Formation and differentiation of magmas

Gorbachev N.S., Kostyuk A.V., Nekrasov A.N., Sultanov D.M. Experimental modeling of mantle-crust interaction: the influence of fluid (H_2O, H_2O+CO_2, H_2O+HCl) on melting, phase composition and critical relationship between melt and fluid

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Abstract. Effect of fluids on melting, phase composition and critical relationship between melt and fluid were studied experimentally in system peridotite-basalt-(Na, $K)_2CO_3$-fluid at P=4.0 GPa, T=1400ºC. Experiments were carried out in anvil-with-hole apparatus by a quenching technique. At H_2O+CO_2, H_2O+HCl fluids and "dry" condition subcritical conditions were observed. Interaction of peridotite with melt and fluid provide pyroxenization and phlogopitization of peridotite, origin of K-containing (up to 1.5 wt.% K_2O) Cpx, formation of SiO_2-rich magma normal or elevated alkalinity. Critical relations between partial silicates melt and H_2O-containing fluid observed in presence of aqueous fluid. The supercritical fluid-melt interacts with Ol, Opx, ± Ca-Cpx restite of peridotite to form a reaction K-containing Cpx, carbonate Cb, and quenching phases – Flog, globules Al-Si glass. Identified effects explain local development phase and chemical heterogeneity of the upper mantle and the mantle magmas.

Key words: experiment, mantle, crust, fluid, interaction, melting, critical relationship, phase composition.

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Introduction. Geophysical and geochemical data indicate on large-scale exchange of matter between crust and mantle. The most important exchange mechanism is the subduction of oceanic slab, leading to formation of volatile-enriched mantle reservoirs with protoliths subducted slab. Fluids have an effective influence on the phase relations and melting of the mantle. Effect of fluids on melting, phase composition and critical relationship between melt and fluid has been studied experimentally in system peridotite-basalt-(Na, $K)_2CO_3$-(H_2O, H_2O + CO_2, H_2O + HCl.

Experiments. Experiments were carried out on an anvil-with-hole apparatus by a quenching technique at P=4 GPa, T=1400°C in IEM RAS, Russia. Mixture of fine powders of tholeiitic basalt, Mss (~10 wt.%) and (Na, $K)_2CO_3$ (~10 wt.%) used as a starting materials. Sources of fluids (20-25 wt.% relative to silicate) were $H_2C_2O_4x2H_2O$; distilled H_2O; 1N HCl. Peridotite ampoule with starting mixture and fluid placed in to the Pt ampoule and hermetically sealed [Gorbachev, 2000]. Duration of experiment was 18-24 hours. Products of experiments were studied by scanning electron microscope CamScan MV2300.

Experimental results. Phase relations and composition melts, formed by partial melting of initial samples, depend on composition of fluids (tabl. 1).

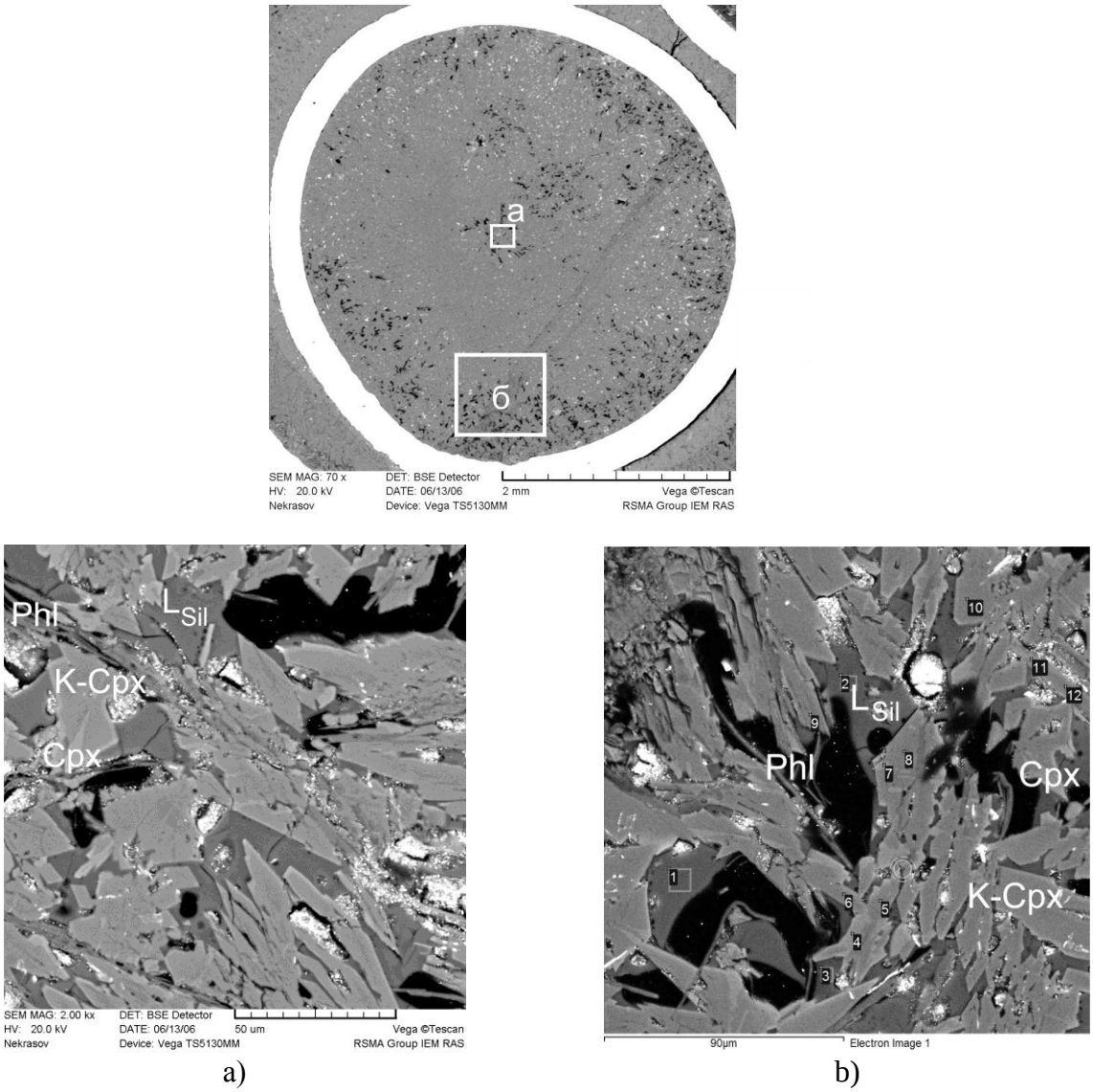
Table 1. Composition (wt.% oxides) of coexist phases at partial melting of peridotite (ampoule)-basalt-(Na, $K)_2CO_3$-fluid system.

