

Litvin¹ Yu. A., Anashkina² N. E. Ultrabasic-basic differentiation of mantle magmas and natural diamond-parental melts by evidence of physico-chemical experiments

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Experimentally at 7 GPa phase relations in two sections of the system garnet peridotite–eclogite–carbonatite are studied in connection with the problem of physico-chemical conditions of differentiation of the upper mantle ultrabasic-basic magmas and formation of continuous series of peridotite–eclogite rocks as well as the syngenesis of diamond and primary inclusions of peridotitic and eclogitic parageneses. Diagrams of equilibrium and fractional crystallization of the boundary silicate multicomponent system peridotite–eclogite are constructed. As a result, a new effect of “peridotite–eclogite tunnel” is established. The tunnel provides formation of the continuous series of peridotite–eclogite rocks of the Earth’s upper mantle. Also, diagrams of equilibrium and fractional crystallization for the polythermal section peridotite₃₀carbonatite₇₀–eclogite₃₅carbonatite₆₅ are constructed. As a result, a combined action of the effects of peridotite–eclogite tunnel and carbonatization of peridotitic magnesian phases is recognized. The effects provide consecutive formation of the phases of peridotitic and eclogitic parageneses in the natural processes of diamond origin.

Key words: upper mantle, mantle magmatism, diamond genesis, peridotite, eclogite, carbonatite, syngenetic inclusions, fractional crystallization, peridotite–eclogite tunnel, experiment

Reference: Litvin, Yu. A., N. E. Anashkina Ultrabasic-basic differentiation of mantle magmas and natural diamond-parental melts by evidence of physico-chemical experiments, *Vestnik ONZ RAS*, 4, (doi:)

This work is based on data presented by two talks [Litvin, 2012a; Anashkina, Litvin, 2012] to Annual Seminar on Experimental Mineralogy, Petrology and Geochemistry, Moscow, GEOCHI – IEM RAS, 2012

1. Melting relations of the upper-mantle peridotite–eclogite system

Xenoliths of peridotite–pyroxenite and eclogite–grosphydite series in kimberlites are basic for the conception of primary garnet peridotitic or pyrrhotitic by A. Ringwood [1962] rocks of the upper mantle. Garnet peridotites and eclogites are the major rocks of the Earth’s upper mantle [Ringwood, 1975]. Peridotites dominate statistically (95%) in respect to eclogites (5%). However, the inverse relationship is ascertained for the Roberts Victor (80% eclogites and 20% peridotites), Bobbeyan, Ritfontein (SA), Orapa (Botswana), Garnet-Ridge, Moses-Rock (USA), Zagadochnaya (RF) and some other pipes. 63% of eclogites are presented by biminerals Cpx–Grt rocks. Mineral phases of peridotite and eclogite parageneses represent most of primary inclusions in natural diamonds [Sobolev, 1974]. With rare exception, minerals of both the parageneses are not coexisted in the same crystal. Petrochemical trends demonstrate continuous transitions between peridotitic and eclogitic rocks [Marakushev, 1984] and compositions of mineral inclusions in diamonds [Sobolev, 1974]. But direct petrogenetic relations of peridotites and eclogites are physico-chemically poorly substantiated.

Formation of primary ultrabasic magma in garnet peridotite system Ol–Opx–Cpx–Grt is under control of quasi-invariant peritectics Ol+Opx+Cpx+Gr+L [Litvin, 1991]. Based on experimental evidence, a topology of the diagram of equilibrium melting relations of peridotite–

eclogite system Ol–Cpx–Crn–Cs has been determined. This makes possible to identify principal details of structure of its liquidus [Litvin, 1991]. It has been found that Ol–Opx–Cpx–Gr–peridotite and Cs–Opx–Cpx–Grt–eclogite peritectics are physico-chemically bounded up by univariant curve Opx+Cpx+Grt+L that has a temperature maximum at the “piercing point” of the boundary plane Opx–Cpx–Grt between peridotitic (olivine-saturated) and eclogitic (silica-saturated) composition tetrahedra. The maximum represents a thermal eclogitic barrier between Ol-saturated peridotitic and SiO₂-saturated Opx–Qtz/Cs- and Ky–Crn–eclogitic compositions. It is an insuperable obstacle for ultrabasic-basic differentiation in case of equilibrium so fractional crystallization of ultrabasic magma. The “eclogitic barrier” will hold its importance for less deep conditions and was discussed in the context of basaltic magmatism [O’Hara, 1968].

Another univariant curve Ol+Cpx+Grt+L links the Ol–Opx–Cpx–Grt peridotite peritectics and the eutectics of rarely occurring olivine eclogites in temperature-lowering way without a thermal maximum. It is known that olivine eclogites are extremely rare among the xenolith of mantle rocks in kimberlites [Dawson, 1980] but frequent among xenoliths in alkaline basalts [O’Hara, 1968]. An existence of the univariant curve Ol+Cpx+Grt+L without a temperature maximum that links the garnet–peridotitic and olivine–eclogitic simplexes is of principal interest in view of the fact that Ol can disappear in reaction with Jd components while Grt, Opx and Na–Mg–silicate are formed above 4.5 GPa [Gasparik, Litvin, 1997]. The reaction of “olivine garnetization” is minimized and can not show itself appreciably in equilibrium process of ultrabasic melt crystallization. Moreover, figurative point of the system composition is not able to go out the limits of the peridotitic composition simplex. But one would expect that effectiveness of the reaction is significantly increased under the conditions of fractional crystallization due to accumulation of jadeitic component in the residual melts. As this takes place, it is important that the figurative point of the system composition is able to transfer into the olivine–eclogitic composition simplex by a natural physico-chemical way, i.e. go out the limits of the peridotitic composition simplex.

Experimental searching of physico-chemical mechanism, that is capable of carrying out a continuous ultrabasic-basic differentiation of the mantle magmas and thus provide petrogenetic links for formation of the rocks of peridotite–eclogite series, has acquired a meaning after experimental discovering of the reaction between olivine and jadeite that gives rise to olivine disappearing [Gasparik, Litvin, 1997]. The question of physico-chemical conditions of formation of the mineral phases of peridotitic and eclogitic parageneses from primary inclusions in natural diamonds has assumed an actual significance in connection with elaboration of the mantle–carbonatite theory of diamond genesis [Litvin, 2007, 2009] and its progression [Litvin, 2010; Litvin et al., 2012]. Beyond any doubt, the problem can be only solved in physico-chemical experiment.

This work is devoted to investigation of physico-chemical conditions of diamond formation in the upper mantle peridotite–eclogite–carbonatite–carbon parental media of multicomponent and changeable compositions. The limits of the parental basic compositions is characterized by the system peridotite₃₀carbonatite–eclogite₃₅carbonatite₆₅–carbonatite [Litvin, 2010b; Litvin et al., 2012] (Fig. 1).

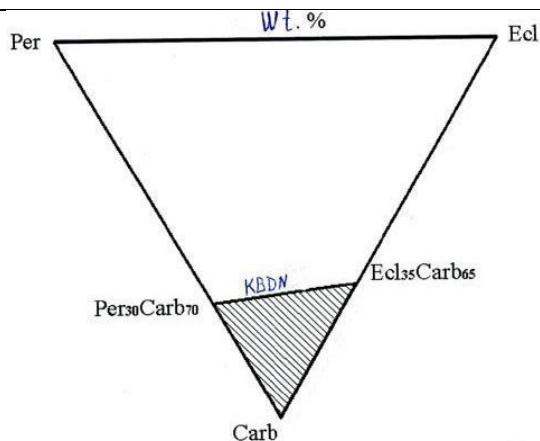


Fig. 1. Composition triangle of the peridotite Per–eclogite Ecl–carbonatite Carb - system. The line of concentration barrier of diamond nucleation (KBDN) restricts the field of parental media for natural diamonds and primary mineral inclusions therein [Litvin, 2010b]. Note: for compositions of the boundary phase see Figs. 2 and 5

2. “Peridotite-to-eclogite tunnel” mechanism

Fractional crystallization of primary komatiitic magma is accompanied by increasing concentration of jadeite component at residual melts. This activates the mechanism of ultrabasic-basic magma differentiation with formation of continuous peridotite-eclogite series. By experimental evidence, “peridotite-to-eclogite tunnel” mechanism is under control of reaction between Ol- and Jd-components [Gasparik, Litvin, 1997; Litvin *et al.*, 2000]. Over liquidus of peridotite-eclogite system, reaction point $Ol+Jd-Cpx=Gr+L$ [Butvina, Litvin, 2010] operates effectively in Ol elimination along the univariant curve $Ol+Cpx+Gr+L$. Under temperature lowering, the reaction brings figurative point of composition of the ultrabasic-basic magma out of peridotite $Fo + Di-Jd-Cpx + L$ divariant field into the eclogitic one $Gr + Jd-Di-Cpx + L$.

The work of the “peridotite-to-eclogite tunnel” under fractional crystallization of ultrabasic-basic magmas is clearly disclosed by equilibrium phase diagram of the system peridotite ($Ol_{60}Opx_{16}Cpx_{12}Grt_{12}$)–eclogite ($Cpx_{50}Grt_{50}$) studied experimentally at 7 GPa (Fig. 2) as well as by diagram of fractional crystallization (Fig. 3) constructed on the base of the equilibrium one. At both cases, olivine is the liquidus phase.

For the equilibrium case, orthopyroxene is lost in solidus peritectic point, and subsolidus is presented as result by two assemblies with olivine – $Ol+Opx+Cpx+Grt$ and $Ol+Cpx+Grt$. For the case of fractional crystallization, olivine is also lost under action of “peridotite-eclogite tunnel”, and following crystallization of the residual melts is determined by the

Fig. 3. Diagram of fractional crystallization of the system peridotite($Ol_{60}Opx_{16}Cpx_{12}Grt_{12}$)–eclogite ($Cpx_{50}Grt_{50}$) at 7 GPa under conditions of the peridotite–eclogite tunnel. Note: signs P and E concerns, respectively, to designation of peridotitic and eclogitic phases of the same name

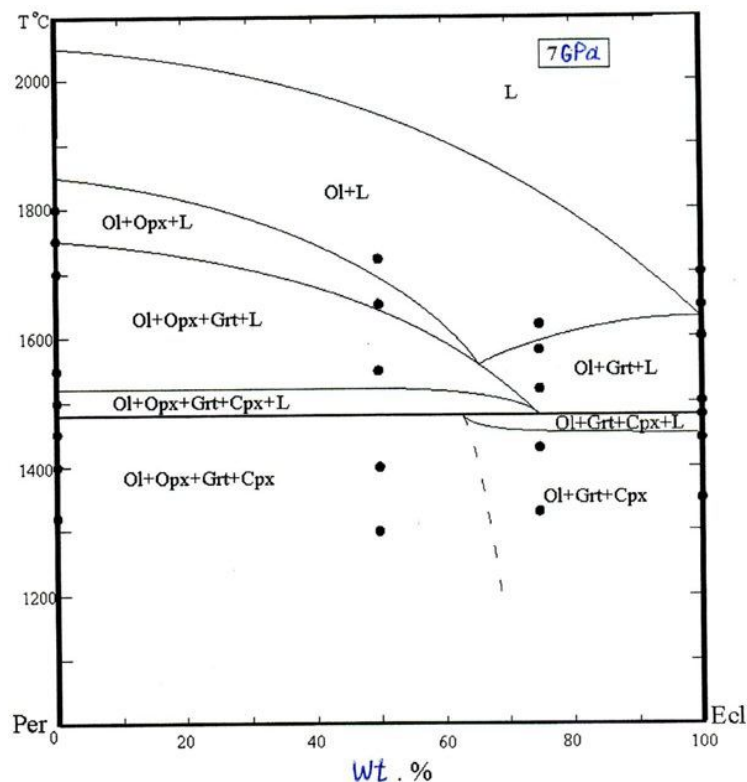
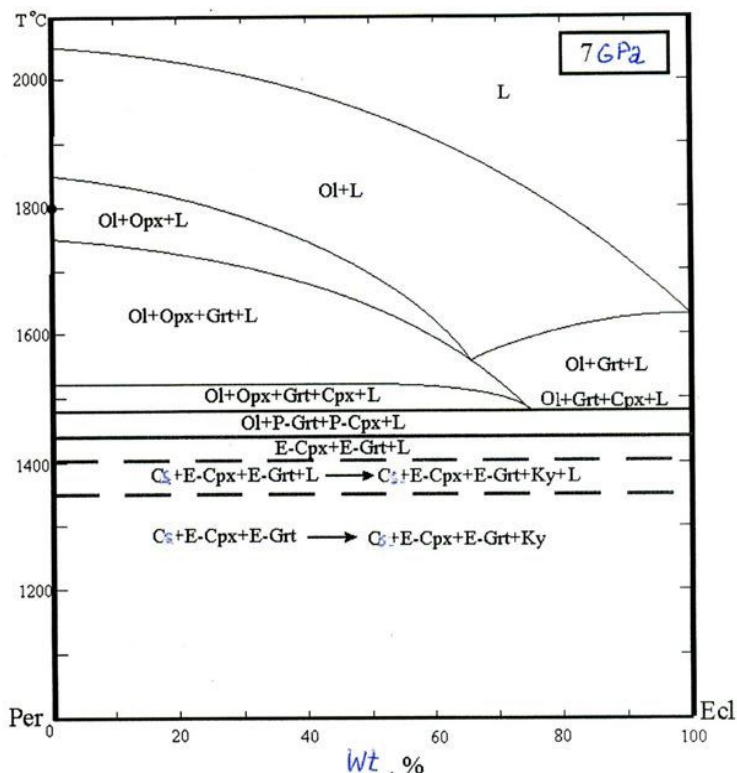


Fig. 2. Diagram of equilibrium crystallization of the system peridotite – eclogite at 7 GPa; starting compositions: Per ($Ol_{60}Opx_{16}Cpx_{12}Grt_{12}$) = Na_2O 0.52, MgO 37.12, FeO 11.35, CaO 2.49, Al_2O_3 3.48, SiO_2 45.04 and, respectively, peridotitic olivine $Ol = MgO$ 45.63, FeO 14.35, SiO_2 40.02, orthopyroxene $Opx = Na_2O$ 0.30, MgO 33.34, FeO 7.26, CaO 0.21, Al_2O_3 0.49, SiO_2 57.80, clinopyroxene $Cpx = Na_2O$ 2.60, MgO 16.88, FeO 4.68, CaO 15.66, Al_2O_3 4.28, SiO_2 55.92, garnet $Grt = MgO$ 20.93, FeO 8.48, CaO 3.97, Al_2O_3 24.07, SiO_2 42.55; (2) eclogite Ecl ($Cpx_{50}Grt_{50}$) = Na_2O 3.71, MgO 8.51, FeO 15.24, CaO 9.04, Al_2O_3 15.76, SiO_2 47.74 and, respectively, eclogitic clinopyroxene $Cpx = Na_2O$ 7.41, MgO 8.50, FeO 6.40, CaO 12.09, Al_2O_3 9.52, SiO_2 56.31, garnet $Grt = MgO$ 8.51, FeO 24.08, CaO 5.98, Al_2O_3 22.19, SiO_2 39.23. Black circles - experimental points



transfer of figurative point of melt from the line Cpx–Grt along the liquidus elements of SiO₂-saturated eclogitic systems.

Fig. 4 is schematically presented liquidus surface of the upper mantle peridotite-eclogite system as a projection onto the boundary plane Ol–Cs–Crm of the complex tetrahedron Ol–Cs–Crm–Cpx in such way that the composition line Cpx–Grt is perpendicularly oriented in respect to the plane Ol–Cs–Crm. The line Cpx – Grt is commonplace for all the peridotitic and eclogitic composition tetrahedra (simplexes) of the system Ol–Cs–Crm–Cpx being a place where all the tetrahedra are contiguous.

