gas phase (neither  $\text{CO}$ ,  $\text{CO}_2$ , nor  $\text{CH}_4$ ). The volatility of oxygen in the experiment was controlled by the CCO buffer. When the temperature drops by  $100^{\circ}\text{C}$  and at a pressure of 3 GPa, the structure of the sample changes, it becomes homogeneous. Pyroxene and quartz do not form, a porous glass remains (fig. 3), saturated with CaO, and there are also large graphite crystals, which are mainly located in the marginal zone of the sample, but there are also large crystals in the central part (fig. 4). It is possible that the crystals were captured by the melt during the experiment. There are no metallic iron droplets. At  $1500^{\circ}\text{C}$  CaO migrates to the sample. In order to avoid such problems, in a further experimental study, the assembly of the ensemble will be methodically changed, which will include a sleeve made of MgO:BN in a mass ratio of 3:1 (Bobrov et al., 2011), placed between a graphite heater and a lithographic stone - a toroid. The average compositions of the initial glass and glass after the experiments are presented in Table 1.

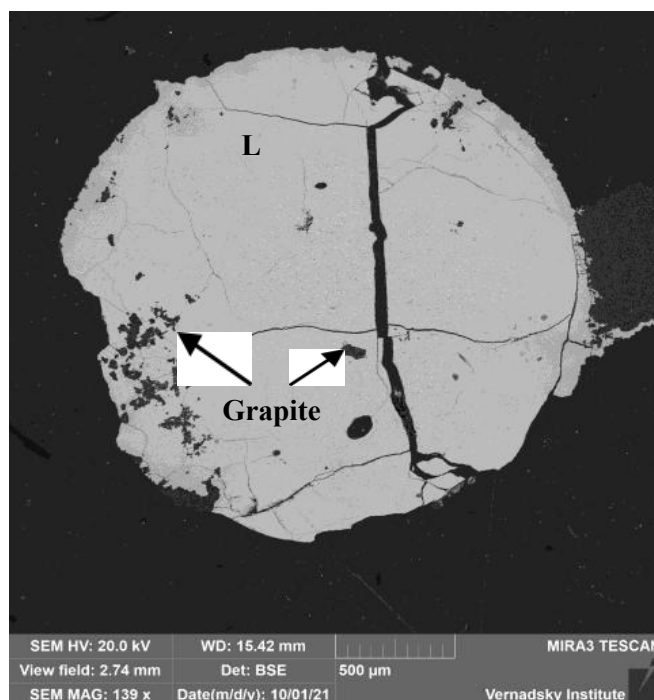
**Table 1.** Average compositions of glasses obtained at 1 atm in a tubular furnace, and average compositions of glasses obtained in experiments at  $T = 1600^{\circ}\text{C}$  and  $P = 2,5$  and 3 GPa.

Nº exp.	Comp.	SiO <sub>2</sub>	MgO	FeO	Total
The original 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 original 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).  $T=1600^{\circ}\text{C}$ ,  $P = 2,5$  and 3 GPa. The data are given in wt. %. X – average values, S – standard deviations. The data indicated in parentheses indicate the number of analyses.

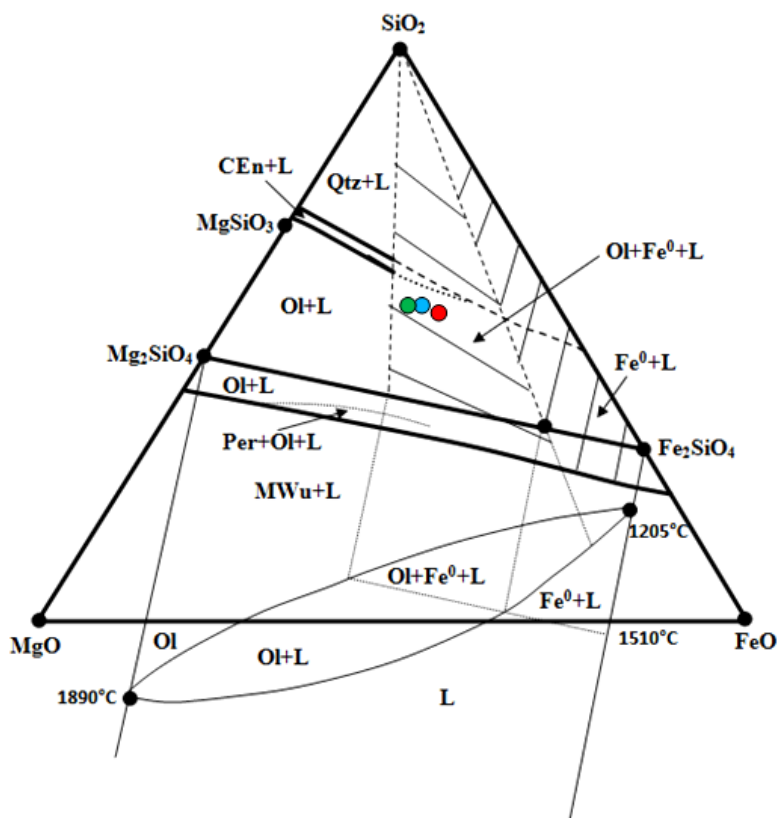
**Fig. 3.** Porous glass ( $T=1500^{\circ}\text{C}$ ,  $P=3\text{GPa}$ , CCO buffer). The image is in BSE.