	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	Cr_2O_3	MnO	FeO	Total
H_2O+CO_2 fluid												
Basalt part												
L_{Sil}	4.19	0.28	22.23	65.69	0.00	1.87	4.87	0.17	0.00	0.00	0.69	100.00
K-Cpx	2.33	19.13	11.72	45.72	0.18	0.67	10.08	0.42	0.67	0.32	3.78	95.02
Cpx	0.84	16.05	8.84	50.95	0.00	0.00	16.51	0.47	0.47	0.17	4.83	99.12
Phl	1.33	22.29	14.44	41.35	0.82	6.76	0.06	0.36	0.38	0.20	2.94	91.2
Peridotite part												
L_{Sil}	4.22	0.31	21.59	65.52	0.54	1.81	4.42	0.13	0.14	0.04	1.29	100.00
K-Cpx	2.38	19.56	11.98	46.77	0.18	0.69	10.31	0.43	0.68	0.33	3.87	97.19
Cpx	0.84	16.02	8.82	50.84	0.00	0.00	16.48	0.46	0.46	0.17	4.82	98.92
H_2O fluid												
Ol	0.38	50.20	0.78	40.23	0.17	0.04	0.18	0.40	2.36	0.12	6.08	100.75
K-Cpx	2.09	14.36	15.02	41.78	0.23	1.50	10.87	0.85	0.10	0.21	6.56	93.6
Cpx	0.89	11.97	11.54	45.82	0.00	0.10	21.69	2.04	0.18	0.00	3.77	98.16
Opx	0.00	33.33	4.88	54.29	0.06	0.00	1.69	0.28	1.03	0.13	3.54	99.23
Phl	1.31	21.92	14.20	40.67	0.81	6.65	0.06	0.35	0.37	0.20	2.89	89.70
L_{Sil}- glob	6.81	0.00	18.60	53.08	0.13	2.83	0.22	0.24	0.04	0.12	0.10	82.30
L_{Carb}	0.89	3.21	0.72	2.59	0.00	0.10	42.89	0.17	0.05	0.48	0.88	52.07
«dry» system												
Contact "peridotite-basalt"												
Opx	0.99	32.86	5.99	54.99	0.57	0.27	3.27	0.39	0.84	0.25	2.59	103.63
Phl	1.25	25.54	13.11	40.77	0.48	8.03	0.13	0.50	1.94	0.00	1.24	93.85
Cht	0.26	20.03	16.61	0.30	0.04	0.15	0.00	0.32	54.95	0.57	5.90	99.99
L_{Sil}	8.69	1.24	22.67	64.00	0.00	1.50	0.69	0.40	0.00	0.16	0.65	100
Peridotite part												
Opx	0.48	32.37	5.48	53.49	0.00	0.00	2.07	0.11	2.14	0.00	2.48	99.23
Cpx	1.87	16.46	5.61	51.05	0.31	0.00	17.57	0.66	0.67	0.25	2.09	96.54
Phl	1.10	25.49	12.71	41.53	0.00	7.37	0.89	0.66	1.41	0.09	1.91	93.15
Cht	0.57	18.62	18.36	0.26	0.69	0.00	0.10	0.21	50.43	0.55	7.17	97.49
L_{Sil}	11.84	0.00	21.29	63.15	0.14	1.64	0.47	0.40	0.06	0.37	0.65	100

	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	Cr_2O_3	MnO	FeO	Total
H_2O+HCl fluid												
L_{Sil}	1.34	2.22	17.74	72.29	0.10	1.53	3.20	0.19	0.00	0.31	0.71	100.00
Ol	0.16	46.82	0.59	40.57	0.07	0.05	0.00	0.90	2.24	0.37	8.20	100.00
Cpx	0.89	15.69	9.98	50.72	0.06	0.04	18.27	0.70	0.86	0.44	3.85	101.42
K-Cpx	2.38	19.72	12.69	46.75	0.05	0.68	10.32	0.49	0.66	0.00	3.63	97.42
Phl	1.56	23.46	12.88	41.55	0.16	7.01	0.18	0.31	0.88	0.41	2.35	90.78

*The compositions of silicate glasses (quenched melts) recalculated to 100%.

H_2O+CO_2 fluid. Quenching samples "inherit" the structure of peridotite ampoules. Distinguished: internal - "basalt" part (Fig. 1a), the reaction zone at the contact of basalt-peridotite and outer peridotite part of the ampoule (Fig. 1b). Partial melting at subcritical conditions. Composition of coexisting phases: Cpx + KCpx + Flog + dacite Gl +/- Opx. (fig.1 a). Feature is the olivine absence among the liquidus minerals. Sulfides are concentrated in the reaction zone. Oval shape sulfides indicate partial melting of the original Mss. Matrix represented by pentlandite and Ni-pyrrhotite compositions with inclusions of Pt-Fe phase.



a) b)

Fig. 1. BSE images of experimental samples (peridotite (ampoule)-basalt-$(Na, K)_2CO_3$- H_2O+CO_2 fluid system, T=1400°C, P=4.0 GPa). Upper figure - a general view of a longitudinal section of the ampoule; a) basalt; b) peridotite.

H_2O fluid. Partial meting at critical relations melt-fluid. The system showed complete disintegration of the sample. Although at cross-sectional of quenching samples (Fig. 2a) can be traced components of peridotite ampoules ("Basaltic" (Fig. 2b), and the reaction zone of the peridotite (Fig. 2c)). Intergran glass is not present. Composition of coexisting phases: (Ol + Opx + Cpx)-relicts of peridotite, + (KCpx + Flog + Cb + Gl globule)-reactionary and quenching phases. (Fig. 2).

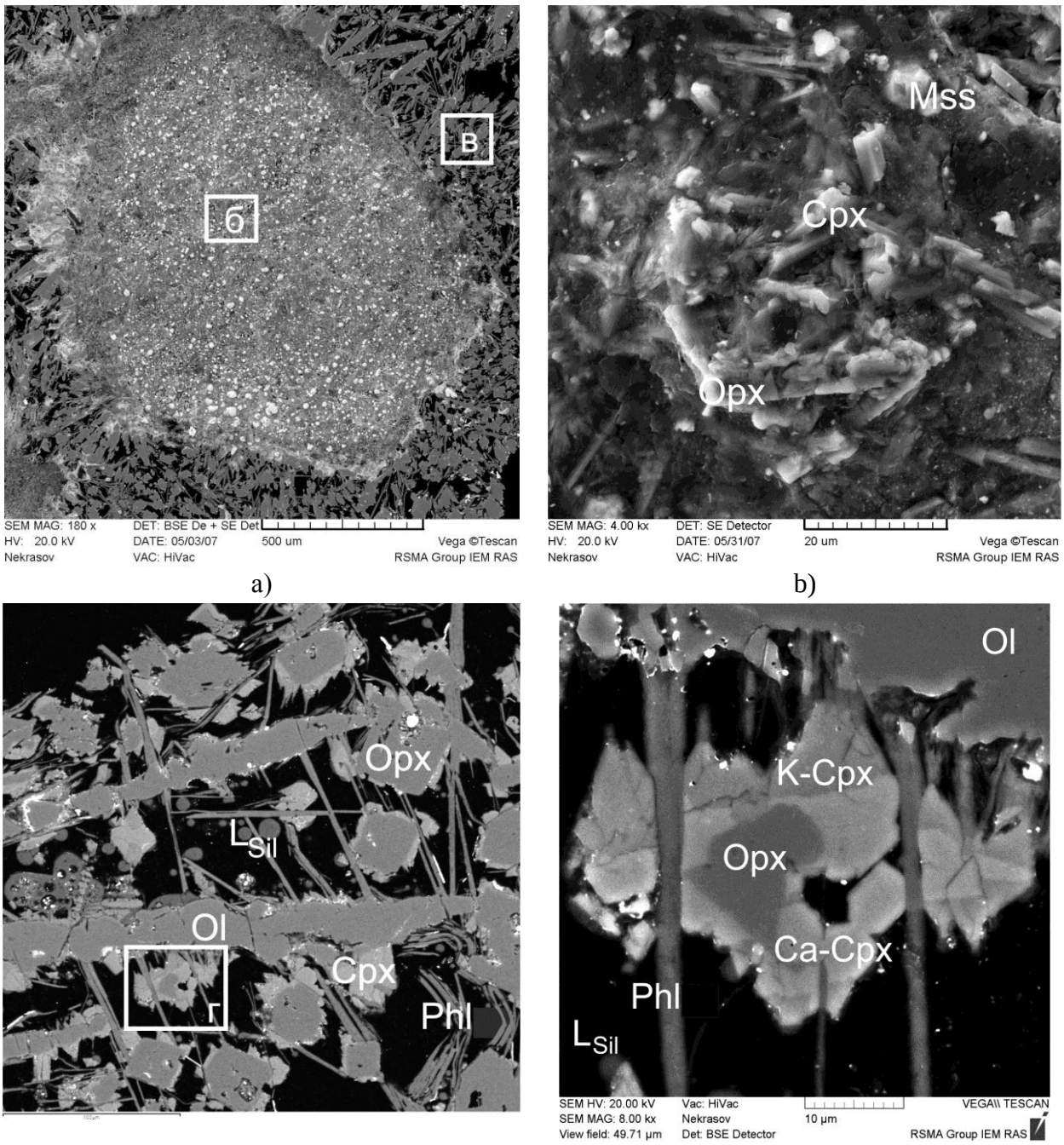


Fig. 2. BSE images of experimental samples (peridotite (ampoule)-basalt-($Na, K)_2CO_3$ - H_2O fluid system, T=1400°C, P=4.0 GPa). a) general view of a longitudinal section of the ampoule; b) basalt; c) peridotite.