Fig. 4 demonstrate that figurative points of residual melt compositions transfer towards to the join Cpx–Grt due to olivine-jadeite reaction. Direction of the transfer of the composition points from the quazi-invariant point Ol+Opx+Cpx+Grt to the composition line Cpx–Grt is marked by thick distorted line over the hatched region of the garnet peridotite liquidus surface. By doing so, a way for transfer of the melt figurative point over liquidus surface of any silica-saturated eclogitic system is opened. In this case, a choice of direction of further fractional crystallization is determined by component ratio in starting composition of ultrabasic melt in the very beginning of its fractional crystallization. Thus, the “peridotite-to-eclogite tunnel” mechanism makes the round the thermal eclogitic barrier and, correspondingly, paves the way for continuous fractional crystallization of ultrabasic-basic magmas with transfer in formation from Ol-bearing peridotite to Cs-bearing eclogite rocks

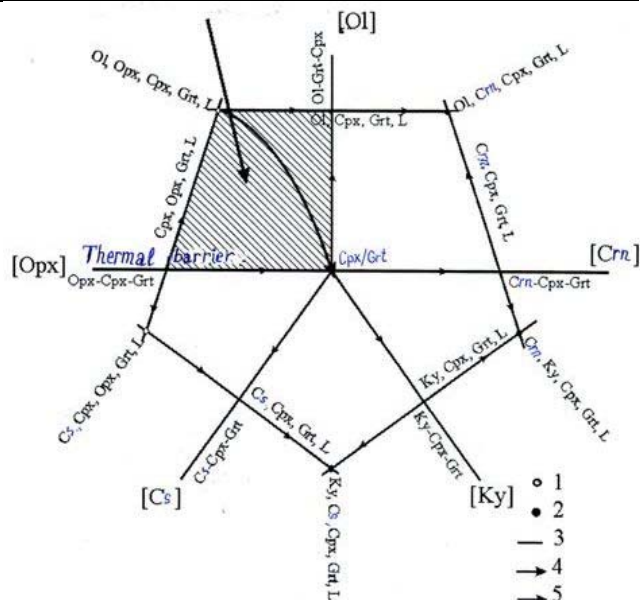


Fig. 4. Divariant liquidus field Cpx+Grt+L (view from the apex Cpx). Conventional signs: 1 – quazi invariant peritectic points; 2 – quazi invariant eutectic points; 3 – thin lines – univariant curves with arrows 4 pointed out directions of temperature lowering; 5 – thick line with arrow contacting the Cpx–Grt line is pointed out a change in direction of the univariant curve Ol+Cpx+Grt+L under conditions of fractional crystallization and acting the mechanism of “peridotite-eclogite tunnel”.

3. Differentiation of silicate-carbonate melts parental for diamond and minerals of peridotite and eclogite parageneses

By experimental evidence, a changeable composition of the peridotite–eclogite–carbonatite parental melts for diamond and mineral inclusions therein is based on the peridotite₃₀carbonatite₇₀–eclogite₃₅carbonatite₆₅–carbonatite system [Litvin, 2010b; Litvin et al., 2012]. Diagrams of equilibrium and fractional crystallization of the boundary system peridotite₃₀carbonatite₇₀–eclogite₃₅carbonatite₆₅ are presented at Fig. 5 and 6, respectively.

By preliminary evidence, differentiation of the parental melts is under definite influence of the mechanism of “peridotite–eclogite tunnel”. But an additional factor connected with the effects of carbonatization of peridotitic Mg-components is coming into play. For the both equilibrium and fractional crystallization cases, olivine, orthopyroxene and garnet are liquidus phases and action of the carbonatization processes are shown up. For the equilibrium case, olivine is lost at the first peritectic

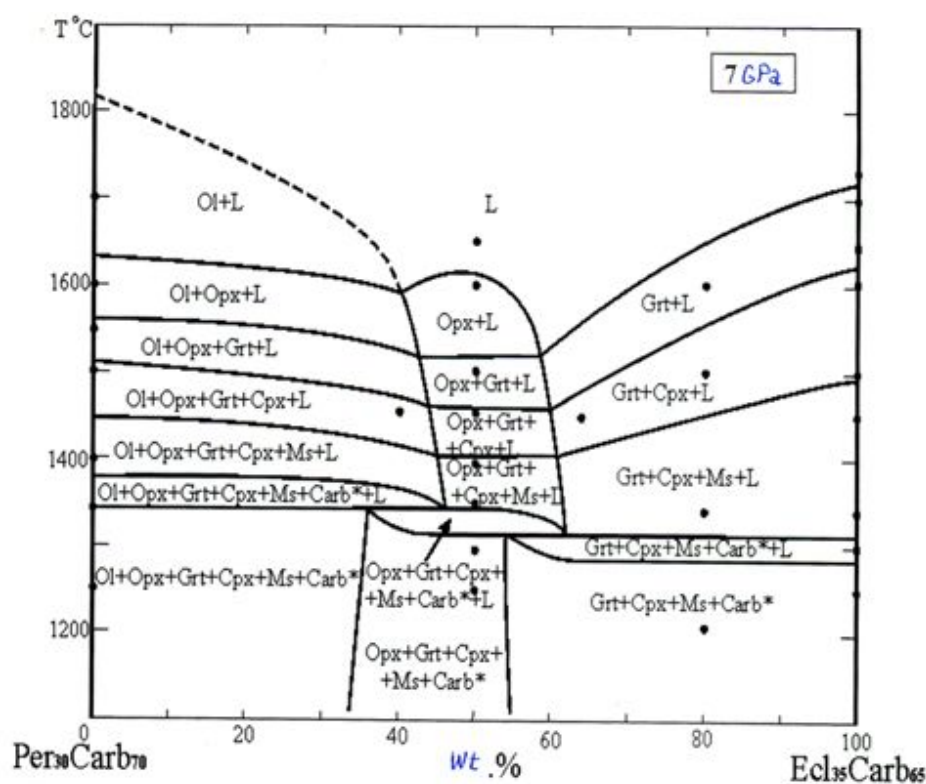


Fig. 5. Preliminary diagram of equilibrium crystallization of the system peridotite₃₀carbonatite₇₀–eclogite₃₅carbonatite₆₅ at 7 GPa; starting compositions: (1) carbonatite – K₂O 18.55, Na₂O 1.69, MgO 8.30, FeO 15.89, CaO 15.08, CO₂ 40.49, (2) peridotite (Ol₆₀Opx₁₆Cpx₁₂Grt₁₂) – for composition of the boundary phase see Figs. 2; eclogite (Cpx₅₀Grt₅₀) – for composition of the boundary phase see Fig. 2. Black circles – experimental points. For carbonate phases, magnesite Ms is separately shown but the other Ca, Fe, Na and K carbonates are symbolized by Carb* to simplify the diagram

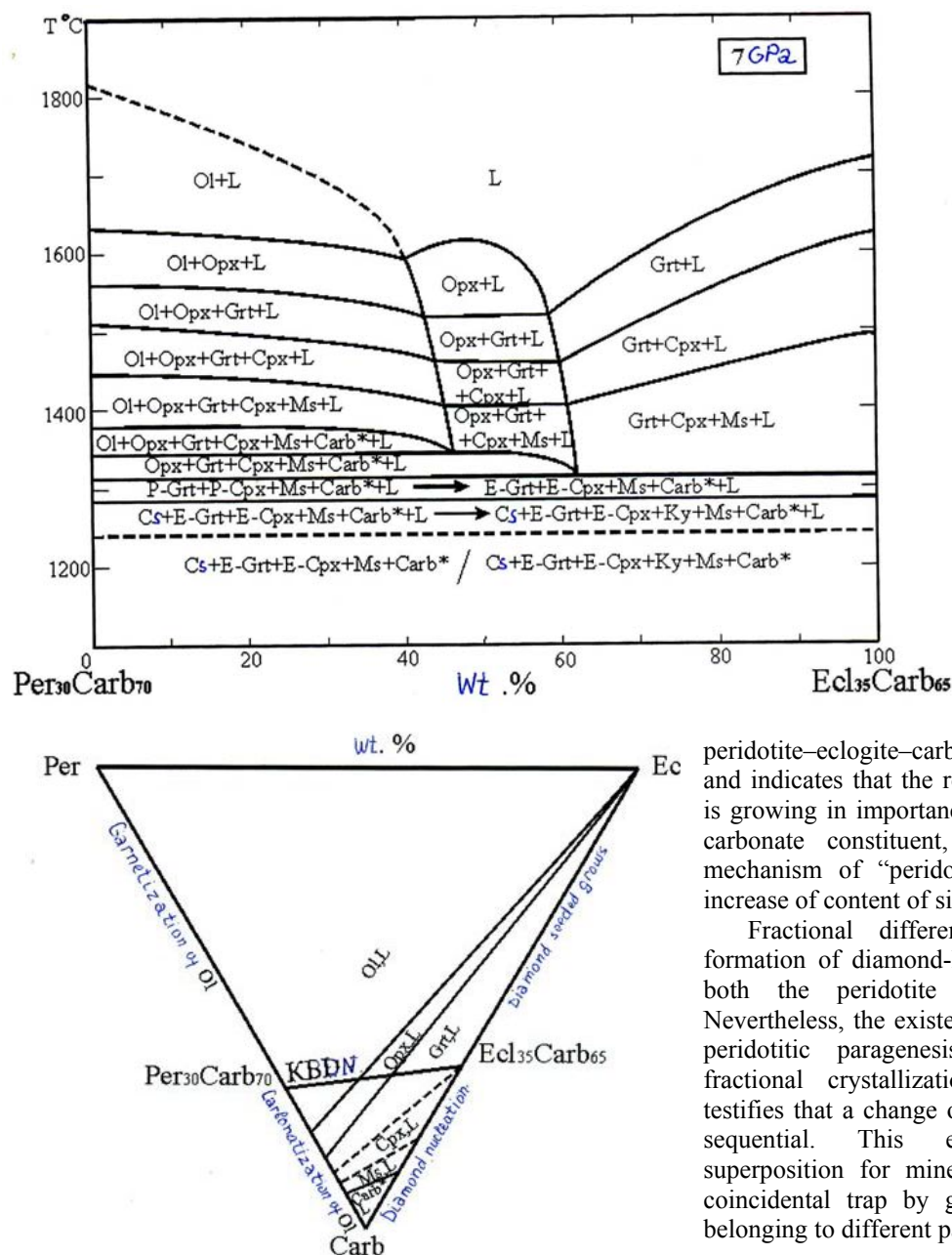


Fig. 6. Preliminary diagram of fractional crystallization of the system peridotite30carbonatite70-eclogite35carbonatite65 at 7 GPa

+ Grt + Ms + Carb*. Nevertheless, in the case of equilibrium crystallization clinopyroxenes and garnets are characterized by peridotitic specialization and, perhaps, these regain eclogitic compositions only under conditions of fractional crystallization. Finally, coesite and kyanite are formed among sublolidus assemblages as the result of fractional crystallization.

Schematic liquidus diagram of the system

peridotite–eclogite–carbonatite is presented at Fig. 7 and indicates that the role of carbonatization process is growing in importance with increase of content of carbonate constituent, whereas the role of the mechanism of “peridotite–eclogite tunnel” – with increase of content of silicate constituent.

Fractional differentiation is responsible for formation of diamond-hosted mineral inclusions for both the peridotite and eclogite parageneses. Nevertheless, the existence of regular transition from peridotitic paragenesis to eclogitic one under fractional crystallization of syngenetic minerals testifies that a change of corresponding conditions is sequential. This excludes the paragenetic superposition for minerals and as a sequence the coincidental trap by growing diamonds of phases belonging to different parageneses. Mineral inclusions

of different paragenetic relation within the same diamond crystal has to be regarded as result of accidental events without physico-chemical basement.

Figs. 8 and 9 demonstrate examples of syngenetic crystallization of diamond and minerals of peridotitic and eclogitic parageneses, respectively, by results of testing experiments at 8.5 GPa.

Fig. 7. Schematic liquidus of the system peridotite – eclogite – carbonatite

point, and orthopyroxene – at the second one; as a result, subsolidus is presented by one assembly with olivine Ol + Opx + Cpx + Grt + Ms + Carb* and two assemblies without olivine – Opx + Cpx + Grt + Ms + Carb* and Cpx

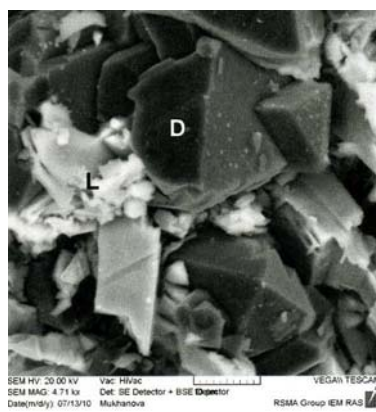
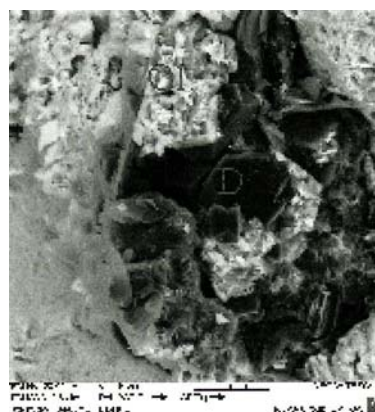


Fig. 8. Syngenetic crystallization of diamond with olivine in peridotite–carbonatite system: D = diamond; Ol = olivine

Fig. 9. Syngenetic crystallization of diamond with Cpx and Grt in eclogite–carbonatite system [Pokrovskaya, Litvin, 2011]: D = diamond, Cpx = clinopyroxene, Grt = garnet, L = melt

This work is supported by the grants of RFBR № 11-05-00401 and Leading Scientific School № 3654-2012-5.

References:

- Anashkina, N. E., Yu. A. Litvin (2012). Paragenetic relations of diamonds and minerals from inclusions by experimental evidence. In: *Abstracts of Annual Seminar on Experimental Mineralogy, Petrology and Geochemistry (ASEMPG-2012)* », 17–18 April 2012, Moscow, GEOKHI and IEM RAS, 2012, p. 3 (in Russian).
- Butvina, V. G., Yu. A. Litvin (2010). Physico-chemical transition from peridotite assemblage to the eclogite one (experimental data at 7.0 GPa), *Geophysical Research Abstracts*. Vol. 12. EGU20103717-1.
- Gasparik, T., Yu. Litvin (1997). Stability of $\text{Na}_2\text{Mg}_2\text{Si}_2\text{O}_7$ and melting relations on the forsterite-jadeite join at pressures up to 22 GPa, *Eur. J. Mineral.*, 9, 311–326.
- Dawson, J. B. (1980). *Kimberlites and Their Xenoliths*, Berlin-Heidelberg-New York: Springer Verlag. 252 p.
- Litvin, V. Yu., T. Gasparik, Yu. A. Litvin (2000). The enstatite-nepheline system in experiments at 6.5–13.5 GPa: an importance of $\text{Na}_2\text{Mg}_2\text{Si}_2\text{O}_7$ for melting of the nepheline-normative mantle, *Geochemistry International*, 38, Issue 1, 100–107.
- Litvin, Yu. A. (1991). *Physico-Chemical Study of Melting Relations of the Earth's Deep-Seated Matter*, Moscow: "Nauka" Publishing House, 312 p. (in Russian).
- Litvin, Yu. A. (2007). High-pressure mineralogy of diamond genesis. In: *Advances in High Pressure Mineralogy (edited by Eiji Ohtani)*, Geological Society of America Special paper 421, 83–103.
- Litvin, Yu. A. (2009). The physico-chemical conditions of diamond formation in the mantle matter: experimental studies, *Russian Geology and Geophysics*, 50 (12), 1188–1200.
- Litvin, Yu. A. (2010a). Origin of diamond and syngenetic inclusions by evidence of physico-chemical experiment, In "Transactions of XXI International Scientific Conference "Fundamental Problems of Geology of Fossiliferous Mineral Deposits and Metallogeny" to 100th Anniversary of Academician V.I. Smirnov". Moscow, MSU, January 26–28, vol. 2, p. 208–226 (in Russian).
- Litvin, Yu. A. (2010b). Physico-chemical conditions of formation of natural diamond and heterogeneous substance of primary inclusions therein, In "XI Meeting RMS – Current mineralogy: from theory to practice. Transactions of International Scientific Conference", Saint-Petersburg, Russia, October 12–15, 2010, p. 77–78 (in Russian).
- Litvin, Yu. A. (2012a). Petrogenetic links of garnet peridotites and eclogites: differentiation of the mantle ultrabasic-basic magmas in physico-chemical experiment, In: *Abstracts of Annual Seminar on Experimental Mineralogy, Petrology and Geochemistry (ASEMPG-2012)* », 17–18 April 2012, Moscow, GEOKHI and IEM RAS, p. 58 (in Russian).
- Litvin, Yu. A. (2012b). Ultrabasic-basic evolution of upper mantle magma: petrogenetic links between diamond-bearing peridotites and eclogites (on evidence of physico-chemical experiments), *Geophysical Research Abstracts*, Vol. 14, EGU2012-3610-1, 2012. EGU General Assembly 2012.
- Litvin, Yu. A., P. G. Vasiliev, A. V. Bobrov, V. Yu. Okoemova, A. V. Kuzyura (2012). Parental media of natural diamonds and primary mineral inclusions therein by evidence of physico-chemical experiment, *Geochemistry International*, №7.
- Marakushev, A. A. (1984). Peridotite nodules in kimberlites as indicators of the deep lithosphere structure, In: *Reports of Soviet Geologists to 27th Session of the International Geological Congress. Petrology*. Moscow: Nauka, 153–160 (in Russian).
- O'Hara, M. J. (1968). The bearing of phase equilibria in synthetic and natural systems on the origin and evolution of basic and ultrabasic rocks, *Earth-Sci. Rev.*, vol. 4, 69–133.
- Pokrovskaya, N. E., Yu. A. Litvin (2011). Experimental modeling of syngensis of diamond and minerals of peridotite and eclogite parageneses, *Vestnik Otdelenia nauk o Zemle RAN*, vol. 3, NZ6079, doi:10.2205/2011 NZ000209.
- Ringwood, A. E. (1962). A model for the upper mantle, *J. Geophys. Res.* 67, 857–866.
- Ringwood, A. E. (1975). *Composition and Petrology of the Earth's Mantle*, New York–London Paris–Tokyo: Mc-Graw-Hill.
- Sobolev, N. V. (1974). Deep-seated Inclusions in Kimberlites and the Problem of Upper Mantle Composition, *Novosibirsk: Nauka*. 264 p. (in Russian).