The liquidus surface of the triple fusibility diagram for the  $\text{SiO}_2\text{-MgO-FeO}$  system was constructed, which shows the area of possible separation of metallic iron droplets under ultra-reducing conditions (the shaded area is shown in fig. 5). To construct the diagram, diagrams of the state of the periclase-quartz, wustite-quartz and periclase-wustite systems at a pressure of 1 atm were used. The diagram of the state of the forsterite-fayalite system shows the stability region of metallic iron, the product of incongruent melting of ferruginous olivine at  $T = 1510^{\circ}\text{C}$ ,  $P = 1$  atm (Yoder, 1979). This makes it possible to approximate the area of compositions in which the metal phase  $\text{Fe}^0$  can be formed in equilibrium with the melt and olivine crystals. The points of the experimental compositions marked with colored circles on the diagram fall into the region of melt, olivine crystals and the  $\text{Fe}^0$  metal phase (red is

**Fig. 4.** CaO supersaturated glass with large graphite crystals (Grf).

the initial composition; blue –  $1600^{\circ}\text{C}$ , 3 GPa; green –  $1600^{\circ}\text{C}$ ; 2,5 GPa). As the pressure increased, the composition of the melt changed to the area of saturation of the system with silica, i.e. to the area of andesite composition.

In nature, there are deposits in the basalts of which there are quite large accumulations of iron, for example, Disco Island. According to E.M. Spiridonov are "Disco Island is a natural metallurgical process." The question of the origin of such deposits remains debatable. One of the points of view is the interaction of platiobasalts with the coal-bearing strata lying on metamorphites. Such iron accumulations could form at oxygen volatility close to the CCO buffer, but at low pressures.



**Fig. 5.** The fusibility diagram for the  $\text{SiO}_2\text{-MgO-FeO}$  system, which shows the area of possible separation of the metallic phase of iron under reducing conditions. Melt compositions: red circle – initial composition; blue –  $T = 1600^\circ\text{C}$ ,  $P = 3$  GPa; green –  $T = 1600^\circ\text{C}$ ,  $P = 2,5$  GPa. Symbols: L – melt, Qtz – quartz ( $\text{SiO}_2$ ), Per – periclase ( $\text{MgO}$ ), Wu – wustite ( $\text{FeO}$ ), MWu – magnesio-wustite ( $(\text{Mg,Fe})\text{O}$ ), CEn – clinoenstatite ( $\text{MgSiO}_3$ ), Ol – olivine ( $\text{Mg}_2\text{SiO}_4$  (forsterite) –  $\text{Fe}_2\text{SiO}_4$  (fayalite)),  $\text{Fe}^0$  is metallic iron.

**Conclusions.** Experiments carried out on the "anvil with a hole" installation in an open system without platinum capsules do not allow to obtain metal droplets when buffering the system with carbon, because this area is at  $f\text{O}_2$  (CCO), which is higher than  $f\text{O}_2$  (IW). In the experiments of the  $\text{SiO}_2\text{-MgO-FeO-C-H}$  system, glasses saturated with calcium oxide were obtained at  $T = 1600^\circ\text{C}$  and  $P = 2,5\text{-}3$  GPa, the phase of calcium pyroxene crystallizes along the edges of the sample and graphite, in the form of inclusions, the central zone is represented by glass and quartz crystals, at  $T = 1500^\circ\text{C}$  and  $P = 3$  GPa, the glass structure becomes homogeneous and porous with large graphite inclusions. In the constructed diagram of the fusibility of the considered system, the composition points of the experimental samples fall into the stability region of the melt, olivine crystals and the  $\text{Fe}^0$  metal phase.

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**Shchekina T.I.<sup>1</sup>, Zinovieva N.G.<sup>1</sup>, Rusak A. A.<sup>2</sup>, Khvostikov V.A.<sup>3</sup>, Kotelnikov A. R.<sup>4</sup>,**