"Dry" system. Partial meting at subcritical conditions. Quenching samples have a massive texture, due to the fact that the massive silicate glass cements solid liquidus phases. There are pyroxenization of peridotite due to fluid-melt-peridotite interaction. Composition of coexisting phases: Opx + Cpx + Flog + Cht + Mss-PtFe + trachyandesite Gl. (Fig. 3).

H_2O+HCl fluid. Partial meting at subcritical conditions. Composition of coexisting phases: Ol + Opx + Cpx + Flog + dacite Gl + NaCl (Fig. 4).

Conclusions. Quenching samples from the experiments with H_2O+CO_2, H_2O+HCl and in the absence of fluid preserving the structure of the starting sample. Signs of partial melting of peridotite and eclogite present in the samples. Intergranular silicate glass cements liquidus phase, samples have massive texture. These features indicate that partial melting of the system H_2O+CO_2, H_2O+HCl and at "dry" conditions occurred at subcritical PT. Since T of experiment (1400°C) is greater than T solidus of fluid-bearing peridotite and eclogite, the absence of intergranular glass - typomorphic telltale signs of partial melting of eclogite and peridotite, has another reason. Abnormal texture and phase composition of the quenching samples from experiment with H_2O fluid can be explained by the existence of critical relations between the partial silicate melt and aqueous fluid. The formation of reactive minerals can be explained by high reactivity of supercritical fluid-melt.

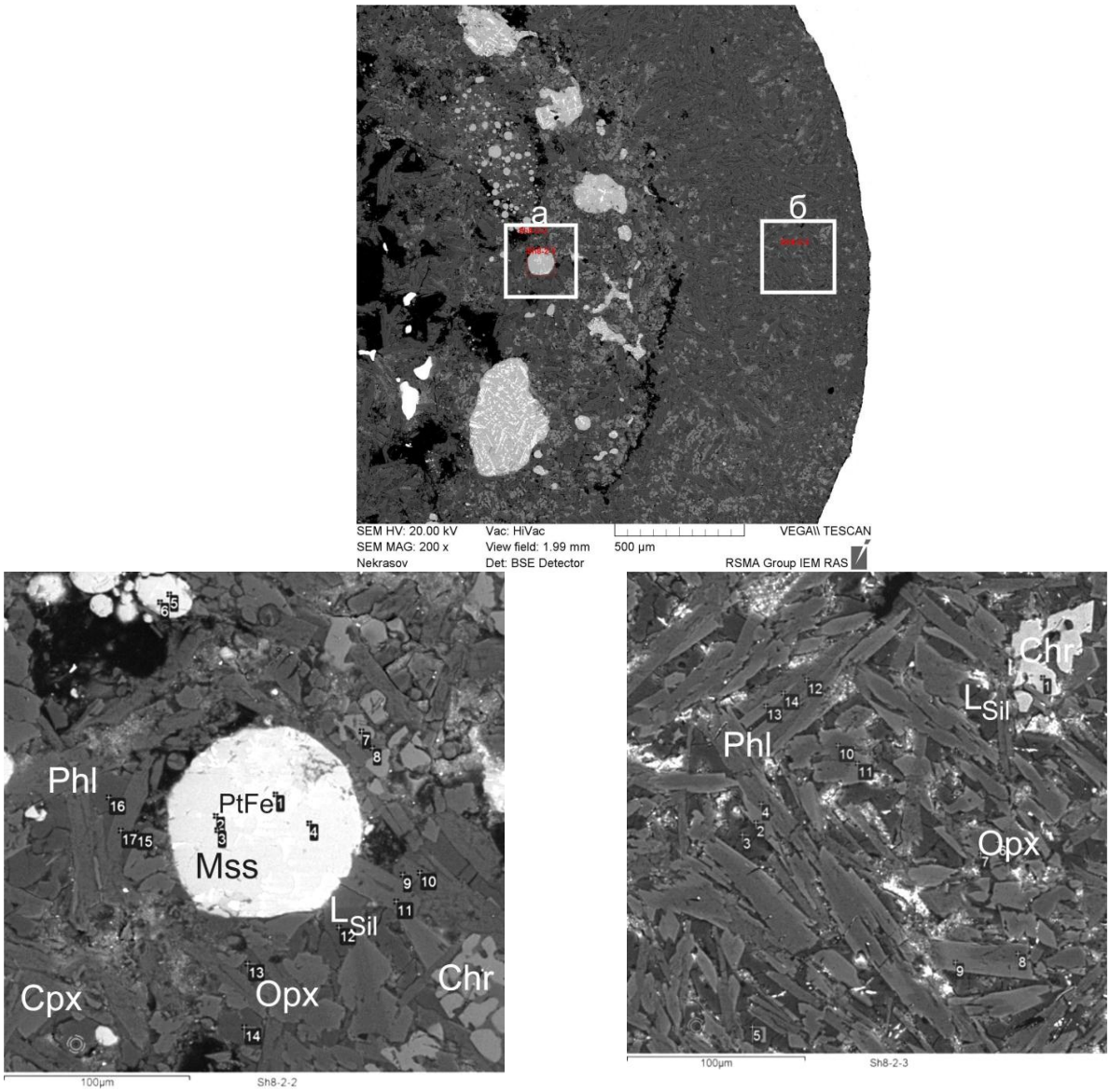


Fig. 3. BSE images of experimental samples (peridotite (ampoule)-basalt-(Na, K)$_2$CO$_3$ system, T=1400°C, P=4.0 GPa). Upper figure - a general view of the ampoule; a) contact basalt-peridotite; b) peridotite.

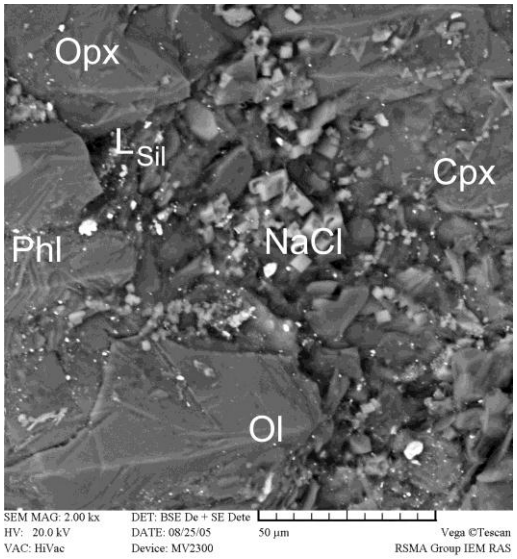


Fig. 4. BSE images of experimental samples (peridotite (ampoule)-basalt-(Na, K)$_2$CO$_3$- H$_2$O+HCl system, T=1400°C, P=4.0 GPa).