Lukanin O. A., Volovetskii M. V., Kargal'tsev A. A. Dependence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio on oxygen fugacity and temperature in melts of granitoid composition on experimental data

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The experiments with melts of granitic and pantelleritic compositions conducted within temperature range 1220–1420°C and fO_2 $10^{-0.7} \div 10^{-11}$ bar ($P_{\text{tot}} = 1$ atm) showed that the dependence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in melt on oxygen fugacity (fO_2) in isothermal conditions is described by equation $\log(\text{Fe}^{3+}/\text{Fe}^{2+}) = k \cdot \log(\text{fO}_2) + q$, where k and q are constants depending on melt composition and temperature. Under given fO_2 – T conditions the degree of iron oxidation in more alkaline and iron enriched pantelleritic melt is higher than that in granitic melt. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio decreases in both types of melts with temperature increase at $\text{fO}_2 = \text{const}$. The data obtained are compared with results of other experimental investigations of granitoid melts, as well as calculations made using a previously proposed empirical equations $(\text{Fe}^{3+}/\text{Fe}^{2+})_{\text{melt}} = f(T, \text{fO}_2, \text{melt composition})$. It is shown that the available empirical equations are in poor agreement with experimental data. We propose new empirical equations, that adequately describe the experimental data for two types of silicic aluminosilicate melts, namely, granite and comendite-pantellerite compositions respectively, within temperature range ~ 1200(1100)–1450°C.

Keywords: redox state of iron, silicic aluminosilicate melts, oxygen fugacity, granite, pantellerite

Reference: Lukanin, O. A., M. V. Volovetskii, A. A. Kargal'tsev (2012), Dependence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio from oxygen fugacity and temperature in melts of granitoid composition on experimental data, *Vestnik ONZ RAS*, 4

Introduction The redox state of iron in melts, which controls to a large extent their physical properties and direction of evolution during crystallization differentiation depends on number of external and internal parameters: temperature, pressure, oxygen fugacity and melt chemistry. The knowledge of the influence of these parameters on ferric-ferrous ratio of natural aluminosilicate melts provides means for the reconstruction of redox conditions of their formation. Up to date, several empirical equations have been derived on the basis of extensive experimental data to connect redox state of iron, temperature, oxygen fugacity and melt composition [Sack et al., 1980; Kilinc et al., 1983; Mysen, 1991; Борисов, Шапкин, 1989; Kress, Carmichael, 1991; Николаев и др., 1996; Jayasuriya et al., 2004]. They describe fairly well the dependence of these parameters at magmatic T–fO₂ conditions for a wide range of natural silicate melts, mainly of basic composition. However, their validity for granitoid melt remains questionable. Although a number of earlier experimental investigations have been reported [Sack et al., 1980; Kilinc, et al., 1983; Bychkov, Borisov, 1992; Moore et al., 1995], the influence of fO₂ and T on $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in silicic aluminosilicate melts is still poorly understood. New experimental data obtained

Abstracts

by us for silicic melts of granite and pantellerite composition [Volovetsky et al., 2012] allow to consider this problem in more detail.

Experimental data Experiments with melts of granite (I2) and pantellerite (P9) compositions (Table 1) were conducted within temperature range 1220 ÷ 1420°C and

fO_2 $10^{-0.7}$ – 10^{-11} bar at a total pressure of 1 atm partial pressure of oxygen during the experiments [Kargal'tsev et al. [Volovetskii et al., 2012] using high-temperature furnace, which provides given *al.*, 2010]. The valence state of iron in quenched glasses obtained after the runs was determined by Mössbauer spectroscopy.

Table 1. Chemical composition of initial samples

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	Cl	ZrO ₂	Σ
Granite I2	70.46	0.06	15.28	3.41	0.05	0.14	2.06	4.07	3.95	-	-	99.53
Pantel. P9	69.28	0.36	7.69	7.82	0.31	0.07	0.34	6.61	4.37	0.51	0.33	97.36

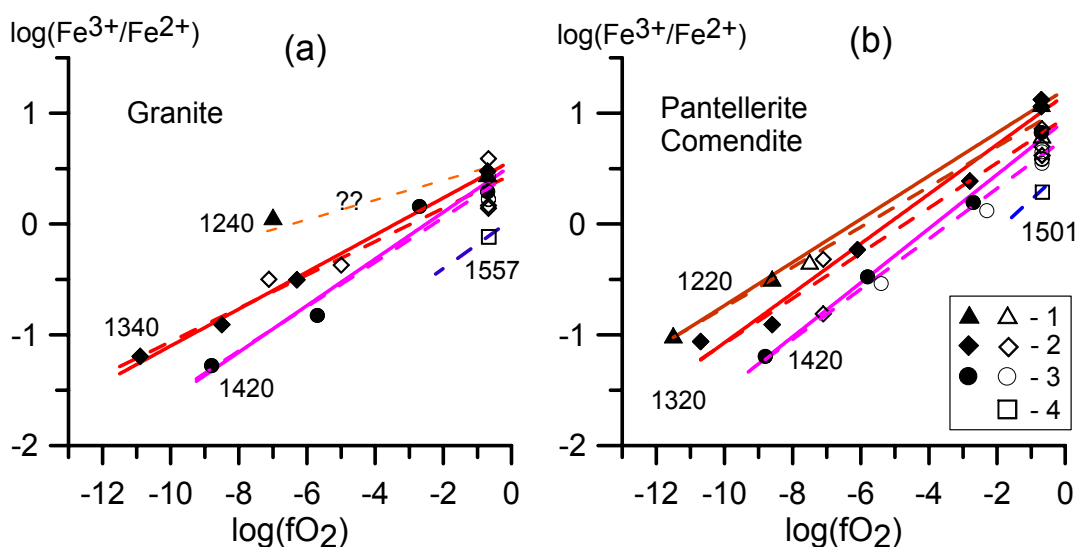


Fig. 1. Dependence of the Fe^{3+}/Fe^{2+} from the oxygen fugacity at different temperatures for granite (a) and pantellerite-comendite (b) melts. 1–4 – experimental data at different T (°C) (filled symbols – for I2 and P9 compositions [Volovetskii et al., 2012], empty symbols – for granitoid compositions according to literature data [Sack et al., 1980; Kilinc et al., 1983; Bychkov, Borisov, 1992; Moore et al., 1995]): 1 – 1200–1250 (1240 for I2 and 1220 for P9), 2 – 1300–1352 (1340 for I2 and 1320 ± 10 for P9), 3 – 1401–1454 (1420 for I2 and P9), 4 – 1557 and 1501 for the granite and comendite-pantellerite compositions, respectively. For I2 at 1240°C and $\log(fO_2) = -7$ equilibrium of melt with furnace atmosphere, obviously, has not been reached

Influence of fO_2 . The results of experiments that demonstrate the dependence of redox state of iron in melts (quenched glasses) from oxygen fugacity at temperatures of 1220, 1340(1320) and 1420°C are shown in Fig. 1. The fO_2 increase under isothermal conditions is accompanied by the increase of ferric iron fraction in both types of silicic melts. The diagrams show linear approximation of the dependence of $\log(Fe^{3+}/Fe^{2+})$ from $\log(fO_2)$ at constant temperature describing experimental data in the form of equations:

$$\log(Fe^{3+}/Fe^{2+}) = k \log(fO_2) + q, \quad (1)$$

where k and q - constants. Under given fO_2 -T conditions the degree of iron oxidation in more alkaline and iron enriched pantelleritic melt is higher than that in granitic melt. This is most clearly expressed under oxidizing conditions at relatively high fO_2 . The coefficient k , which determines the slope of the isothermal line on the plot of $\log(Fe^{3+}/Fe^{2+})$ – $\log(fO_2)$ slightly differs for two melt compositions investigated: for I2 series 0.17 ± 1 at 1340°C and 0.21 ± 3 at 1420°C; for P9 series at the same temperatures 0.22 ± 2 and 0.24 ± 1 , respectively. The value of coefficient k for each composition slightly increases

with temperature increase. It should be noted that initial I2 and P9 melts undergo some changes during the experiments, especially at high temperatures 1320(1340) and 1420°C, mainly related to partial Na_2O loss and increasing content of Al_2O_3 , due to the interaction of melt with the container material [Volovetsky et al., 2012].

Therefore, isothermal straight lines corresponding to different temperatures in

each of the plots for I2 and P9, present the experimental data for melts of slightly different composition.

The plots in Fig. 1 also shows the experimental data of other investigators obtained at 1 atm and different T– fO_2 conditions for natural granitoid melts of different composition. All experimentally studied melts, including I2 and P9, were divided into two groups (in wt.%): *granite* $SiO_2 > 70$ (73–76), $FeO < 3.5$ (3.1–3.4), $Al_2O_3 \geq 12$ (12.0–13.3), $Na_2O+K_2O = 5.7$ –7.0 (Fig. 1a) and *comendite-pantellerite* (granites with high alkalinity and iron content) $SiO_2 > 69$ (69.3–75), $FeO > 5$ (5.2–8.6), $Al_2O_3 < 12$ (8.1–11.2), $Na_2O+K_2O = 7.0$ –11 (Fig. 1b). The molar ratio $(Na_2O+K_2O)/Al_2O_3$ for the first group of melts is 0.6–0.8 (mean 0.75), for the second group 1.1–1.8 (mean 1.3). Dependences of $\log(Fe^{3+}/Fe^{2+})$ on $\log(fO_2)$ for each of these groups of compositions under conditions close to isothermal (at 1225 ± 25 , 1326 ± 25 и $1427 \pm 27^\circ C$) can also be described by linear equations of the form (1) (dashed lines in Fig. 1a and b), that are generally in good agreement with data for I2 and P9 (Table 2).

Isothermal coefficients k for comendite-pantellerite melts have higher values as compared to granite melts. Their value for both types of melts increases with temperature increase (Table 2). Thus, the involvement of

experimental data of other investigators confirmed the possibility of k value increase with temperature. However, this conclusion obviously requires further examination, due to the uncertainties of the experimental data used in

the derivation of equations, that are connected with their scatter in temperature and chemical composition of the melt.

Table 2. Empirical equation $Y = k \cdot X + q$, where $X = \log(fO_2)$, $Y = \log(Fe^{3+}/Fe^{2+})$ describing the effect of fO_2 on the Fe^{3+}/Fe^{2+} ratio in granite and comendite-pantellerite melts under isothermal conditions

$T, ^\circ C$	I2, Granite group	$T, ^\circ C$	P9, Comendite-Pantellerite group
1240	-	1220	$Y = 0.195 \cdot X + 1.21$; $R^2 = 0.999$
-	-	1225±25	$(Y = 0.181 \cdot X + 1.06$; $R^2 = 0.986)$
1340	$Y = 0.167 \cdot X + 0.57$; $R^2 = 0.995$	1320±10	$Y = 0.224 \cdot X + 1.17$; $R^2 = 0.980$
1322±22	$(Y = 0.150 \cdot X + 0.45$; $R^2 = 0.942)$	1326±25	$(Y = 0.204 \cdot X + 0.96$; $R^2 = 0.939)$
1420	$Y = 0.211 \cdot X + 0.53$; $R^2 = 0.958$	1420	$Y = 0.244 \cdot X + 0.93$; $R^2 = 0.995$
1430±12	$(Y = 0.201 \cdot X + 0.46$; $R^2 = 0.957)$	1427±27	$(Y = 0.227 \cdot X + 0.78$; $R^2 = 0.979)$

Note: in parentheses - equations for the two groups of melts obtained by processing all available experimental data, including data for I2 and P9.

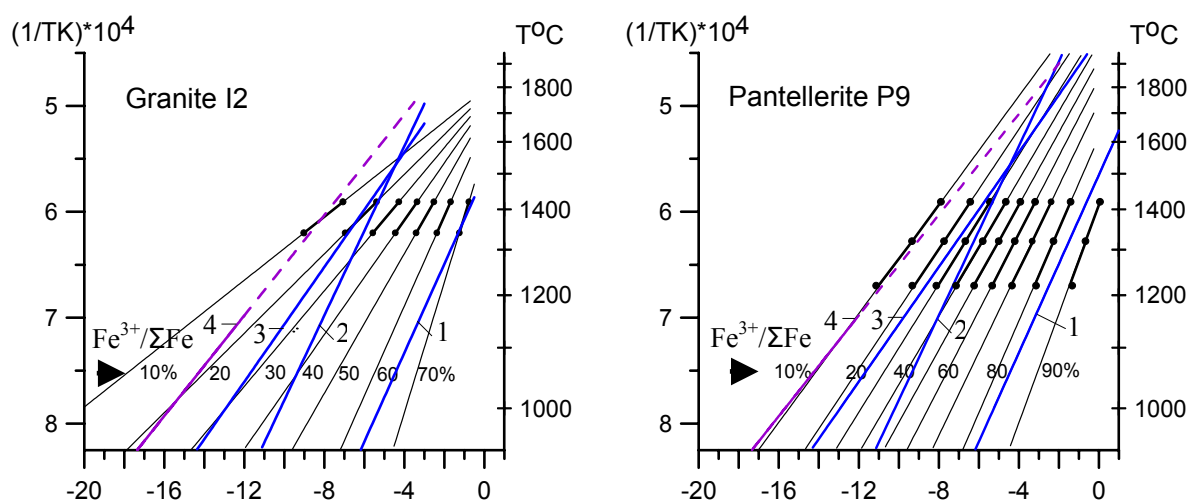


Fig. 2. Effect of temperature influence on fO_2 in granite I2 (a) and pantellerite P9 (b) melts with $Fe^{3+}/\Sigma Fe = \text{const}$. The points are connected by thick lines – empirical data for the investigated temperature range. Thin line – extrapolation of these data in a wide temperature range. 1–3 – buffer equilibrium: 1 – magnetite-hematite (MH), 2 – Ni–NiO (NNO), 3 – wustite-magnetite (WM). 4 – change of intrinsic fO_2 of tektite glasses with temperature by electrochemical data [Kadik et al, 2003]: the solid line in the range of measurements, dashed – the extrapolation to higher temperatures.

Effect of temperature Temperature increase at constant fO_2 leads to reduction of Fe^{3+} to Fe^{2+} in both types of melts. In a closed system, when the Fe^{3+}/Fe^{2+} in the melt is constant, a rise in temperature is accompanied by increase of fO_2 and vice versa – lowering T causes the decrease of fO_2 . Fig. 2 shows the changes in fO_2 with temperature for melts I2 and P9 with a constant ratio of $Fe^{3+}/\Sigma Fe$ based on the calculated data from empirical equations (Table 2). The relatively narrow temperature range in which there are reliable experimental data (especially for I2), as well as the uncertainty arising in the derivation of empirical equations, are the cause a very approximate extrapolation of the lines with $Fe^{3+}/\Sigma Fe = \text{const}$ outside the studied range of temperatures. However, the plots in Fig. 2 reflect some important features of the temperature influence on the regime of fO_2 in granite and pantellerite melts in a closed system.