Feature of fluid-containing silicate systems is the existence of critical relationships between silicate melts and fluids due to their high mutual solubility. There is complete miscibility between melt and fluid at supercritical pressures and temperatures $P_кT_к$. The complete miscibility between the liquidus phases, melt and fluid occurs in the second critical end point ($2P_кT_к$) at equality solidus P-T of silicate and $P_кT_к$ of two-phase equilibrium melt-fluid. Critical pressure and temperature of $P_кT_к$ and $2P_кT_к$ studied experimentally in H_2O-containing silicate systems of monomineral (SiO_2, albite, nepheline, jadeite) and granitic compositions. In these systems, $P_кT_к$ are in the range P=0.7-2.3GPa, T=550-1050ºC, increasing in the sequence Q, Ne, Ab, Jd, granite [Bureau, Keppler, 1999]. In systems of basic and ultrabasic composition focused on $P_кT_к$ of the second critical end point $2P_кT_к$. In the system Fo-En-H_2O pressure of $2P_кT_к$ estimated at 12-13GPa [Stalder et al. 2001], basalt (eclogite) + H_2O at 6.5GPa [Kessel et al., 2005], basalt (eclogite) + peridotite + H_2O at 3.8-4.0 GPa [Gorbachev, 2000], peridotite + H_2O at 3.8GPa [Mibe et

al., 2007]. In the system Fo + En + H_2O + CO_2 pressure of $2P_кT_к$ estimated at 12-15GPa [Willy, Rhyabchikov, 2000]. Information on the critical relationship between the partial melts and fluids is virtually nonexistent.

Thus, a review of publications on the critical relations in the silicate-fluid systems does not contradict the hypothesis that abnormal texture and phase composition of the quenching samples with H_2O fluid due to the existence of critical relationships between the above-solidus silicate melt and aqueous fluid.

Experimental results show an effective influence of fluid on the phase relations and melt composition. Absence of olivine in the quenching samples, piroksenization and phlogopitization of peridotite ("dry" conditions, H_2O + CO_2 fluid) can be explained by the interaction of partial melts and fluid with peridotite. Galite and quenching globules of Al-Si glass formed with H_2O + HCl fluid. Composition of the melt depends on the composition of the fluid: H_2O + CO_2 fluid - tonalite melts composition; H_2O + HCl fluid – riodacitic melts; "dry" system - alkaline melts as feldspathic syenite.

The critical correlation between partial silicate melt and water-based fluid were observed in the presence of H_2O fluid. The supercritical fluid-melt interacts with Ol, Opx, ± Ca-Cpx restite of peridotite to form a reaction K-Na-containing clinopyroxen, carbonate, and by quenching – phlogopite, globules Al-Si glass. After quenching intergranular silicate glass is not formed, its absence leads to destruction of quenching samples. Identified effects explain local development of phase and chemical heterogeneity of the upper mantle and the mantle magmas.

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References:

1. Gorbachev N.S. (2000). Supercritical state in hydrous mantle according to an experimental study of fluid-containing peridotite at P=40kb, T=1400°C. DAS (in Russian). 370.3. C. 365-368.
2. Bureau H., Keppler H. (1999). Complete miscibility between silicate melts and hydrous fluids in the upper mantle: experimental evidence and geochemical implications. Earth and Planetary Science Letters. 165. P. 187-196.
3. Stalder R., Ulmer P., Thompson A.B., Gunther D. (2001) High pressure fluids in the system MgO–SiO_2–H_2O under upper mantle conditions. Contrib. Mineral. Petrol. V.140. P.607-618.
4. Kessel R., Ulmer P., Pettke T., Schmidt M.W., Thompson A.B. (2005). The water-basalt system at 4 to 6 GPa: Phase relations and second critical endpoint in a K-free eclogite at 700 to 1400°C. Earth and Planetary Science Letters. 237. P. 873-892.
5. Mibe K., Kanzaki M., Kawamoto T., Matsukage K.N., Fei Y.W., Ono S. (2007). Second critical endpoint in the peridotite–H_2O system. Jour. Geophys. Res. V.112. B03201, doi:10.1029/2005jb004125
6. Wyllie P.J., Ryabchikov I.D. (2000). Volatile components, magmas, and critical fluids in upwelling mantle. Jour. Petrol. V.41. P.1195-1206.

Gorbachev N.S., Kostyuk A.V. Distribution of rare and rare earth elements between Grt, Cpx and Cb at mantle P-T (from experimental data)

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Abstract. Distribution coefficients D of trace elements between Cpx, Grt and carbonatite melt Cb at P = 4 GPa, 1100-1350°C showed broad (2.5-3 order) variation. High affinity for carbonate (D silicate / carbonate <1) have P, LREE, Sr, Ba, U, Th, Ta, and to silicates - Sc, Ti, Cr, Mn, Co, Ni, Cu, Zn . Grt is more efficient concentrator of trace elements than Cpx. Variations in D indicates the effectiveness fractionation of trace elements in silicate-carbonate systems.

Key words: experiment, trace and rare earth elements, distribution, garnet, clinopyroxene, carbonate.

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Introduction. Carbonatite melts play an important role in the upper mantle metasomatism, enriching its volatile and incompatible elements. For understanding the behavior of trace elements in these processes, it is important to know their distribution between minerals of peridotite, carbonate and homogeneous silicate-carbonate melts. Distribution of trace elements between Cpx, Grt and carbonate melt (Cb) at high P (> 4 GPa), T (up to 1600°C) and different compositions was studied in a number of papers [Adam, Green, 2001; Klemme at al., 1995; Sweney et al., 1995; Dasgupta et al., 2009; Grassi, Schmidt, 2011; Grassi et al., 2012; Girnis et al., 2006; Yao et al., 2012]. In experimental studies of Girnis et. al. (2013) describes the features the behavior of trace elements in silicate (Cpx, Grt, Opx) - carbonate systems, the application of the experimental data to the genesis of kimberlites, proposed recommended values of D Cpx, Grt/Cb. Our investigation of the distribution of trace and rare-earth elements between clinopyroxene (Cpx), garnet (Grt) and carbonate (Cb) cover the least studied interval of P-T (3.8-4 GPa, 1100-1350°C). Furthermore, unlike the majority data obtained in "dry" conditions, our experiments carried out with H_2O-fluid.

Methods. Experiments were carried out in Au and Pt capsules on an anvil-with-hole apparatus by a quenching technique. Mixture of fine powders of silicate (Si) and carbonate (Cb) was placed in hermetically sealed ampoule. Cpx from Kovdor pegmatites of $Ca_{1,02}Mg_{0,89}Fe_{0,09}Al_{0,05}Si_{1,94}O_6$ composition, Grt from Grt-containing dikes of UHP carbonatites of Tromso area, Norway ($Mg_{0,76}Ca_{0,94}Fe_{1,30}Al_{1,94}Fe_{0,10}Si_{2,94}O_{12}$ composition), and calcite (Cc) carbonatite from Kovdora were used as the starting materials. Na_2CO_3, K_2CO_3, H_2O were used as volatile components. Temperature was measured with Pt30Rh/Pt6Rh thermocouple, pressure at high temperatures calibrated for the curve of quartz - coesite equilibrium. The accuracy of determining the temperature and pressure in the experiments measured at ± 5°C and ±1 kb [Litvin, 1991]. Duration of the experiment was 18-24 hours. Products of experiments were studied and analyzed by electron microprobe. Concentrations of trace elements in silicate and carbonate phases were determined by ICP MS in Chernogolovka.

Results. Table 1 shows representative chemical compositions of Cb and Si fractions of quenching samples; on Fig. 1 - their microphotograph; on Fig. 2 - partition coefficients of trace elements between Cpx, Grt and Cb.

Table 1. Composition of coexisting phase in Cpx-Cb and Grt-Cb systems.

Cpx-Cb system

	1200°C		1250°C		1300°C		1350°C	
	Cpx	Cb	Cpx	Cb	Cpx	Cb	Cpx	Cb
SiO_2	54.22	2.44	53.87	0.13	53.15	0.53	54.80	1.70
TiO_2	0.00	0.05	0.63	0.00	0.31	0.04	0.00	0.08
Al_2O_3	1.09	0.16	1.55	0.00	1.17	0.03	1.08	0.07
FeO	0.13	0.03	0.97	0.22	2.94	0.04	0.00	0.00
MnO	0.07	0.07	0.09	0.02	0.01	0.00	0.00	0.00
MgO	16.75	1.17	24.12	0.76	16.41	0.67	17.60	0.49
CaO	23.00	47.63	10.89	50.72	25.24	50.70	24.87	50.15
Na_2O	0.72	0.16	2.90	0.00	0.21	0.12	0.70	0.26
K_2O	0.11	0.07	2.96	0.15	0.15	0.14	0.12	0.97
P_2O_5	0.08	0.20	2.04	0.04	0.00	0.00	0.01	0.56
Cr_2O_3	0.00	0.00	0.00	0.12	0.00	0.00	0.00	0.00
SrO	0.25	0.49	0.14	0.51	0.27	0.46	0.33	0.45
Total	96.44	52.63	100.17	52.64	100.03	52.73	100.22	54.91

Grt-Cb system

	1100°C		1200°C		1250°C		1350°C	
	Grt	Cb	Grt	Cb	Grt	Cb	Grt	Cb
SiO_2	38.92	0.10	40.01	0.87	39.34	1.54	37.08	3.36
TiO_2	0.04	0.11	0.33	0.61	0.10	0.00	0.88	0.03
Al_2O_3	21.24	0.32	22.10	0.43	22.29	0.51	23.59	1.66
FeO	22.00	4.10	22.22	4.81	9.25	0.92	5.96	1.39
MnO	0.11	0.01	0.65	0.09	0.33	0.12	0.21	0.11
MgO	6.81	8.23	6.53	7.40	4.59	1.11	5.72	1.28
CaO	9.63	35.40	10.15	40.21	23.79	47.52	22.31	44.34
Na_2O	0.02	0.00	0.15	0.00	0.13	0.39	0.96	0.17
K_2O	0.07	0.00	0.00	0.09	0.00	0.35	0.11	0.57
P_2O_5	0.01	0.00	0.18	0.00	0.00	0.05	1.01	0.00
Cr_2O_3	0.08	0.05	0.05	0.04	0.00	0.00	0.14	0.10
SrO	0.64	0.21	0.41	0.38	0.18	0.43	0.52	0.57
Total	99.59	48.52	102.78	54.93	100.01	52.94	99.64	53.77

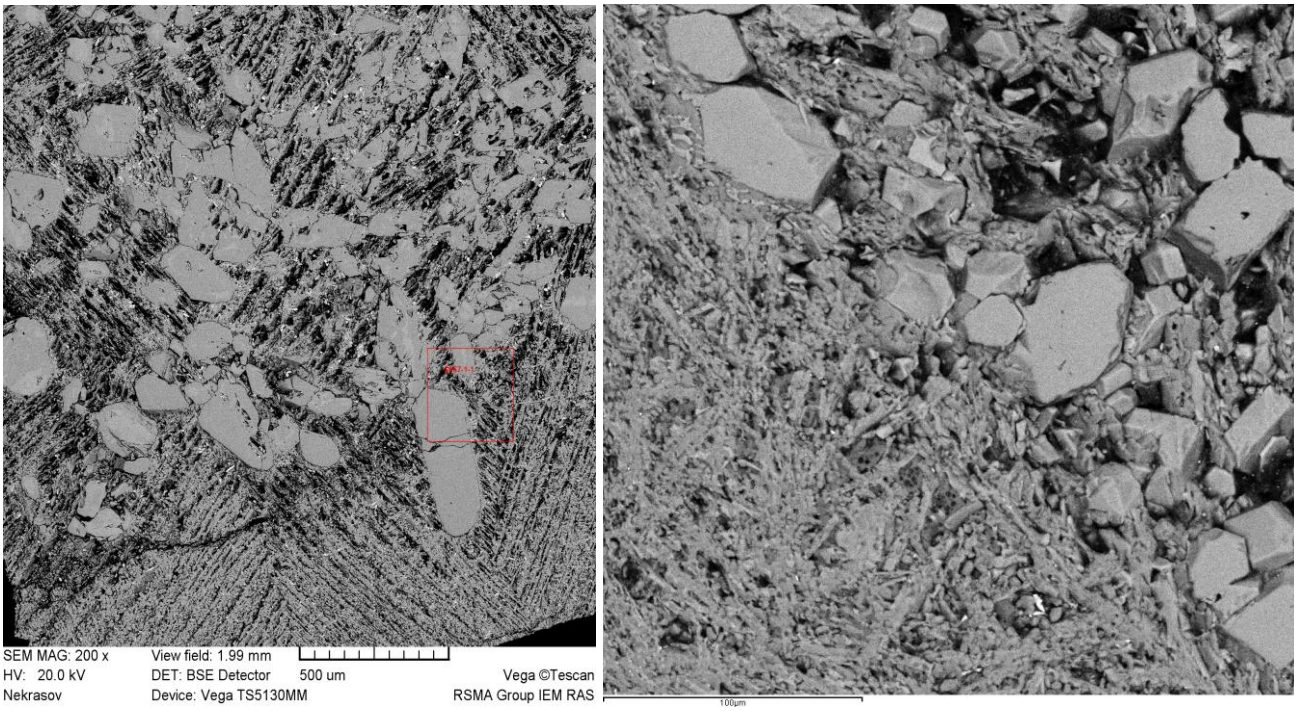
The main results and their discussion. Wide (2.5-3 order) variation of the distribution coefficients D Si/Cb of trace elements between Si and Cb were identified. High affinity for carbonate (concentrated in carbonates, D silicate/carbonate <1) possess P, LREE, Sr, Ba, U, Th, Ta, and to silicates (D silicate/carbonate > 1) - elements of Fe group - Sc, Ti , Cr, Mn, Co, Ni, Cu, Zn (Fig. 2-3). Garnet in association with carbonate is more effective concentrator of microelements than clinopyroxene for the majority of trace elements. Trend D REE Si/Cb is positive. With the increase in N D REE Grt/Cb increases for La from $n\times10^{-1}$ up to 10 or more for Lu. A lesser extent changes D REE Cpx/Cb, from $n\times10^{-2}$ to 2, respectively.

Effect of temperature on the distribution coefficients D Grt/Cb, Cpx/Cb were considered for typomorphic carbonatites elements - Ba, REE, Hf, Pb, Th, U (Fig. 3).

Complicate dependence of the distribution D Grt/Cb of medium and heavy REE (from Eu to Lu, and Th, U) occurs in the system Grt/Cb and characterized by dependence on temperature. Dependence of D Cpx/Cb on T for all REE is positive. The most significant, more than an order of magnitude, this dependence is in strongly incompatible for Cpx elements Ba, LREE, D Cpx/Cb Ba, La with increasing T from 1200 to 1350°C increases from $n\bullet10^{-3}$ to $n\bullet10^{-1}$.

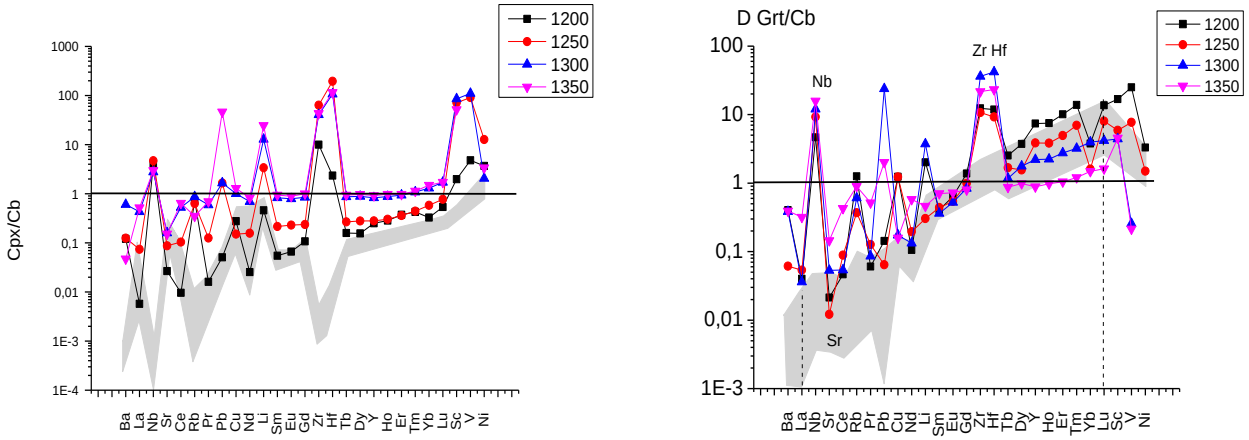
Our research covers the least studied interval of P (3.8-4 GPa), and unlike the majority data obtained in the "dry" conditions, were carried out with H_2O-fluid. On the Fig. 2, our experimental data are compared with the recommended data [Girnis et al., 2013], presented in this paper. Overall, similar trends are observed in the distribution, especially in the distribution of REE. There are also differences. First of all, these include higher D Cpx, Grt/Cb of incompatible elements, positive anomalies of D Nb, Zr, Hf, higher D Cpx/Cb Sc, V.