As can be seen from the plots the slope of the lines with a constant ratio of $Fe^{3+}/\Sigma Fe$ depends on the degree of oxidation of iron in the melt. For oxidized melts ($Fe^{3+}/\Sigma Fe > 60\text{--}70\%$) the slope is close to the slope of the line buffer equilibrium magnetite-hematite. The slope of the lines decreases with decrease in the proportion of Fe^{3+} in the melt. This appears especially noticeable for granitic composition. The slope for a much more reduced melts ($Fe^{3+}/\Sigma Fe < 30\text{--}40\%$) becomes less than the slope of wustite-magnetite buffer. It should be noted that tektite glasses with $Fe^{3+}/\Sigma Fe \leq 10\%$ have similar slope, according to measurement of intrinsic oxygen fugacity [Kadik et al, 2003]. Thus, in closed system, the lowering of temperature will be accompanied by much more significant decrease in fO_2 in reduced melts in comparison with that in oxidized melts.

Empirical equations $(Fe^{3+}/Fe^{2+})_{\text{melt}} = f(T, fO_2, \text{melt composition})$ In Fig. 3 the experimental results for I2 and P9 expressed in the form of equations (1) (Table 2) are compared with calculations for the same melt, made with previously proposed empirical equations describing the

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dependence of iron redox state from the oxygen fugacity, temperature and melt composition:

$$\lg(\text{Fe}^{3+}/\text{Fe}^{2+}) = h/\text{TK} + k \lg(f\text{O}_2) + \sum d_i X_i + c, \quad (2)$$

where c – constant; h , k , and d_i – regression coefficients, which are derived by processing of large sets of experimental data for the whole spectrum of magmatic silicate melts (from ultrabasic-basite to silicic) in wide range of T and $f\text{O}_2$; X_i – mole fractions of oxides of major elements.

1983, and others]. The last equations significantly underestimate the degree of oxidation of iron in the investigated granitic melts at given $f\text{O}_2$ - T conditions.

We obtained new empirical equation of the form (2) for the two types of silicic aluminosilicate melts of granitic and comendite-pantellerite compositions by least squares method using all available experimental data. Granite group includes the results of 17 runs, mostly in the range 1300–1450 °C (+ one run at 1557°C), comendite-pantellerite group consists of 33 runs, mainly in the range 1196–1454°C (+ one run at 1005, 1103 and 1501°C). Regression coefficients values for each of these equations

are presented in Table 3. The h and k coefficients are constant values and do not depend on melt composition and temperature.

The agreement between experimental and calculated data for these equations is shown in Fig. 4 and 5. In almost all cases $\text{Fe}^{3+}/\Sigma\text{Fe}$ calculated values for granite melts differ from those measured in experimental samples by no more than 3%. Determination of $\lg(f\text{O}_2)$ from the known

$\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in melt makes the difference for most of the experiments ± 0.2 log. units, but this discrepancy for

significantly reduced or oxidized melts may reach up to 0.5–0.8 log. units. Testing for comendite-pantellerite melts demonstrates a more considerable variation between the calculated and experimental data: $\text{Fe}^{3+}/\Sigma\text{Fe}$ within 4–5%, in some cases up to 8–9%, and $\lg(f\text{O}_2)$ for the main part of the experiments ± 0.4 log. units (maximum of ± 1.1 log. un.) (Fig. 5). It is quite expected, due to significantly greater heterogeneity of the samples in this group, both in composition and temperature.

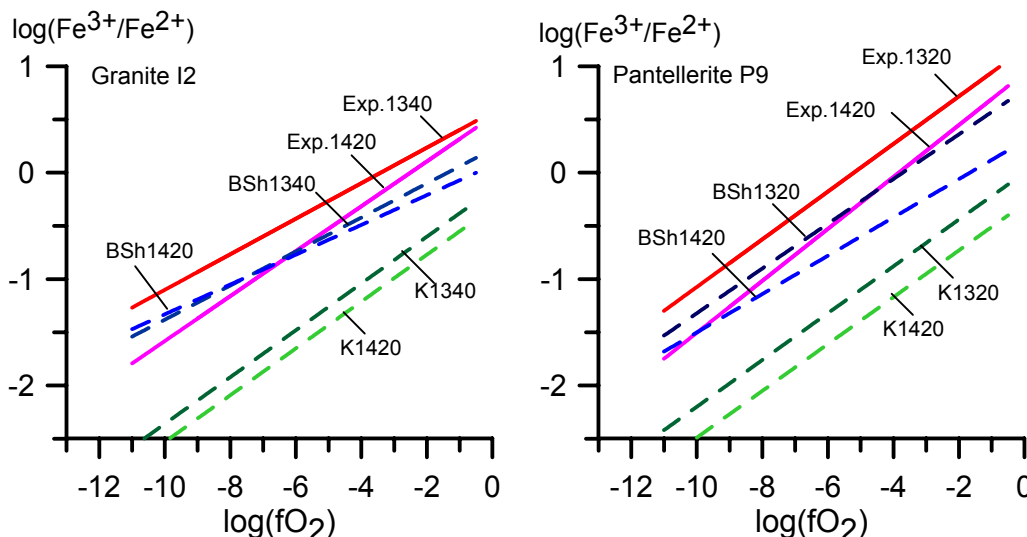


Fig. 3. Comparison of experimental data for I2 (a) and P9 (b) melts at temperatures of 1340(1320) and 1420°C (solid lines) with the calculation results from empirical equations *Borisov and Shapkin* [1989] (dashed lines BSh) and *Kilinc et al.* [1983] (dashed line K)

The values of k coefficient calculated from these equations are close to values found experimentally for the I2 and P9. However, the results of calculations in general are in poor agreement with experimental data. Borisov and Shapkina equation [Borisov, Shapkin, 1989], which takes into account the dependence of h and k on the composition of the melt, much better describes the results of experiments with granite and pantellerite melts in the investigated $f\text{O}_2$ - T area in comparison with similar equations with constant values of h and k [Kilinc et al.,

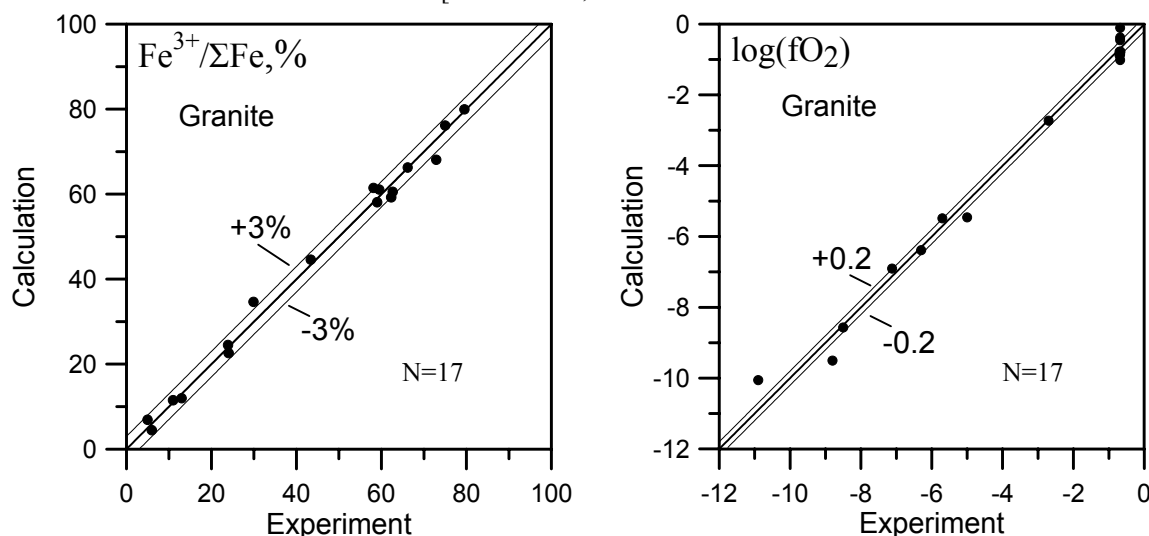


Fig. 4. Comparison of experimental and calculated data for granite melts for temperature range 1300–1557°C. (N – number of experimental points).

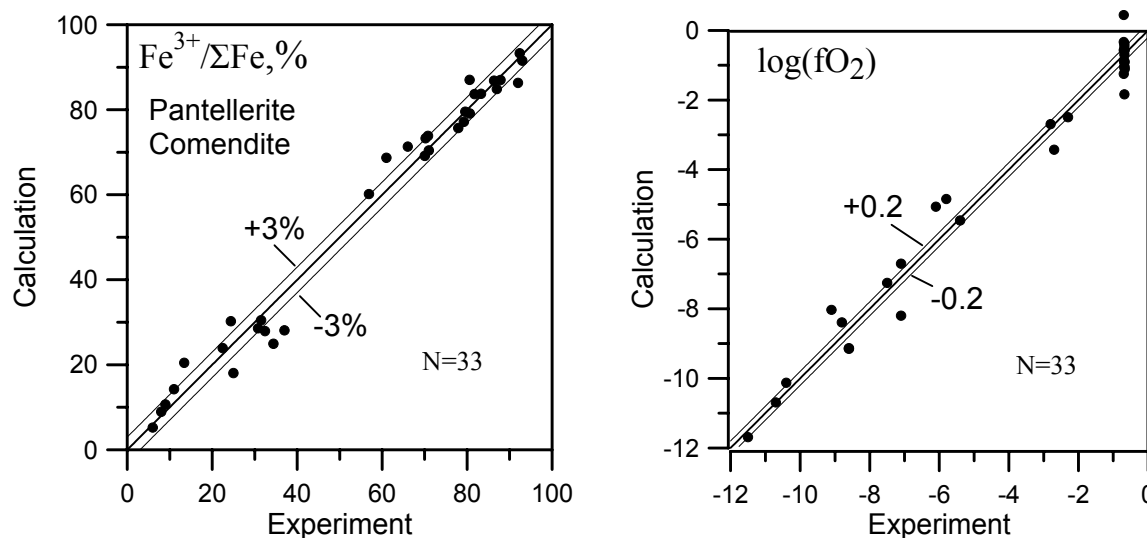


Fig. 5. Comparison of experimental and calculated data for comendite–pantellerite melts for temperature range 1005–1557°C. (N – number of experimental points)

Table 3. Regression coefficients of equation (2) for two types of silicic melts–granite and comendite–pantellerite compositions

Type of melt	k	h	c	d_{SiO_2}	d_{TiO_2}	$d_{Al_2O_3}$	d_{FeO^*}	d_{MgO}	d_{CaO}	d_{Na_2O}	d_{K_2O}
Granite	0.181	619	-45.2	41.4	485.9	64.5	-6.8	1.2	35.6	62.1	134.1
Comed.-panteller.	0.196	3226	35.8	-38.6	-2.3	-35.4	-32.1	-93.0	-17.6	-32.7	-29.7

A similar regression equation obtained for the combined population of granitoid melts reveals a much larger discrepancy with the experimental data in comparison with the equations for each of the two groups. Deviations of more than half of the experiments on $Fe^{3+}/\Sigma Fe \geq 5\%$ ($\log(fO_2) \geq 0.5$ log. units) and almost a quarter of the experiments $\geq 10\%$ (respectively, $\log(fO_2) \geq 1.2$ log. units). Thus, only the equations proposed for each of the abovementioned granitoid groups may in first approximation satisfactorily describe the dependence of $(Fe^{3+}/Fe^{2+})_{melt} = f(T, fO_2, \text{composition})$ obviously still in a relatively limited range of temperatures $\sim 1200(1100)–1450^\circ\text{C}$. The improvement of empirical equations of this kind (increasing their accuracy and extending the range of compositions and temperatures) appears to require additional experimental data that will enable to take into account the influence of composition and temperature on k and h coefficients in the equations.

Conclusions

1. The influence of oxygen fugacity on the Fe^{3+}/Fe^{2+} in granite and pantellerite melts under isothermal conditions (in the range 1220–1420 °C) is described by the equation $\log(Fe^{3+}/Fe^{2+}) = k \cdot \lg(fO_2) + q$, where k and q – constants that depend not only on the composition of the melt, but also on the temperature (Table 2). Under given fO_2 – T conditions the degree of iron oxidation in alkaline and iron enriched pantelleritic melt is higher than that in granitic melt.

2. Temperature increase at constant fO_2 causes reduction of Fe^{3+} to Fe^{2+} in both types of melts. In closed system, when the Fe^{3+}/Fe^{2+} in melt is constant, the increase of temperature is accompanied by increase in fO_2 and vice versa – lowering the temperature leads to a decrease in fO_2 . Decrease in T causes significant decrease in fO_2 in relatively more reduced melts in comparison with oxidized melts.

3. New empirical equations (Table 3), obtained by processing our own and the available experimental data allow satisfactorily in first approximation to describe the dependence of $(Fe^{3+}/Fe^{2+})_{melt} = f(T, fO_2, \text{melt composition})$ for two types of acidic silica-alumina melts granite and comendite-pantellerite compositions in relatively limited range of temperatures $\sim 1200(1100)–1450^\circ\text{C}$.

This work was supported by RFBR (grants 08-05-00022, 11-05-00926).

References:

- Borisov, A. A., A. I. Shapkin (1989). A new empirical equation of the ratio of Fe^{3+}/Fe^{2+} in natural melts from their composition, oxygen fugacity and temperature, *Geokhimiya*, № 6, pp. 892–898 (In Russian).
- Bychkov, A.M., A. A. Borisov (1992). Effect of temperature and oxygen fugacity on the structural and valence state of Fe in rhyolitic melts, *Geokhimiya*, № 11, pp. 1507–1511 (In Russian).
- Nikolaev, G. S., A. A. Borisov, A. A. Ariskin (1996). Calculation of the ratio of Fe^{3+}/Fe^{2+} in magmatic melts: testing and additional calibration of empirical equations for various petrochemical series, *Geokhimiya*, № 8, pp. 713–722 (In Russian).
- Volovetskii, M. V., O. A. Lukanin, V. S. Rusakov, A. A. Kargal'tsev (2012). Influence of oxygen fugacity and temperature on the redox state of iron in natural silicic aluminosilicate melts, *Geochemistry International*, v. 50, No. 4, pp. 330–343.
- Kadik, A. A., O. A. Lukanin, E. V. Zharkova, V. I. Fel'dman (2003). Oxygen and hydrogen (water) regime during tektite formation, *Geochemistry International*, v. 41, No 9, pp. 865–880.
- Kargal'tsev, A. A., M. V. Volovetskii, A. A. Kadik, O. A. Lukanin (2009). A high-temperature furnace with a controlled oxygen regime for studying phase and redox reactions in silicate and oxide systems at 1 atm, *Geochemistry International*, v. 47, No. 7, pp. 725–730.

7. Kilinc, A., I. S. E. Carmichael, M. L. Rivers, R. O. Sack (1983). The ferric-ferrous ratio of natural silicate liquids equilibrated in air, *Contrib. Mineral. Petrol.*, v. 83, pp. 136–140.
8. Kress, V. C., I. S. E. Carmichael (1991). The compressibility of silicate liquids containing Fe₂O₃ and the effect of composition, temperature, oxygen fugacity and pressure on their redox states, *Contrib. Mineral. Petrol.*, v. 108, pp. 82–92.
9. Mysen, B. O. (1991) Relations between structure, redox equilibria of iron and properties of magmatic liquids, *Physical Chemistry of Magma* (eds.: L.L. Perchuk and I. Kushiro). Springer Verlag, Chapter 2, pp. 41–98.
10. Jayasuriya, K. D., H. St. C. O'Neil, A. Berry, S. J. Campbell (2004). A Mössbauer study of the oxidation state of Fe in silicate melts, *Amer. Mineral.*, v. 89, pp. 1597–1609.
11. Moore, G., K. Righter, I. S. E. Carmichael (1995). The effect of dissolved water on the oxidation state of iron in natural silicate liquids, *Contrib. Mineral. Petrol.*, v. 120, No 1, pp. 170–179.
12. Sack, R. O., I. S. E. Carmichael, M. Rivers, M. S. Ghiorso (1980). Ferric-ferrous equilibria in natural silicate liquids at 1 bar, *Contrib. Mineral. Petrol.*, v. 75, pp. 369–376.