Conclusions. Significant (2.5-3 order) variation of the distribution coefficients D trace elements between Grt, Cpx and Cb indicate their effective fractionation in silicate- carbonate systems. High affinity for carbonate (D silicate/carbonate <1) possess P, LREE, Sr, Ba, U, Th, Ta, and to silicates - elements of Fe group, Sc, Ti, Cr, Mn, Co, Ni, Cu, Zn. In association with the carbonate for the majority of microelements Grt is more efficient concentrator of microelements than Cpx. Effect of T on D REE Cpx/Cb is positive, on D Grt/Cb is negative. The experimental data allow us to quantitatively model and predict the formation of deposits trace and REE in carbonatites.



a) b)

Fig. 1. BSE images of experimental samples: a - Di+Cb. T=1250°C, P=4 GPa; b - Grt+Cb, T=1250°C, P=4 GPa.



a) b)

Fig. 2. Distribution coefficients of trace elements between: a) Cpx and Cb; b) Grt and Cb at P=4 GPa, T=1200-1350°C. Points – our datas; color fields - Girnis, et.al. [2013].

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References:

1. Adam J., T. Green (2001). Experimentally determined partition coefficients for minor and trace elements in peridotite minerals and carbonatitic melt, and their relevance to natural carbonatites. *Europian Journal of Mineralogy*. 13. P.815-827.
2. Dasgupta R., Hirschmann M.M., McDonough W.F., Spiegelman M., Withers A.C. (2009). Trace element partitioning between garnet lherzolite and carbonatite at 6.6 and 8.6 GPa with applications to the geochemistry of the mantle and of mantle-derived melts. *Chemical Geology*. 262. P. 57-77.
3. Girnis A.V. (2003). Equilibrium olivine-orthopyroxene-melt as thermobarometry for mantle magmas. *Petrology*. V.11. №2. P. 115-127.
4. Girnis A.V., V.K. Bulatov, J. Lae, G.P. Bray (2006). Distribution of trace elements between carbonate-silicate melts and mantle minerals: experiment and petrological investigations. *Petrology*. V.14. №5. P. 524-547.
5. Girnis A.V., V.K. Bulatov, Y. Lahaye, and G.P. Brey (2006). Partitioning of trace elements between carbonate-silicate melts and mantle minerals: experiment and petrological consequences. *Petrology*. V.14. No. 5. PP. 492-514.
6. Girnis A.V., V.K. Bulatov, G.P. Brey, A. Gerdes, H.E. Hofer (2013). Trace element partitioning between mantle

minerals and silico-carbonate melts at 6-12 GPa and applications to mantle metasomatism and kimberlite genesis. *Lithos*. 160-161. P. 183-200.
7. Grassi D., M.W. Schmidt, D. Gunther (2012). Element partitioning during carbonated pelite melting at 8, 13 and 22 GPa and the sediment signature in the EM mantle components. *Earth and Planetary Science Letters.* 327-328. P.84-96.
8. Grassi D., M.W. Schmidt (2011). Melting of carbonated pelites at 8-13 GPa: generating K-rich carbonatites for mantle metasomatism. *Contrib Mineral Petrol*. 162. P.169-191.
9. Klemme S., Van Der Laan S.R., Foley S.F., Gunther D. (1995). Experimentally determined trace and minor element partitioning between clinopyroxene and carbonatite melt under upper mantle conditions. *Earth and Planetary Science Letters*. 133. P. 439-448.
10. Litvin Yu.A. (1991). Physical and chemical studies of the melting of depth-material of the Earth. Moscow. Publ. Nauka.
11. Sweney R.J., Prozesky V., Przybylowicz W. (1995). Selected trace and minor element partitioning between peridotite minerals and carbonatite melts at 18-46 kb pressure. *Geochemica and Cosmochimica Acta.* 59. P. 3671-3683.
12. Yao L., C. Sun, Y. Liang (2012). A parameterized model for REE distribution between low-Ca pyroxene and basaltic melts with applications to REE partitioning in low-Ca pyroxene along a mantle adiabat and during pyroxenite-derived melt and peridotite interaction. *Contrib Mineral Petrol.* 164. P. 261-280. DOI 10.1007/s00410-012-0737-5.

Kostyuk A.V., Gorbachev N.S. Effect of TP on the solubility of accessory minerals in carbonated alkali silicate melts (based on experimental data)

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Abstract. Solubility of apatite, Ni-containing pyrrhotite, ilmenite and zircon experimentally investigated P = 0.3-0.5 GPa and T = 1100-1250ºC in the peridotite - basalt - $(K, Na)_2CO_3$ + H_2O system. It was found that at temperature increase from 1100 to 1250°C (P = 0.5 GPa) concentration of ZrO_2 in the silicate melt increases from 0.68 to 1.44 wt.%. Concentration of TiO_2, P_2O_5 and SO_3 not change significantly (it's above 0.7 - 0.6 - 1.5 wt.% respectively). At pressure increases from 0.3 to 0. 5 GPa (T = 1250ºC) the concentration of ZrO_2 in the silicate melt increases from 0.89 to 1.44 wt.%; SO_3 icreases from 0.66 to 1.63 wt.%; but concentration of P_2O_5 opposite decreases from 1.33 to 0.78 wt.%; values of TiO_2 in the range of 0.85 wt.%.

Key words: experiment, geochemistry, solubility, melts, accessory minerals.

Citation: Kostyuk A.V., N.S. Gorbachev (2014). Effect of TP on the solubility of accessory minerals in carbonated alkali silicate melts (based on experimental data). Experimental geochemistry. V. 2. No.

The accessory minerals – apatite, Ni-containing pyrrhotite, ilmenite and zircon are important concentrators of P, S, Ti, Zr in zoned magmatic complexes of ultramafic and alkaline rocks and carbonatites. They determine their behavior in the formation and differentiation of magmas. Solubility of apatite, Ni-containing pyrrhotite, ilmenite and zircon has been experimentally investigated at pressures range 0.3-0.5 GPa and temperature range 1100-1250ºC.

Experiments were carried out in the peridotite - basalt - $(K, Na)_2CO_3$ + H_2O + accessory minerals (ilmenite, apatite, zirconia, Ni-containing pyrrhotite) system on a high gas pressure setting in IEM RAS. Duration of experiments was 48 hours.

For the experimental study of fluid- and sulfide-containing systems we used a special multi-ampoule quenching technique with peridotite container [Gorbachev, 1990]. Specially prepared peridotite container protected the platinum ampoule from aggressive sulfide melt and prevented loss of iron by melt during its interaction with the Pt ampoule. The peridotite of xenoliths from the kimberlite pipe Grib (Arkhangelsk region) was the starting material for the peridotite container. Container was filled by fine powder of initial sample consisting of a mixture of the basalt glass (70%) - K_2CO_3 (5%) - Na_2CO_3 (5%) - Ni-containing pyrrhotite (10%) - ilmenite (5%) - apatite (5%) - zircon grain (1-2 mm). Alkali carbonates $(K, Na)_2CO_3$ used because the alkaline carbonate fluid plays an important role in the mantle metasomatism, and also because of the close spatial and genetic relationship between carbonatite rocks and alkaline complexes. Peridotite container was placed in a platinum ampoule added to the system 10 wt.% of H_2O and hermetically sealed. Finished sample was placed in a buffered Pt ampoule of larger diameter. Sulfur and oxygen fugacity buffered by PtPtS and CoCoO respectively. Under our experimental conditions log fO_2 = -8.6 -10.3, log fS_2 = -0.7 -1.5.