Medvedev V. Ya., Ivanova L. A., Egorov K. N. Experimental modeling of the transformation of kimberlite barophilic minerals in the pipe condition

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Experimental and physico-chemical modeling of pyropes and picroilmenites regressive transformation processes allowed studying their transformation kinetics and obtaining the duration of stay of kimberlite pipes at active state. Kelyphitic rims on the kimberlites high-pressure minerals composed both of primary and secondary minerals that replaced the primary minerals of kelyphyte have been studied. It was shown that formation of secondary chlorite-calcite-serpentine rims on garnets occur only after the primary kelyphitic rim. Results of physico-chemical modeling of garnets transformation agree well with the experiment and correspond to native analogues.

Key words: experiment, pressurefile minerals of kimberlites, kinetic of process

Citation: Medvedev, V. Ya., L. A. Ivanova, K. N. Egorov (2012), Experimental modeling of the transformation of kimberlite barophilic minerals in the pipe condition, *Vestn. Otd. nauk Zemle*, 4,

Persikov ¹E. S., Newman ²S., Bukhtiyarov ¹P. G. Concentration dependences of the molar absorption coefficients of the two type of dissolved water (OH⁻ и H₂O) in silicate and magmatic melts (glasses) in the series acidic-basic

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The structural chemical model has been developed to calculate and predict the concentration dependences of the molar absorption coefficients for the two type of dissolved water (OH⁻ и H₂O) in silicate and magmatic melts (glasses) in a wide range of the melt composition from obsidian to basalt. This model was suggested to correct determination of water content in the glasses (melts) and along the diffusion profiles for various types of dissolved water (OH⁻ groups, 4500 cm⁻¹ band) and molecular H₂O, 5200 cm⁻¹ band) by quantitative IR micro spectroscopy.

Key words: IR-spectroscopy, molar absorption, dissolved water, concentration, silicate glasses, structure, model

Citation: Persikov, E. S., S. Newman, P. G. Bukhtiyarov (2012). Concentration dependences of the molar absorption coefficients of the two type of dissolved water (OH⁻ и H₂O) in silicate and magmatic melts (glasses) in the series acidic-basic, *Vestn. Otd. nauk Zemle, RAS*, 4

FTIR spectroscopy in the infrared and near-infrared spectral region is the one of the effective methods to quantitative determination the concentrations of water which is dissolved in silicate melts (glasses) at high pressures. Moreover it is really a single method for quantitative determination of water content along the diffusion profiles. Water content in silicate glasses and along the diffusion profiles for various types of dissolved water (OH⁻ groups and molecular H₂O) have been determined by FTIR spectroscopy using of the Beer-Lambert equation:

$$C = 100 \cdot 18.015 \cdot A / \rho \cdot \delta \cdot \epsilon \quad (1),$$

where *C* is the concentration (in wt %) of various H₂O species (OH⁻ or H₂O) in the melt (glass), *A* is the height of the absorption peak (relative %), *ρ* is the density of the glass (g/l), *δ* is the thickness of the platelet (cm), *ε* is the molar absorption coefficient of the corresponding water type (l/mol·cm), and 18.015 is the molecular mass of water (g/mol).

The IR spectra of the hydration and diffusion samples were recorded on a Nicolet Magna_IT 860 IR spectrometer equipped with a Nicolet Continuum IR microscope (Caltech, USA). Total water contents (C(H₂O) = the sum of water dissolved as OH⁻ groups and H₂O molecules) along the diffusion profiles in the quenched experiments were determined for the samples by FTIR spectroscopy.

Molar absorption coefficients for OH⁻ and H₂O bands in the infrared and near-infrared regions are known to vary with glass composition. Experimental study of the molar absorption coefficients for OH⁻ and H₂O bands even for a single composition of silicate glass is not so easy. Dixon et al. (1995) and Mandeville et al. (2002) showed that the molar absorption coefficients for the 5200 cm⁻¹ and 4500 cm⁻¹ bands can be approximated as linear functions of the cation fraction of tetrahedral cations (*T* = (Si⁴⁺ + Al³⁺)/(total cations)) over a significant compositional range. [Ohlhorst et al., 2001] were used of the content of SiO₂ in silicate glasses to predict the concentration dependence of molar absorption coefficients for OH⁻ and H₂O bands in the near-infrared regions. In order to enhance the accuracy and reliability of the measured (by IR spectroscopy) concentrations of various water species (OH⁻ and H₂O), a structural-chemical model was developed that makes it possible to calculate and predict the concentration dependence of the molar absorption coefficients of various water species (*ε*) dissolved in silicate melts (glasses) within the andesite-basalt compositional range [Persikov et al., 2010]. In order to characterize the chemical composition, this model employs a structural-chemical parameter (*100NBO/T*): the degree of depolymerization or the coefficient of the relative basicity of silicate melt, which can be readily calculated from the chemical composition of the melt [Persikov, 1991; 1998]. It has been established that this parameter is optimal for expressing distinctive features of the chemical composition and structure of silicate and magmatic melts [Persikov, 1991; 1998].

In this study mentioned model has been used for a wide range of the composition of silicate glasses (melts)

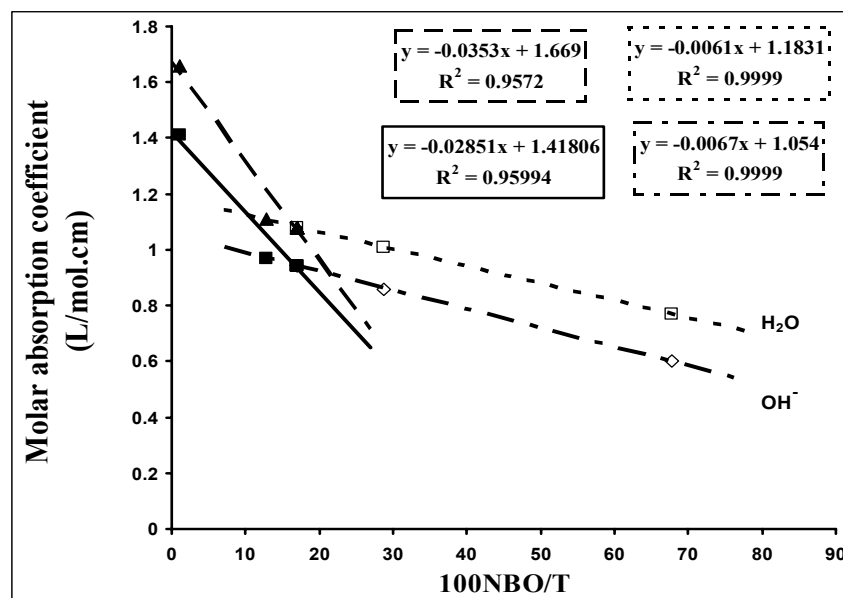


Fig. 1. Compositional dependence of molar absorption coefficients in silicate glasses for hydroxyl groups (4500 cm^{-1} band) and molecular water (5200 cm^{-1} band) within the obsidian – basalt compositional range (open symbols are the andesite–basalt compositional range [Persikov *et al.*, 2010]; closed symbols are the rhyolite–dacite compositional range [Ohlhorst *et al.*, 2001])

from obsidian to basalt. The results obtained using of this model are shown at the Fig. 1.

Simple linear equations proposed for calculating the molar absorption coefficients of the two water species in silicate and magmatic melts (glasses) within the obsidian–basalt compositional range based on the established correlation (Fig. 1) are as follows:

1) for hydroxyl groups (OH^-)

within the obsidian–dacite compositional range

$$4500 \text{ cm}^{-1} = 1.67 - 0.035 \cdot K, \quad (2)$$

within the andesite–basalt compositional range

$$4500 \text{ cm}^{-1} = 1.06 - 0.007 \cdot K, \quad (3)$$

2) for water molecules (H_2O)

within the obsidian–dacite compositional range

$$5200 \text{ cm}^{-1} = 1.42 - 0.028 \cdot K, \quad (4)$$

within the andesite–basalt compositional range

$$5200 \text{ cm}^{-1} = 1.183 - 0.006 \cdot K, \quad (5),$$

where $K = 100 \cdot \text{NBO}/T$ – is mentioned above structural–chemical parameter.

In accordance with the structural model of silicate and magmatic melts [Persikov, 1991; Persikov, 1998] the calibration lines used here (Fig. 1) have the two inflection points at the $K \approx 17$ which corresponds to the anhydrous andesite average composition. At this value of $100\text{NBO}/T$ the dramatic change of melt structure has been done that is the full polymerized framework structure of acidic silicate melts is break down at these points.

The calculated errors of this approximation are ± 0.10 and ± 0.09 l/mol·cm for the molar absorption coefficients for the 4500 cm^{-1} and 5200 cm^{-1} bands, respectively. These errors of the molar absorption coefficients are less than the errors which may obtained using the [Dixon *et al.* 1995, Ohlhorst *et al.*, 2001 and Mandeville *et al.*, 2002] correlation. The values of the molar absorption

coefficients (extinction coefficients) obtained by Eqs. (3 - 5) for the two water species dissolved in silicate melts (glasses) studied are as follows:

1. obsidian

$$4500 \text{ cm}^{-1} = 1.36 \pm 0.10$$

$$5200 \text{ cm}^{-1} = 1.6 \pm 0.09$$

2. haplodacite (Ab90Di8Wo2)

$$4500 \text{ cm}^{-1} = 1.11 \pm 0.10$$

$$5200 \text{ cm}^{-1} = 1.29 \pm 0.09$$

3. haploandesite (Ab77Di19.5Wo3.5)

$$4500 \text{ cm}^{-1} = 0.86 \pm 0.10$$

$$5200 \text{ cm}^{-1} = 1.01 \pm 0.09$$

4. haplobasalt (Ab45Di37Wo18)

$$4500 \text{ cm}^{-1} = 0.6 \pm 0.10$$

$$5200 \text{ cm}^{-1} = 0.77 \pm 0.09$$

In conclusion it should be note that the structural chemical model suggested is allowed to improve the accuracy of the predicted compositional dependence of molar absorption coefficients in silicate glasses for hydroxyl groups (4500 cm^{-1} band) and molecular water (5200 cm^{-1} band) within of acidic-basic range of composition.

We thank E.M. Stolper for his helpful ssions.

This work was supported by RFBR, grant No 12-05-00164 and by DES, program No 9.

References:

1. Dixon, J. E., E. M. Stolper, J. R. Holloway (1995). An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids, Part I: Calibration and solubility model, *J. Petrol.*, v. 36, p. 1607–1631.
2. Mandeville, C. W., J. D. Webster, M. J. Rutherford, B. E. Taylor, A. Timban, K. Faure (2002). Determination of molar absorptivities for infrared absorption bands of H_2O in andesitic glasses, *Am. Mineral.*, v. 87, p. 813–821.
3. Ohlhorst, S., H. Behrens, F. Holtz. (2001). Compositional dependence of molar absorptivities of near-infrared OH^- and H_2O bands in rhyolitic to basaltic glasses, *Chem. Geol.*, v. 174, p. 5–20.
4. Persikov, E. S. (1991). The viscosity of magmatic liquids: experiment, generalized patterns. A model for calculation and prediction. Applications, *In: Physical chemistry of magmas. Advances in Physical Geochemistry*. L. L. Perchuk & I. Kushiro, Eods., Springer-Verlag. New York, v, 9, p. 1–40.
5. Persikov, E. S. (1998). The viscosity of model and magmatic melts under P–T-parameters of the Earth's crust and upper mantle, *Russian Geology and Geophysics*, v. 39, No 12, Allerton Press, Inc, New York, p. 1780–1792.
6. Persikov, E. S., S. Newman, P. G. Bukhtiyarov, A. N. Nekrasov, E. M. Stolper (2010). Experimental study of water diffusion in haplobasaltic and haploandesitic melts, *Chemical Geology*, v. 276, p. 241–256.

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Experimental study of the effect of concentration
of dissolved water on diffusion of H_2O in
haplodacite melts at high pressures

Abstracts

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Diffusion of H₂O and the concentration dependence of water diffusivity in haplodacite melts (Ab90Di8Wo2, mole %) has been experimentally study in a wide range of water content in the melts (0.2–6.0 wt. %), at the P(H₂O) up to 160 MPa and the temperature 1200°C using a new small gradient methodology. Exponential dependence of water diffusion on water content in haplodacite melts at mentioned parameters has been established by a strict experimentally.

Key words: diffusion, water, concentration dependence, melt, temperature, pressure, haplodacite, model, IR-spectroscopy

Citation: Persikov, E. S., P. G. Bukhtiyarov, S. Newman (2012). Experimental study of the effect of concentration of dissolved water on diffusion of H₂O in haplodacite melts at high pressures, Vestn. Otd. nauk Zemle, RAS, 4

The experimental study of water diffusivity in silicate melts was not solved the problem of the concentration dependence of D(H₂O) on C(H₂O) including for polymerized melts such as albite, obsidian, granite, rhyolite and dacite [Shaw, 1974; Nowak, Behrens, 1997; Zhang, Behrens, 2000, ect.]. Moreover, the all diffusion studies which were used a high gradient method, including our results [Persikov et al., 2010] have not been designed in such a way as to provide a definitive experimental determination of the functional relationship between of D(H₂O) and C(H₂O) over the full range of water contents for each experiment. A new small gradient methodology to study the dependence of water diffusivity on water content in synthetic and magmatic melts has been developed to provide a definitive experimental determination of this dependence over a wide range of water content (up to ~ 6 wt. %) which is independent of any assumptions regarding such dependence and mechanisms of water diffusion in these melts [Persikov, et al., 2010; Persikov et al., 2010]. Based on our results, we conclude that one approach that would allow such a determination would be determination of (D(H₂O) values using experiments that have only a small range in C(H₂O), determination of D(H₂O) for a series of small water gradient experiments that collectively span a wide

range in C(H₂O) could yield a robust model independent form of the variation of D(H₂O) as a function of C(H₂O). The main features of this method are as follows: a) do not assume any functional relationship between D(H₂O) and C(H₂O); b) goal is to build this relationship from multiple experiments (5 -7 runs); c) concentration limits at the ends of profiles vary by no more than ~0.5–1.0 wt. % H₂O. We report here new results of experiments to determine the diffusivity of water (D(H₂O)) in haplodacite melts (Ab90Di8Wo2, мол. %), at 1200°C and P(H₂O) up to 160 MPa in a wide range of water content up to ≈ 6 wt. % using this methodology.

An internally heated pressure vessel (IHPV) was used to carry out such kind diffusion experiments. Note that the samples run in the IHPV were undeformed during these experiments. Two different types of small gradient experiments were done: first type of hydration experiments for dry haplodacite melts at the T = 1200°C and P(H₂O) 20 MPa has been described in detail in our resent published paper [Persikov et al., 2010]. Another type of hydration diffusion experiments has been used for water diffusivity in water bearing haplodacite melts. In this case the experiments were included of the three stages: a) first stage was a hydration (saturation) of dry glasses during 3 hours at T = 1200°C and water pressure for example 50 MPa without quenching; b) second stage was a direct diffusion of water into water saturated melt which is started immediately after first stage by isothermal increasing of water pressure up to 70 MPa value; c) third stage was isobarical quenching by turnig off the power to the heater. Measured initial cooling rates were ≈ 300 °C/min down to 900 °C, followed by ≈ 100 °C/min down to room temperature.

Water contents and concentration-distance profiles of the diffusion samples were determined by Fourier transform infrared spectroscopy (FTIR). D(H₂O) values were determined by best fitting these profiles using Boltzmann-Matano method [Crank, 1975]. Our results show that D(H₂O) increases with increasing water content, the increase with

water content is exponential for haplodacite melts (see equation at the Fig. 1). This result is disagree with the result of [Zhang, Behrens, 2000] where the linear dependence of D(H₂O) on C(H₂O) has been established. Predicted dependence of D(H₂O) on C(H₂O) in haplodacite melts is represented at the Fig. 1 too which was obtained using a new structural chemical model to calculate and predict the water diffusivity in magmatic melts [Persikov E.S., P.G. Bukhtiyarov, 2009; Persikov et al., 2010].

Demonstrably (see Fig. 1), that the experimental and predicted dependencies of D(H₂O)) on C(H₂O) are in a good agreement inside of the

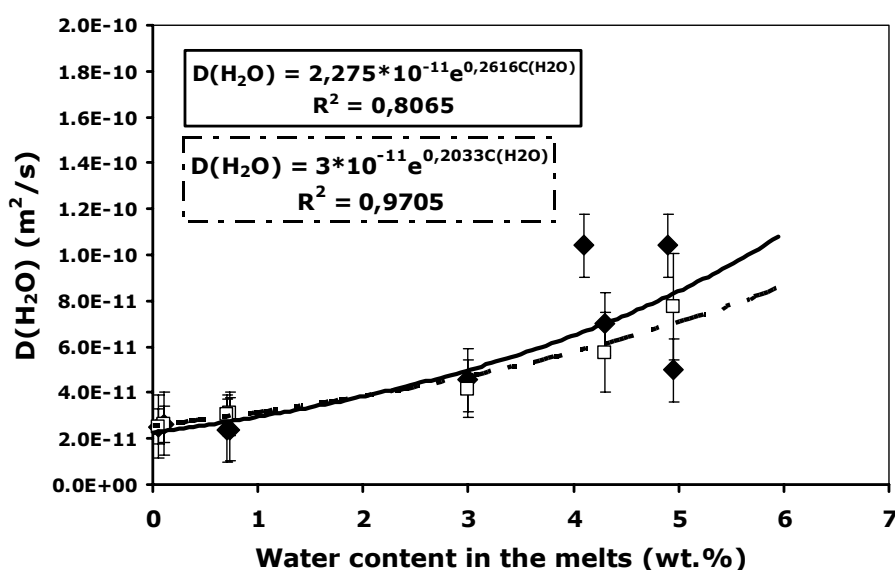


Fig. 1. Concentration dependence of water diffusivity in haplodacite melts, T = 1200°C and P(H₂O) up to 160 MPa (dark symbols – an experimental data, open symbols – predicting data which were obtained using a new model; [Persikov et al., 2010])

experimental ($\pm 30\%$ relative) and predicted ($\pm 35\%$ relative) data precision. This is an additional evidence that the mentioned model [Persikov *et al.*, 2010] may be used with the success to calculate and predict the concentration dependence of water diffusivity in magmatic melts.

We thank E.M. Stolper for his helpful discussions.

This work was supported by RFBR, grant No 12-05-00164 and by DES, program No 9.

References:

1. Shaw, H. R. (1974). Diffusion of H₂O in granitic liquids; Part I. Experimental data; Part II. Mass transfer in magma chambers, In: Hofmann, A.W., et al. (Eds.), *Geochemical Transport and Kinetics*, 634. Carnegie Institute Washington Publ., Washington, pp. 139–170.
2. Nowak, M., H. Behrens. (1997). An experimental investigation on diffusion of water in haplogranitic melts, *Contrib. Mineral. Petrol.*, 126, pp. 365–376.
3. Zhang, Y., Behrens, H. (2000). H₂O diffusion in rhyolitic melts and glasses, *Chem. Geol.*, 169, pp. 243–262.
4. Crank, J. (1975). *The Mathematics of Diffusion*, Clarendon Press, Oxford, 414 p.
5. Persikov, E. S., P. G. Bukhtiyarov, and A. N. Nekrasov (2010). Water diffusion in basalt and andesite melts under high pressures, *Geochemistry International*, vol. 48, No 3, pp. 213–224.
6. Persikov, E. S., S. Newman, P. G. Bukhtiyarov, A. N. Nekrasov, E. M. Stolper. (2010). Experimental study of water diffusion in haplobasaltic and haploandesitic melts, *Chemical Geology*, vol. 276, pp. 241–256.
7. Persikov, E. S., P. G. Bukhtiyarov (2009). Interrelated structural chemical model to predict and calculate the viscosity of magmatic melts and water diffusion in a wide range of compositions and T-P parameters of the Earth's crust and upper mantle, *Russian Geology and Geophysics*, v. 50, № 12, pp. 1079–1090.

Shchekina T. I., Alferieva Ya. O., Alferieva Ya. O., Gramenitskiy E. N. Topaz, cryolite and villiaumite crystallization conditions in the system SiO₂–Al₂O₃–Na₂O–K₂O–Li₂O–H₂O–F and in nature

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It is shown that the composition of rocks containing high fluorine minerals, corresponds to the composition of the melts in the experimental phase diagram of the granite and nepheline-syenite system at 650–800 °C and 1 kbar. This is a proof of the magmatic nature of accessory cryolite, topaz and villiaumite, as well as of the cryolite large bodies crystallization from the molten salt.

Key words: cryolite-, topaz- bearing granites, villiaumite-bearing rocks, saturated with fluoride melts, aluminosilicate and aluminofluoride melts, liquid immiscibility, the total composition of rocks.

Citation: Shchekina, Ya. O. Alferieva, E. N. Gramenitskiy (2012), Topaz, cryolite and villiaumite crystallization conditions in the system SiO₂–Al₂O₃–Na₂O–K₂O–Li₂O–H₂O–F and in nature, *Vestn. Otd. nauk Zemle*, 4,

A sequential increase in the concentration of volatile components, including water and fluorine will occur in the process of magmatic melts differentiation. As the limit of solubility of fluoride-bearing phases is reached, they are

crystallized from a magmatic melt in the form of accessory, sometimes minor rock-forming minerals. In the system we have studied (SiO₂–Al₂O₃–Na₂O–K₂O–Li₂O–H₂O–F) at temperatures from 650 to 800 °C and pressure of 1000 bar, the high-fluorine of these phases would be cryolite Na₃AlF₆, elpasolite NaK₂AlF₆, villiaumite NaF and topaz Al₂SiO₄(F, OH)₂. [Gramenitskiy *et al.*, 2005].

In addition to these minerals, fluoride melt may occur in the system at the equilibrium with aluminosilicate melt. The stability field of fluoride melt expands substantially in the presence of Li [Alferieva *et al.*, 2011]. Each silicate melt in the system has a fixed content of fluorine, thus demonstrating the solubility of fluoride in it. It has been established that in the experimental glasses, as well as in the bulk composition of the rocks, containing high-fluorine minerals, there is a tendency for the concentration of fluoride, to decrease, when contents of SiO₂ increases.

The chemical composition of phases obtained in the experiment was studied by means of the electron microprobe energy dispersive micro analyzer based on scanning electron microscope Jeol JSM-6480LV (INCA-Energy Spectrometer 350) of Department of Petrology, Moscow State University.

Most of the bulk compositions of cryolite-bearing rocks belong to the normal- and moderate-alkali or alkaline series, i.e. to a group of subalkaline, and alkaline leucogranites, respectively. Most of them fall in the category of the agpaitic, and some to peraluminous series. The alkali sum (Na₂O + K₂O) varies from 8 to 13 wt.%. The ratio of Na / K (at.%) is always in favor of sodium and usually equals 1.5–2. Topaz-bearing granites are acidic plutonic rocks of moderately alkaline or subalkaline series and belong to the microcline-albite granites. All topaz-bearing (Li-F) granites and their subvolcanic equivalents - ongonites and elvanes - belong to peraluminous series of rock compositions with agpaitic coefficients from 0.65 to 0.98. Villiaumite-bearing rocks are represented by sodium-potassium alkaline medium rocks – nepheline- and feldspathoid-syenite. Villiaumite is found in agpaitic nepheline syenites and their pegmatites only. Usually in the rocks with villiaumite SiO₂ content varies from 51 to 58%, the alkali sum (Na₂O + K₂O) from 14 to 21%.

In general, the experimental data in the system Si–Al–Na–O–F at 800 °C and 1 kbar are confirmed in the petrochemical features of rocks: a) the topaz-, cryolite and villiaumite-containing rocks form a separate field of figurative points of the compositions; b) fields position themselves in that order with progressively increasing agpaitic coefficients; c) fields of rocks with topaz and villiaumite don't touch each other, the paragenesis of these minerals is prohibited. Bulk composition of cryolite- and topaz-bearing rocks are consistent with well-defined compositions of melts in equilibrium with these minerals in the experimental diagram.

On the other hand, there is some controversy, since the experimental data refer to the phase relations in the simplified composition, moreover, they are tied to certain conditions. Thus, most of the figurative points of compositions of villiaumite-bearing rocks, as well as of inclusions in them, fall in the agpaitic part of the field of equilibrium cryolite + melt, stretched along the line of joint crystallization of cryolite and villiaumite, rather than in the melts in equilibrium with villiaumite. The field of cryolite + melt at the experimental diagram is distributed

in the region of nepheline-normative area and is much wider than field of real cryolite-bearing rocks.

If Na is substituted by Li in the system, the field of cryolite is replaced by field of equilibrium of aluminosilicate and fluoride melt (liquid immiscibility) in nepheline normative area. Confirmation of these relationships have not been identified in nature. The equilibrium of cryolite-villiaumite doesn't occur on the border of the suitable fields, but it is well defined in the experiments in the system without Li. It is possible that other components, besides lithium, may influence the change of phase relations. The displacement of field boundaries of cryolite and villiaumite towards a less agpaite area, according to schematic reaction – cryolite + agpaite melt → villiaumite + aluminous melt, - may be attributed to the presence of a component in the system which enters into villiaumite and expands the field of its stability, or to a change in temperature, or in pressure. Verification of these hypotheses requires further experiments.

The experimental data show the presence in the high-alumina part of model system of an immiscible area of aluminosilicate with fluoride melt, while the solidus of fluoride liquid refers to much lower temperatures than in the case of aluminosilicate melt. This field corresponds to the rich in fluorine corundum nepheline syenites, very rarely found in nature. As already mentioned, the field of liquid immiscibility significantly expands with the replacement of sodium (and potassium) by lithium. The concentration of 1% of Li in the system would suffice to replace the field of cryolite by the field of fluoride melt, which overlaps compositions of most natural granites and syenites. It has been traced up to 650 ° C. Liquid immiscibility manifests itself by the formation of large-scale isolations (salt globules) in the silicate melt. Manifestations of immiscibility process may occur also in nature.

These include the segregation of cryolite in the form of large, almost monomineralic bodies found in a number of cryolite-bearing granites, of great economic value. Examples of such formations are: Ivigtut deposit in Greenland, Pitinga in Brazil, Ulug-Tanzek and Zashihinskoe in Eastern Siberia. Undoubtedly, a cryolite crystallization from a melt (or highly concentrated brine) occurred in these deposits. Similar formations were discovered in alkaline rocks. In the Khibiny massif are found syenitic pegmatites with the villiaumite core, constituting up to 30% of the pegmatite. Schlieren-like segregations of villiaumite form big blocks in association with natrolite, sodalite and gaskmanite, and are encountered in pegmatite horizon of the same complex. Apparently, separation processes of magmatic melts in the liquid silicate and essentially salt compositions have played an important role during villiaumite bodies formation.

Thus, the magmatic nature of accessory topaz, cryolite and villiaumite in granites and nepheline syenites has been proved by way of comparison between petrological and experimental data. It has been shown that the large ore bodies of cryolite and villiaumite geologically connected with granites and pegmatites may be formed from the fluoride salt melt, created as a result of liquid immiscibility with the fluorine saturated silicate melt.

References:

1. Gramenitskiy, E. N., T. I. Shchekina, V. N. Deviatova (2005). Phase relations in the fluorine-bearing granite and nepheline syenite systems and the element distribution between phases (experimental research), M: GEOS, 186 p. (in Russian).
2. Alferieva, Ya. O., E. N. Gramenitskiy, T. I. Shchekina (2011). Experimental study of phase relations in the lithium-bearing fluorine-rich and gaplogranite and nefelinsyenite system, *Geochemistry*, № 7, p. 713–728 (in Russian).

Simakin A. G., Zakrevskaya O. Yu., Salova T. P. Estimate of Kamchatka cortlandites crystallization conditions by amphibole compositions

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Nickel Sulfide deposits containing PGE had been found in Central Kamchatka Ridge (CKR). These ores are localized in amphibole-bearing ultramafic rocks cortlandites. We estimate crystallization pressure of cortlandites while employing our novel Al^{VI} in amphibole geo-barometer. We calibrate pressure dependence of the maximum asymptotic (calculated for $Fe^{3+}+Ti = 0$ apfu) content of octahedral aluminum in amphibole with using of our and published data obtained in experiments on hydrous andesitic and basaltic melts. Processing of amphibole compositions from CKR cortlandites yields pressure ca 8 kbar close to the peak pressure of cortlandites hosting metamorphic rocks of 6.3–8 kbar. Such high pressure corresponds to the depth 24–27 km at the present day crust thickness at CKR edge of 35–40 km. These observations stay for pronounce Kamchatka crust thickening at the arc collision in Eocene time.

Key words: Amphibole, cortlandite, geo-barometer, tholeiitic magma

Citation: Simakin, A. G., O. Yu. Zakrevskaya, T. P. Salova (2011), Estimate of Kamchatka cortlandites crystallization conditions by amphibole compositions, *Vestn. Otd. nauk Zemle*, 4

Large part of Kamchatka was formed at the accretion of Achaivayam-Valaginskaya and Kronotskaya island arcs in Eocene and Pliocene respectively. Collision of island arcs with North-East edge of Asia caused impulses of magmatism of silicic (52 mln yrs ago [Luchitskaya, et al., 2008]) and ultrabasic-basic (Eocene [Konnikov, et al., 2010]; [Selyangin, 2009].) compositions. Mafic-ultramafic formation is represented by the concentric dunite-pyroxenite-gabbro intrusions [Selyangin, 2009] and small to medium size cortlandite-pyroxenite-gabbro-norite ones [Selyangin, 2007].

Ultrabasic-basic cortlanditic intrusions are localized along edge of central metamorphic massif of Kamchatka in the zone extended in meridian direction on 300 km and 30–50 km across. Totally about 50 small to medium size Cu–Ni ore bearing intrusions are encountered in this zone. The largest deposits belong to Dukuk and Shanuch clusters (Fig.1). Cortlandite is defined as a magmatic rock containing 60–70 vol.% of hornblende. Origin of cortlandites is a matter of discussions. However, it is clear that high water content (reflected in amphibole abundance) in the parent high-magnesium picrito-basalt magma somehow is linked with Cu–Ni sulfide ore formation. In the given work we present results of the application of the novel amphibole geo-barometer [Simakin, et al., 2012] to cortlandites of Kamchatka.