After experiment the sample was opened and polished for microprobe study (Fig. 1). Products of experiments were studied using electron probe microanalysis on a digital scanning electron microscope Tescan VEGA TS 5130MM.

The Fig.1 shows that original structure of the sample has remained after the experiment with visible boundaries between peridotite container ("peridotite" in Fig. 1) and glass ("basalt" in Fig. 1).

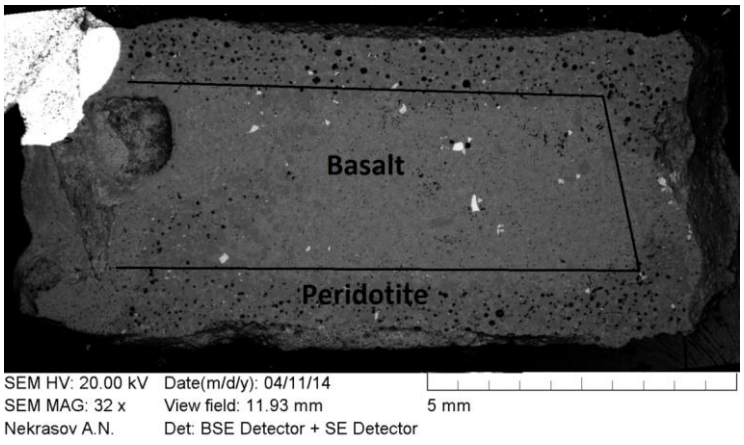

Fig. 1. Microphotograph of polished sample after the experiment in the peridotite-basalt-$(K, Na)_2CO_3$ + H_2O + accessory minerals system at T = 1250°C, P = 0.3GPa.

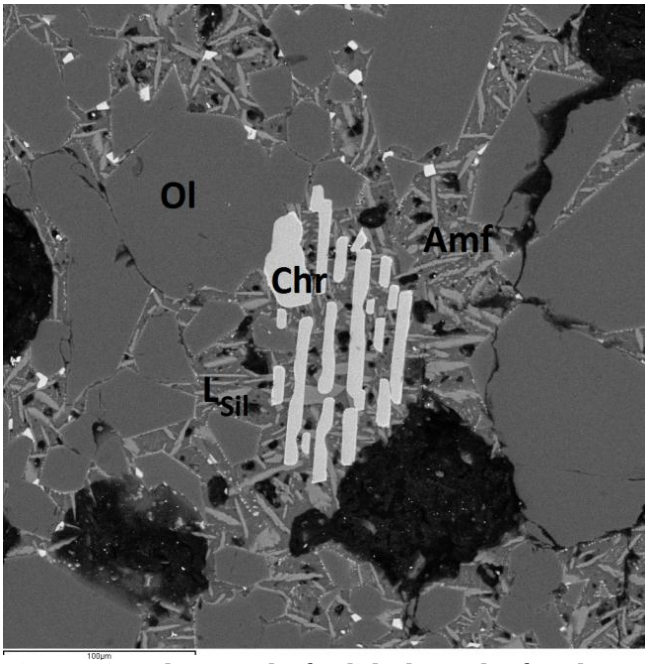

Fig. 2. Microphotograph of polished sample after the experiment in the backscattered electron at T = 1250°C, P = 0.3 GPa.

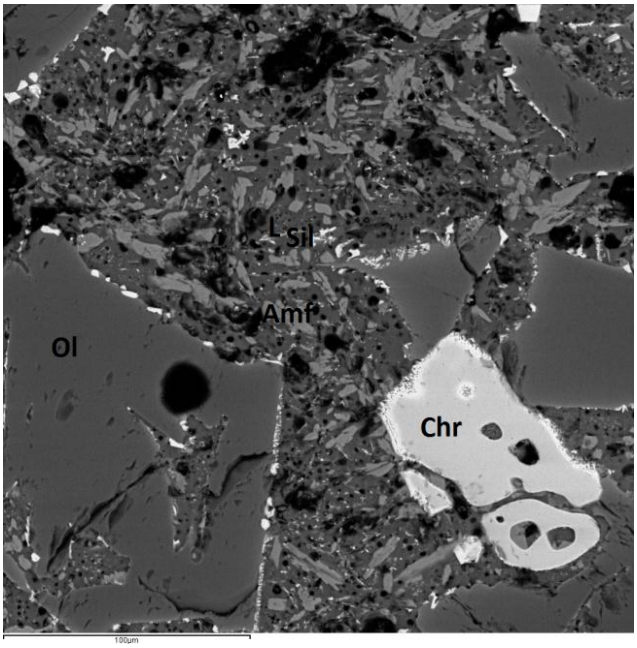

Fig. 3. Microphotograph of polished sample after the experiment in the backscattered electron at T = 1250°C, P = 0.5 GPa.

Effect of pressure. In all experiments, regardless of the temperature and pressure, the complete equilibrium occurred between the reaction melt (in the basalts part of the ampoule) and intergranular melt (in the peridotite). This is evidenced by the identical chemical composition of the melt, and equal concentration of ore elements in the melt around the perimeter of the sample. The reaction melt is formed by the interaction of basaltic melt with peridotite. Intergranular melt is formed by partial melting of peridotite and and holds (cements) the liquidus phase. Liquidus association is represented by olivine, chromite, titanium magnetite, quench amphibole (Figs. 2 and 3), as well as few very small ilmenite phases. Because zircon was added to the system in the form of one or two grains and not in the form of powder as the other phases, these grains easily detected at the center of the sample when polishing (see Figure 1, two white spot in the center). The melt composition changes from andesite (at P = 0.3 GPa) to trachyandesites (at P = 0.5 GPa). Compositions of coexisting phases are shown in Table 1.

Table 1. Chemical compositions of coexisting phases during partial melting of peridotite in the presence of carbonates, alkali, water and accessory minerals.

	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	SO_3	P_2O_5	Cr_2O_3	ZrO_2	Total
P = 0.3 GPa, T = 1250°C														
L_{Sil}	59.99	0.91	11.50	2.41	0.07	0.56	3.49	2.92	3.65	0.66	1.33	0.06	0.89	88.55
Ol	41.45	0.09	0.22	6.22	0.20	50.76	0.25	0.08	0.05	0.06	0.32	0.21	0.08	99.99
Chr	0.11	1.22	4.30	26.16	0.71	16.72	0.11	0.00	0.00	0.03	0.17	50.17	0.00	99.70
Amf	47.12	3.15	5.85	11.58	0.32	9.30	21.19	1.28	0.54	0.20	1.05	0.09	0.87	102.54
Ti-Mag	0.85	4.02	1.21	79.45	0.37	4.31	0.22	0.23	0.14	0.00	0.14	1.18	0.00	92.15
P = 0.5 GPa, T = 1250°C														
L_{Sil}	60.59	0.81	10.37	2.56	0.11	0.29	2.73	3.46	3.53	1.63	0.78	0.05	1.44	88.42
Ol	40.66	0.09	0.25	8.41	0.18	49.89	0.21	0.11	0.11	0.08	0.32	0.31	0.09	100.71
Chr	0.00	0.83	3.39	22.44	0.29	16.25	0.20	0.37	0.11	0.15	0.00	53.49	0.01	97.53
Amf	45.46	2.70	4.32	11.11	0.32	9.92	21.30	1.09	0.22	0.40	1.07	0.11	1.63	99.65
Ti-Mag	3.69	3.38	1.78	72.15	0.12	6.07	1.02	0.02	0.09	0.13	0.21	2.95	0.00	91.60
P = 0.5 GPa, T = 1100°C														
L_{Sil}	62.92	0.69	11.65	1.72	0.11	0.81	2.32	3.95	2.94	1.51	0.55	0.04	0.68	89.89
Amf	48.19	2.69	4.96	10.84	0.23	11.56	20.75	1.35	0.17	0.47	0.89	0.06	1.43	103.63
Chr	0.73	0.93	6.17	26.52	0.74	14.82	0.24	0.96	0.20	0.23	0.05	49.34	0.00	100.93
Ol	41.85	0.14	0.08	6.48	0.11	51.82	0.23	0.14	0.00	0.02	0.05	0.01	0.21	101.13
Anh	19.25	0.53	3.12	1.20	0.17	2.30	31.46	1.89	0.94	35.95	5.11	0.25	1.77	103.93