All previously derived amphibole based geobarometers (with exception of the last model [Ridolfi,

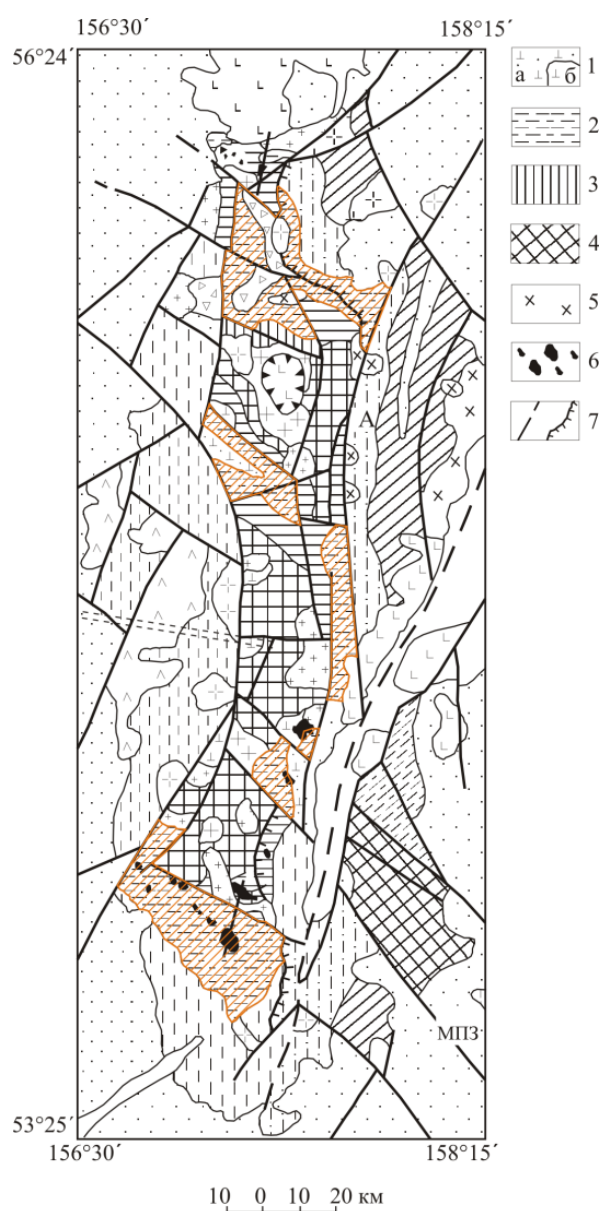


Fig.1. Geologic map of Central Kamchatka massif and localization of Ni-bearing intrusions [Selyagin, 2009 with modifications].
1: a) alistrovskaya and chimkinskaya suites, b) comagmatic subvolcanic intrusions; 2) heivanskaya suite (labeled by orange hatching); 3) andrianovskaya suite; 4) Ganai massif; 5a) levoandrianovskiy intrusive complex b) Dukuk cortlandite-orthopyroxenite-gabbro-norite intrusive complex; 7 – faults: a – steep, b – thrusts 8 erase

Table 1. Representative compositions of Ca-amphiboles from Shanuch ore field, Kamchatka from [Selyagin, 2003].

oxides	1	3	8	9	10	11	12	13	17
SiO ₂	52.37	44.30	45.79	45.51	53.20	53.63	43.42	44.07	45.64
TiO ₂	-	1.17	1.85	1.55	0.15	-	2.80	2.16	2.45
Al ₂ O ₃	30.04	13.16	11.39	11.84	3.46	29.22	12.74	12.63	12.31
FeO	0.10	15.34	11.86	13.60	11.47	0.23	11.19	15.18	9.91
MnO	0.06	0.07	0.09	0.10	0.01	-	-	0.13	0.09
MgO	-	10.54	13.71	11.95	15.56	0.03	13.22	10.30	13.32
CaO	12.14	11.87	10.70	10.74	12.32	11.71	11.21	11.21	10.61
Na ₂ O	4.56	1.23	1.92	1.38	0.35	5.42	1.65	1.72	1.65
K ₂ O	0.07	0.64	0.57	0.55	0.09	0.16	0.67	0.83	0.58
Cr ₂ O ₃	-	-	-	-	-	-	-	-	0.04
Sum	99.34	100.35	99.95	99.27	98.68	100.40	98.96	100.26	98.87
oxides	21	24	27	34	35	37	40	42	
SiO ₂	42.44	41.34	45.43	44.86	55.07	45.25	45.33	45.33	
TiO ₂	2.56	1.98	1.39	1.31	-	2.42	3.85	3.85	
Al ₂ O ₃	13.83	15.17	12.84	13.16	1.22	13.39	11.26	11.26	
FeO	14.73	18.34	11.14	8.93	17.58	8.50	8.78	8.26	
MnO	0.06	0.12	0.03	0.02	0.69	-	-	-	
MgO	10.08	7.59	1.35	14.47	20.11	14.18	14.2	15.76	
CaO	11.43	11.34	11.29	11.28	1.83	11.36	11.28	10.97	
Na ₂ O	1.55	1.36	1.60	1.76	0.07	1.37	1.83	2.19	
K ₂ O	0.67	0.79	0.43	0.54	0.04	0.57	0.41	0.51	
Cr ₂ O ₃	-	-	0.09	0.17	-	0.36	0.7	0.26	
Sum	99.36	100.01	99.64	98.56	98.68	99.53	99.72	99.73	

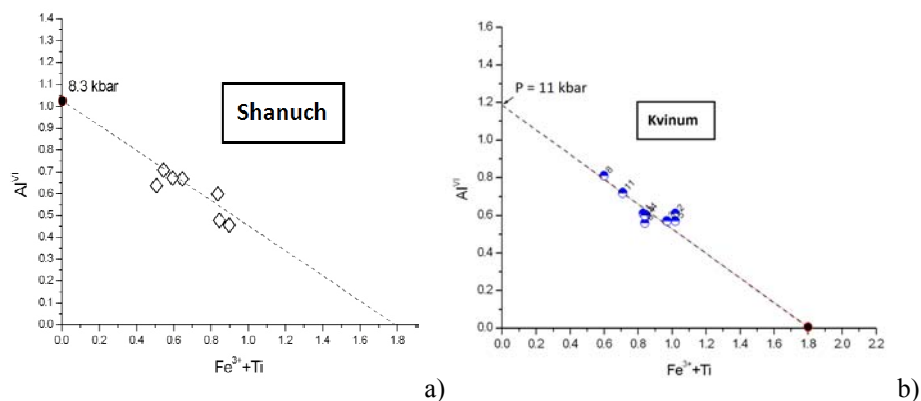


Fig.2. Estimates of pressure by amphibole compositions for Kamchatka cortlandites: a) Shanuch, selected data from [Selyangin, 2003] b) Kvinum, our data.

et al., 2010] inaccurate for pressure determination) are applicable for dacite-rhyolite magmas. In our model we consider content of the octahedral Al in amphibole in the equilibrium with andesitic to basaltic hydrous melts [Simakin, *et al.*, 2009]. It is well known that pressure increase causes transition of aluminum from tetrahedral (like Si) to pentahedral and octahedral cation-modifier positions. This structural transformation is reflected in the increase of Al^{VI} content in amphibole calculated with 13cCNK model. To eliminate effect of octahedral Al substitution by high charge cations we calculate asymptotic Al^{VI}_{max} content in amphibole at the sum $Fe^{3+} + Ti^{4+} + Cr^{3+} = 0$. Parameter Al^{VI}_{max} is linearly correlated with pressure in the range 2–12 kbar ($T=950\text{--}1100^{\circ}C$).

Published and our amphibole compositions were used to estimate cortlandite crystallization pressure (see Table 1).

Our pressure estimate for Shanuch cortlandite (see Fig. 2) coincides with peak pressure of surrounding metamorphic rocks [Selyangin, 2009]. Deep metamorphic complex with cortlandite intrusions is now exposed due to erosion. At the present day crust thickness at the CKR of 38–40 km [Levin, *et al.*, 2002b] this pressure estimate implies maximum crust thickness of 65–70 km gained at collision. Correspondent depth of oceanic slab underlying CKR on some stage of collision was close to the eclogite transition depth (80 km). Densification of oceanic slab at such depth may initiate new subduction zone.

Cu–Ni deposits are genetically linked with high-magnesium basic magmas. High-magnesium tholeiites of N-MORB type are proposed as parental magma for Kamchatka cortlandites [Selyangin, 2009]. Such magmas arise at the high degree of adiabatic decompression melting of dry mantle in mid-ocean ridges. Similar physical mechanism of decompressional melting is expected in the all ascending mantle flows: in back-arc basins, tectonic windows in subduction zones [Levin, *et al.*, 2002a] etc. At the accretion at active continental margins strong ascending mantle flows can be induced by subduction zone transformation including old slab delamination [Luchitskaya, *et al.*, 2008] and start of new slab edge submerge.

In the frame of this interpretation origin of cortlandites may be explained by the assimilation of metamorphic rocks with water bearing minerals (essentially micas) by dry picro-basalts at the PT parameters of amphibolite formation. Reflected by the lowest values of $Fe^{3+} + Ti^{4+}$ sum (0.4–0.5 apfu) low oxygen fugacity well correlates with c their weak magnetization opposite to the common island arc volcanic rocks with magnetite [Sidorov, 2006].

Low fO_2 in cortlandites is explained by high graphite content in the assimilated shists of Heivanskaya series [Selyangin, 2009]. Presence of graphite tends to buffer oxygen fugacity on the level of C–CO₂ buffer (around QFM-3). At the transition to the low temperature postmagmatic stage of cortlandite evolution oxygen fugacity rises that is also recorded in the values of $Fe^{3+} + Ti^{4+}$ sum increasing to 1.1 apfu.

This study was supported by RFBR grants #10-05-00046-a and #10-05-00697-a.

References:

1. Bindeman, I. N. *et al.*, (2002). Archean protolith and accretion of crust in Kamchatka: SHRIMP dating of zircons from Sredinny and Ganai massifs, *Journal of Geology*, vol.110, p. 271–289.
2. Konnikov, E. G. *et al.*, (2010). Geochemical characterization of ultra-basic lavas of Central Kamchatka Ridge, *Doklady Earth Sciences*, vol.435(4), p. 1–5 (in Russian).
3. Levin, V. *et al.*, (2002a). Seismic evidence for catastrophic slab loss beneath Kamchatka, *Nature*, vol.418 (15), p. 763–767.
4. Levin, V. *et al.*, (2002b). Crust and upper mantle of Kamchatka from teleseismic receiver functions, *Tectonophysics*, vol.358, p. 233–265.
5. Luchitskaya, M. V. *et al.*, (2008). Two Stages of Granite Formation in the Sredinny Range, Kamchatka: Tectonic and Geodynamic Setting of Granitic Rocks, *Geotectonics*, vol.42 (4), p. 286–304.
6. Ridolfi, F. *et al.*, (2010). Stability and chemical equilibrium of amphibole in calc-alkaline magmas: an overview, new thermobarometric formulations and application to subduction-related volcanoes, *Contributions to Mineralogy and Petrology*, vol.160, p. 45–66.
7. Selyangin, O. B. (2003). Petrology of Ni-bearing basic rocks of Shanuch ore field, Kamchatka, *KRAESC Bulletin Earth Sciences*, vol.2, p. 33–55.
8. Selyangin, O. B. (2007). New data on the structure and evolution of Kuvargol Ni-bearing intrusion, Southern Kamchatka, *KRAESC Bulletin Earth Sciences*, vol.1 (9), p. 111–126.
9. Selyangin, O. B. (2009). On the tectonic position of Ni-bearing intrusions of Central Kamchatka massif, *KRAESC Bulletin Earth Sciences*, vol.13, p. 123–138.
10. Sidorov, M. D., V. A. Stepanov (2006). Geophysical fields and nickel productivity of Central Kamchatka massif, *KRAESC Bulletin Earth Sciences*, vol.2 (8), p. 140–150.
11. Simakin, A. G. *et al.*, (2009). Amphibole crystallization from a water-saturated andesite melt: experimental data at $P = 2$ kbar, *Petrology*, vol.17 (6), p. 591–605.
12. Simakin, A. G. *et al.*, (2012). Novel amphibole geobarometer with application to mafic xenoliths, *Earth Science Research* (in Press).

Sinyakova¹ E.F., Kosyakov V.I.² One-dimensional solidification of the CuFe₂S₃ melt

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To elucidation the mechanisms of cubanite formation, a sample composed of Fe 33.3, Cu 16.7, S 50.0 at.% is subjected to quasi-equilibrium directional crystallization. The crystallized ingot consisted of three parts: (1) a pyrrhotite solid solution (*poss*), (2) a cubanite (*cb*), and (3) *poss* + *cb*. Curves of the component distribution in the sample are plotted; their partition coefficients between solid and sulfide melt are measured, the change of microstructures in the sample at cooling is defined. The obtained data indicate the existence of the primary crystallization field of cubanite on Cu-Fe-S phase diagram.

Key words: Cu-Fe-S system, cubanite, pyrrhotite, one-dimensional solidification

Reference: Sinyakova, E. F., V. I. Kosyakov (2012), One-dimensional solidification of the CuFe₂S₃ melt, *Vestnik ONZ RAS*, 4.

Introduction Cubanite (*cb* – CuFe₂S₃) is one of the main minerals of massive ore bodies at copper-nickel deposits. It occurs as tabular and grained inclusions [Genkin et al., 1981; Distler et al., 1998], large crystals [Sereda, 2004] and solid polycrystalline aggregates [Distler et al., 1996]. Among the massive ores of the Norilsk deposits there occur varieties with the relative content of cubanite up to 60 – 70% [Genkin et al., 1966; Distler, 1994; Distler et al., 1998]. In these ores orthorhombic cubanite is often associated with cubic cubanite or cubic chalcopyrite [Genkin et al., 1966].

Liquidus surface of the Cu-Fe-S system was plotted by Greig [Greig et al., 1955] but the primary crystallization field of cubanite from sulfide melt was absent on this surface. On the high-temperature isothermal cross-sections on the solid-liquid diagram one can observe the crystallization field of *iss* in its middle part and no signs of equilibrium sulfide melt with other intermediate phases [Kullerud et al., 1969; Tsujimura, Kitakaze, 2004]. On the other hand, Kullerud (1963-1964) and Dutrizac (1976) report results of thermal analysis of CuFe₂S₃, which evidence that this substance melts with decomposition. These data suggest the presence of a two-phase cubanite – liquid equilibrium in the Cu-Fe-S system. Some researchers also suggest the probability of formation of cubanite directly from sulfide magma [Distler et al., 1996; Distler et al., 1988]. This opinion agrees with the above experimental results [Kullerud, 1963-1964; Dutrizac, 1976] and conflicts with the traditional notion of the phase diagram of the Cu-Fe-S system [Kosyakov, 2008].

Elimination of this contradiction requires additional studies of phase relationships with participation of melts in the middle part of the Cu-Fe-S system. To reveal the mechanisms of cubanite formation in this work, we used the method of directional crystallization, which allows determination of the sequence and composition of phases formed from melt [Kosyakov, Sinyakova, 2005].

Experimental methods One-dimensional crystallization of the melt with composition of Fe 33.3, Cu 16.7, S 50.0 at.% was carried out by vertical Bridgman method. The ampoule with homogenous melt had been dropped from the hot zone to the cold one with 2.3×10^{-8} m/s rate. The process occurred in quasi-equilibrium regime

under these conditions [Kosyakov, Sinyakova, 2005]. Length of cylindrical specimen was 90 mm and its diameter was 7 mm. It was cut into 17 samples perpendicular to the longitudinal axis, and each one was weighed. The samples were examined with microscopic, electron microprobe analyses, and X-ray diffraction. The melt composition and partition coefficient of the components were calculated from material balance of components.

Results

Distribution curves and distribution coefficients of components Distribution curves Fe and Cu, reflecting the crystallization process of sulfide melt up to $g \approx 0.83$, are shown in Fig. 1. The same figure shows the curves of variations in melt composition during crystallization. The starting zone of ingot (I) ($0 \leq g \approx 0.06$) is formed of pyrrhotite solid solution (*poss*) with impurity of Cu. Melt composition during crystallization of *poss* changes slightly from Fe 33.3, Cu 16.7, and S 50.0 to Fe 32.5, Cu 17.61, and S 49.88 at.%. Because of the short crystallization range of *poss*, its composition within the limits of error can be considered constant and equal to Fe 44.77 ± 0.15 , Cu 2.65 ± 0.18 , S 52.58 ± 0.17 at.%.

In zone II ($\sim 0.06 \leq g \leq \sim 0.83$) cubanite crystallizes from melt. At the point of the phase reaction related to the termination of *poss* crystallization and the beginning of *cb* crystallization, the pathway of solid phase composition is broken while the pathway of the melt composition is subjected to bending (Fig. 1). The transition from one segment to another may be interpreted as a monovariant phase reaction: $L + poss \rightarrow cb$. The *cb* composition (Fe 33.25 ± 0.18 , Cu 16.64 ± 0.27 , S 50.09 ± 0.21 at.%) within the limits of error is identical to the stoichiometric composition CuFe₂S₃. During *cb* crystallization the melt becomes depleted in iron ($k_{Fe} = 1.02 \div 1.14$) and sulfur ($k_S = 1.00 \div 1.02$) and enriched in copper ($k_{Cu} = 0.94 \div 0.78$). Crystallization of cubanite is finished when melt composition is equal to Fe 29.20, Cu 21.88, S 48.92 at.%. The finite part of ingot ($0.83 \leq g < 1$) consists of multiphase mixture, the composition and structure of which was not studied by us in detail.

Microscopic description of the sample The first part of the sample represented a low-temperature monoclinic modification of pyrrhotite solid solution. Lamellar inclusions of cubanite present in the *poss* matrix (Fig. 2a). The composition of inclusions is close to Cu_{1.1}Fe_{1.9}S₃, that is somewhat different from the stoichiometric CuFe₂S₃ formula. According to the data of X-ray analysis the lattice parameter "a" of the Cu_{1.1}Fe_{1.9}S₃ is 5.280 (3) Å, which coincides with the data for synthetic cubanite [Caye et al., 1988].