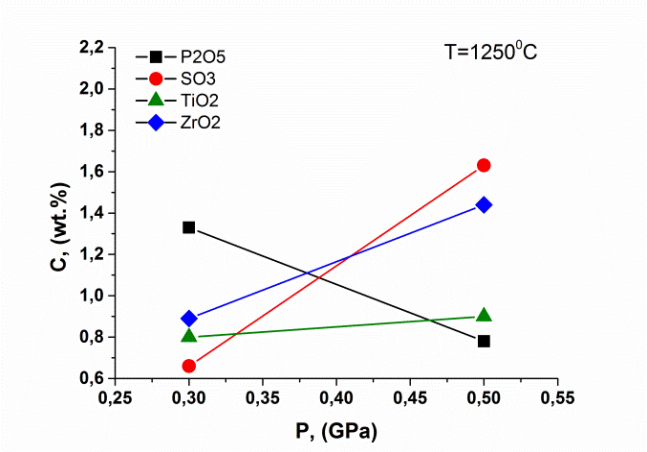

Fig. 4. Influence of pressure on the solubility of accessory minerals in the peridotite-basalt-(K, Na)$_2$CO$_3$ + H$_2$O system

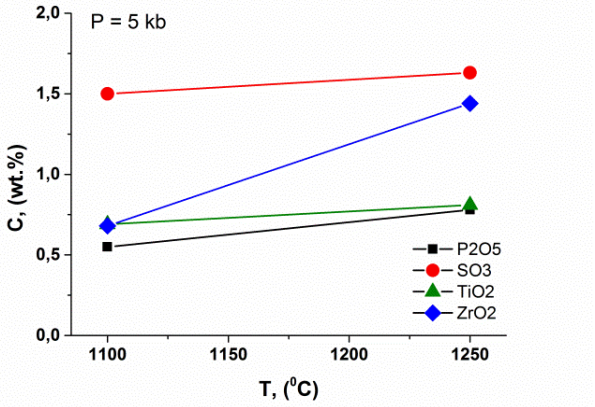

Fig. 5. Influence of temperature on the solubility of accessory minerals in the peridotite-basalt-(K, Na)$_2$CO$_3$ + H$_2$O system

Carbonate and sulphide melts are not found due to their high solubility in the alkali fluid-containing silicate melts. Solubility of Ni-containing pyrrhotite and zircon (Zr_2SiO_4) in alkaline silicate melt increases at pressure increases from 0.3 to 0.5 GPa. This is evidenced by an increase in concentrations of SO_3 from 0.66 to 1.63 wt.% and ZrO_2 from 0.89 to 1.44 wt.% at P = 0.3-0.5 GPa, respectively. Concentration of P_2O_5 on the contrary, decreased from 1.33 to 0.78 wt.%; values of TiO_2 in the range 0.8-0.9 wt.% (Fig. 4).

Effect of temperature. Experiments on the effect of temperature on the solubility of accessory minerals were carried out in the same system at P = 0.5 GPa. The melt composition changed from a trachy-dacite to trachy-andesites with increasing temperature from 1100°C to 1250°C, respectively (see Table. 1). Carbonate and sulfide melts were also not detected. Acidic alkaline melt cements association of olivine - amphibole - chromite - anhydrite (CaSO4) in the experimental samples at T = 1100°C (Fig. 6). Zircon grains is also saved in the sample. No significant variations in the concentrations of TiO_2, P_2O_5 and SO_3 when the temperature changes. Their values are: TiO_2 - 0.7-0.8 wt.%; P_2O_5 - 0.5-0.8 wt.%; SO_3 - about 1.5 wt.%. Significantly increases the concentration of ZrO_2 - from 0.68 to 1.44 wt.% with increasing temperature (Fig. 5).

Conclusions. During the experimental study of the influence of TP on the solubility of accessory minerals in carbonated alkali silicate melts has been established:

- Compositions of water-containing silicate melts of basalt and peridotite parts in the sample are similar in the peridotite-basalt-(K, Na)$_2$CO$_3$ + H$_2$O system. This effect can be explained by the fact that the compositions of silicate melts within the entire sample are buffered by aqueous fluid.
- In any of the experiments were not detected carbonate and sulphide melts after the experiment, due to the high solubility of these phases in the fluid-containing alkali-silicate melt and fluid.
- Apatite absence in the system after the experiment points to its complete dissolution, as well as the fact that we have not reached the saturation limit of the melt by phosphorus.
- Presence of single anhydrite globule ($CaSO_4$) in silicate glasses indicates the formation of sulphate melt. This is indirectly confirmed by high concentrations of SO_3 in the melt (about 1.5 wt.%) at such low pressures. According to the available experimental data, the solubility of sulphide sulphur in hydrous melts at P ≤ 0.5 GPa are 0.1-0.2 wt.% [Kostyuk et al, 2011; Kostyuk et.al, 2013], and sulfate sulfur greater than 1 wt.% [Jugo at.al., 2005]. Therefore, in water-containing basalt melts at fO_2 buffered by CoCoO buffer occurs oxidation of sulfide sulfur (S^{2-}) to sulfate (SO_4^{2-}).
- Established that the solubility of the accessory minerals depends largely on pressure than temperature.

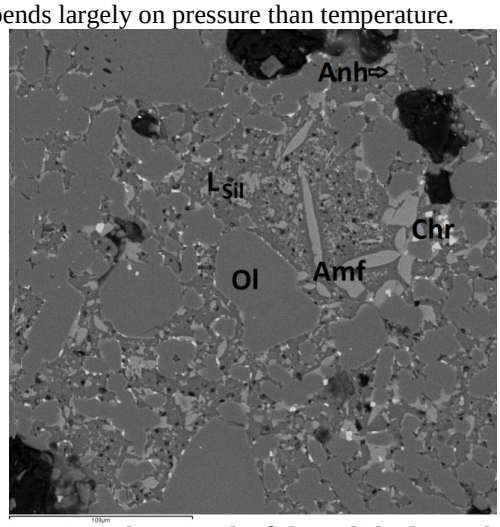

Fig. 6. Microphotograph of the polished sample after experiment in the backscattered electron at T = 1100°C, P = 0.5 GPa.

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References:

1. Gorbachev N.S. (1990) Fluid-magmatic interaction in sulfide-silicate systems. *Intern.Geolog.Rev.* 32. 8. P. 1749-1831.
2. Jugo P.J., Luth R.W.and Richards J.P. (2005) An experimental study of the sulfur content in Basaltic melts saturated with immiscible sulfide or sulfate liquids at 1300°C and 1GPa. *Journal of Petrology*, V.46, N.4, P.783-798
3. Kostyuk A. V., N. S. Gorbachev (2011) Extreme pressure dependence of sulfur solubility in silicate melts (experimental data), *Vestn. Otd. nauk Zemle*, 3, NZ6045, doi:10.2205/2011NZ000175
4. Kostyuk A.V., N.S. Gorbachev (2013). Is there an extreme pressure dependence of sulphur solubility in hydrous silicate melts?. *Mineralogical Magazine*, July 2013, v. 77, p. 1414-1534, published online August 7, 2013, doi:10.1180/minmag.2013.077.5.11