Fig. 2b demonstrates a cubanite matrix with inclusions of slightly depleted in iron pyrrhotite with 0.4–0.6 at.% Cu. These inclusions are result of partial breakdown of primary CuFe₂S₃. It should be formed the phase with composition near to cubanite, but with less iron content. Fig. 2c shows that the cubanite matrix is two-phase. One of the phases are present in the form of thin bars (≤ 1 – $2 \mu\text{m}$ in width and 4 – $8 \mu\text{m}$ in length), oriented at right angles to each other. It has a composition of Cu_{1.1}Fe_{1.9}S₃ and cubic lattice with parameter 5.280(3) Å. The matrix phase corresponds to stoichiometric cubanite CuFe₂S₃ with parameter 5.303(3) Å.

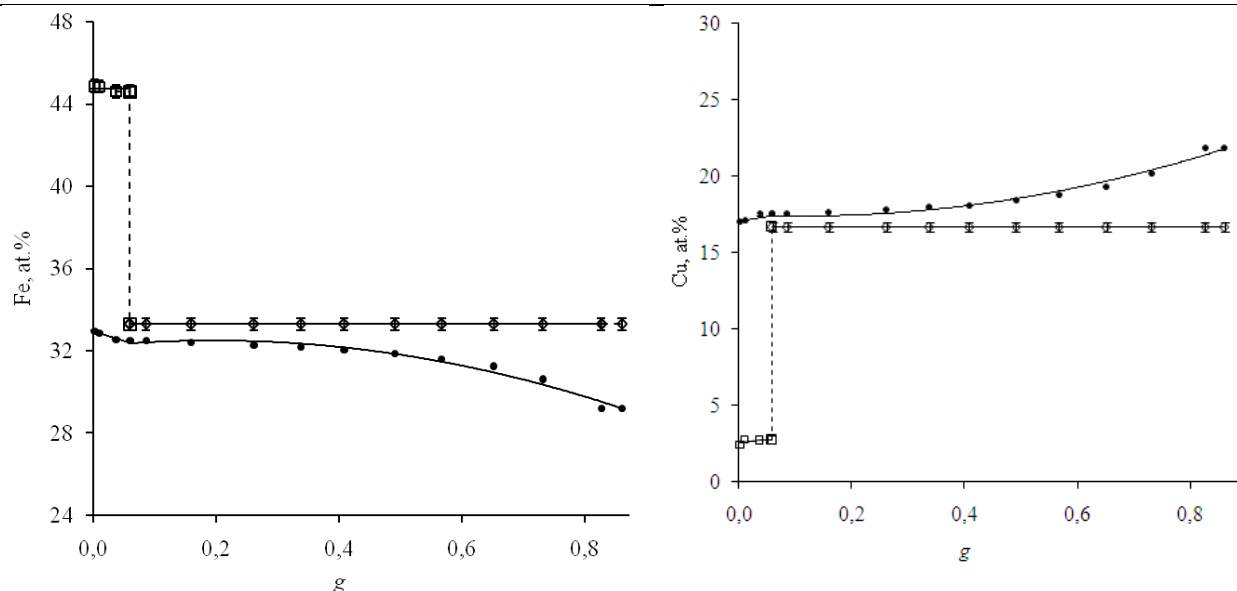


Fig. 1. Distribution of Fe and Cu in *poss* (square), *cb* (rhombus), and in the melt (close circle)

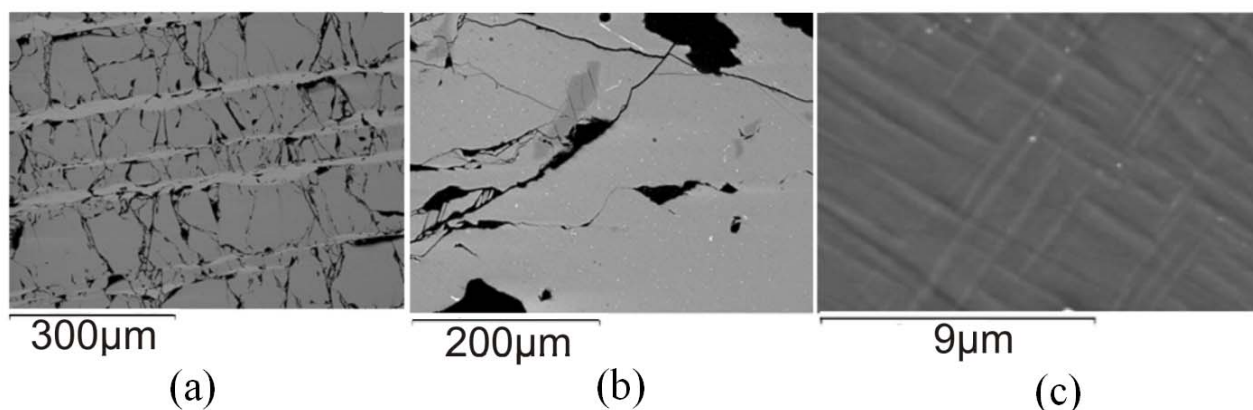


Fig. 2. Microstructure of the sample after one-dimensional solidification and following cooling to room temperature. Back-scattered electron images: (a) zone I, ($g = 0.01$): in the gray pyrrhotite matrix are light grey lamellar inclusions of cubanite; (b, c) zone II, ($g = 0.09$): (b) in light grey cubanite matrix are dark grey inclusions of pyrrhotite; (c) heterogeneous structure of the matrix from figure (b). Black sites are cracks and pores in the sample

Results of our work confirm the data of Kullerud (1963-1964) and Dutrizak (1976) on possibility of cubanite crystallization from sulfide melt. It means that an area of cubanite primary crystallization should be on the phase diagram of Cu-Fe-S system. From Fig. 1 follows that this area borders with field of primary crystallization of pyrrhotite solid solution. Thus revision of the liquid-solid phase diagram of Cu-Fe-S system is need in the region of *poss* and *iss* crystallization.

The obtained data confirm possibility of formation coarse-crystalline cubanite in sulfide ores during fractional crystallization sulfide melt. On the other hand, presence of lamellar inclusions of cubanite in association with other Cu-Fe sulfide minerals is possible to explain by solid phase decay of primary phases at their cooling.

This work was supported by the grant of RFBR No 12-05-00099a and by the grant of Otdelenia nauk o Zemle – 2.

References:

1. Caye, R., B. Cervelle, F. Cesbron et al. (1988). Isocubanite, a new definition of the cubic polymorph of cubanite CuFe_2S_3 , *Mineral. Magazine*, vol. 52, pp. 509–514.
2. Distler, V.V. (1994). *Platinum mineralization the Noril'sk deposits, Geology and Genesis of PGE deposits*, Laverov N.P., Distler V.V. eds. Izdatelstvo Nauka, pp. 7–35 (in Russ.).
3. Distler, V.V., T.L. Grokhovskaia, T.L. Evstigneyeva et al. (1988). *Petrology of the sulphide magmatic ore-formation*. Izdatelstvo Nauka, p. 230 (in Russ.).
4. Distler, V.V., E.A. Kulagov, S.F. Sluzhenikin, I.P. Laputina (1996). Quenched sulfide solid solutions in the ores of Noril'sk deposit, *Geology of ore deposits*, vol. 38, pp. 41–53.
5. Dutrizak, J.E. (1976). Reactions in cubanite and chalcopyrite, *Canad. Mineral.*, vol. 14, pp. 172–181.
6. Genkin, A.D., A.A. Filimonova, T.N. Shadlun et al. (1966). On cubic cubanite and cubic chalcopyrite, *Geology of ore deposit*, vol. 1, pp. 41–54.
7. Genkin, A. D., V. V. Distler, G. D. Gladyshev et al. (1981). *Copper-Nickel Sulfide Ores of the Norilsk Deposit*. Izdatelstvo Nauka, p. 234 (in Russ.).
8. Greig, J.W., E. Jensen, H.E. Mervin (1955). The system Cu-Fe-S, *Carnegie Inst. Washington Year Book*, vol. 54. pp. 129–134.

9. Kosyakov, V. I. (2008). Topological analysis of the melting diagram of the Cu–Fe–S system, *Russ. J. Inorg. Chem.*, vol. 53, No 6, pp. 946–951.
10. Kosyakov, V.I., E.F. Sinyakova (2005). Directional crystallization of Fe–Ni sulfide melts within the crystallization field of monosulfide solid solution, *Geochem Intern.*, vol. 43, pp. 372–385.
11. Kullerud, G. (1963-1964). The Cu–Fe–S system, *Carnegie Inst. Washington Year Book* 63, pp. 200–202.
12. Kullerud, G., R.A. Yund, G.H. Moh (1969). Phase relations in the Cu–Fe–S, Cu–Ni–S and Fe–Ni–S systems, *Econ. Geol. Monograph.*, vol. 4, pp. 323–343.
13. Sereda, E.V. (2004). *Standart collection of the rocks, ores and minerals of Noril'sk deposits. Bowels of Taimyr. A Selection of Scientific Papers. Simonov O.N. ed.* Issue 2, Dudinka, pp. 306–309 (in Russ.).
14. Tsujimura, T., A. Kitakaze (2004). New phase relation in the Cu–Fe–S system at 800 °C; constraint of fractional crystallization of a sulfide liquid, *N. Jb. Miner. Mh.*, vol. 10, pp. 433–444.

Sirotkina ¹E.A., Bobrov ¹A.V., Litvin ²Yu.A., Dubrovinsky ³L.S. Experimental study of the system MgO–SiO₂–Cr₂O₃ at 7–16 GPa and 1200–1800°C

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The first results of experimental investigation of phase relations in the system MgO–SiO₂–Cr₂O₃ at 7–16 GPa are summarized. Samples synthesized at 7 GPa from different starting compositions contain chromium-bearing enstatite and eskolaite (Cr₂O₃). Increase of pressure (12–16 GPa) results in replacement of pyroxene by garnet of the majorite–knorringite series. The cubic symmetry with a space group *Ia-3d* and cell parameters *a* = 11.5718(1) Å, *V* = 1549.54(2) Å³ was established for the most knorringite-rich garnet by single-crystal X-ray diffraction.

Key words: experiment at high temperatures and pressures, knorringite, majorite

Citation: Sirotkina, E. A., A. V. Bobrov, Yu. A. Litvin, L. S. Dubrovinsky (2012), Experimental study of the system MgO–SiO₂–Cr₂O₃ at 7–16 GPa and 1200–1800°C, *Vestnik ONZ RAS*, 4, (doi: -

Numerous results of investigations of crystalline inclusions in diamonds provide evidence for the formation of most of them within the pressure range of 4–7 GPa, which corresponds to depths of 150–250 km [Taylor, Anand, 2004 and others]. Garnets are widely abundant as inclusions in diamonds and those of the ultrabasic paragenesis are characterized by significant chromium admixture in the composition of knorringite (Mg₃Cr₂Si₃O₁₂, *Knr*) end-member. It was established that incorporation of knorringite in garnet occurred from 3 GPa (beyond the diamond depth facies), and the concentration of chromium reached significant values (5–10 wt % Cr₂O₃ and more) in the pressure range of stability of most of natural diamonds (4–7 GPa) [Malinovskii et al., 1975],

which is an indicative feature of diamondiferous dunite–harzburgite paragenesis of the lithospheric mantle.

Incorporation of majoritic component is another important peculiarity of mantle garnets. The concentration of aluminum and chromium in garnets decreases with pressure [Akaogi, Akimoto, 1977; Irifune, 1987], whereas the content of silicon in the octahedral site, as well as the concentration of divalent cations (Ca, Mg, Fe) and sodium regularly increase [Ono, Yasuda, 1996], which this results in the formation of garnet with the silicon content of >3 p.f.u. This is controlled by the beginning of dissolution of pyroxene (mainly (Mg,Fe)SiO₃) components in garnet already from 5 GPa [Akaogi, Akimoto, 1979]. The solubility of pyroxene in garnet increases with pressure reaching significant values at 10–15 GPa, which corresponds to the lowermost upper mantle and transition zone.

The relationship of majorite and knorringite with pressure providing evidence for similarity in their behavior, but, at the same time, for possible concurring reaction on pressure increase arose our interest to the experimental investigation of the knorringite–majorite (in chemical expression, MgO–SiO₂–Cr₂O₃) system in a wide range of *PT*-parameters. Here we report the first results of performed experiments.

Experiments on investigation of the system MgO–SiO₂–Cr₂O₃ were performed on high-pressure toroidal “anvil-with-hole” apparatus NL-13T in the Institute of Experimental Mineralogy, Russian Academy of Sciences, and multi-anvil apparatus in the Bayerisches Geoinstitut, Bayreuth, Germany.

At 7 GPa and 1200–1900°C (in the field of the enstatite (MgSiO₃, *En*) stability) the starting compositions of *Knr*₅₀*En*₅₀, *Knr*₇₀*En*₃₀, *Knr*₃₀*En*₇₀ и *Knr*₁₀₀*En*₀ (mol %) were studied. The phase associations in all runs included enstatite (up to 3.2 wt % Cr₂O₃) and eskolaite (Cr₂O₃, *Esk*). Fig. 1a demonstrates the typical texture of obtained samples with relatively large enstatite crystals and small, often interstitial eskolaite segregations. Increase of chromium content in enstatite with temperature was observed (Table 1).

As is evident from Table 1, all orthopyroxenes are characterized by some depletion in magnesium (in relation to 1 p.f.u.), and it is this fact that illustrates chromium incorporation in the mineral structure. We should unlikely consider the scheme of heterovalent isomorphism like Mg²⁺+Si⁴⁺→2Cr³⁺ in this case, when chromium enters both octahedral (replacing Mg) and tetrahedral (replacing Si) sites, by the analogy with orthorhombic corundum (AlAlO₃) component of orthopyroxene [Berman, Aranovich, 1996]. Based on the single-crystal X-ray diffraction study of chromium-bearing enstatite (Luca Bindi, personal communication), we suggest the structural formula Mg_xCr_{1-x}Si_{(3-x)/4}□_{(1-x)/4}O₃, according to which chromium replaces magnesium in octahedrons being accompanied by appearance of vacancies instead of silicon atoms in tetrahedrons.

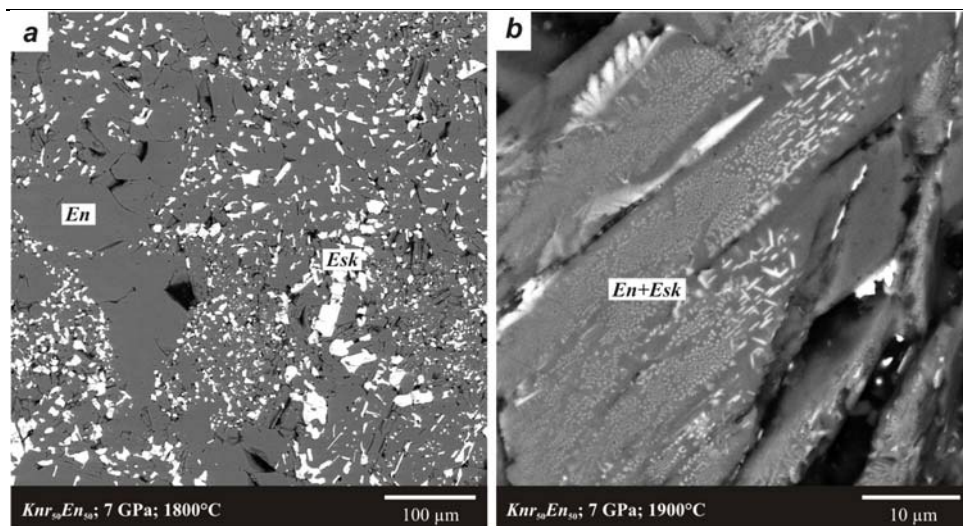


Fig. 1. Back-scattered electron images of textural peculiarities of experimental samples obtained in the system $\text{MgO-SiO}_2\text{-Cr}_2\text{O}_3$ at 7 GPa. (a) Relatively large grains of chromium-bearing enstatite and small grains of eskolaite in the groundmass ($\text{Knr}_{50}\text{En}_{50}$, $T = 1800^\circ\text{C}$); (b) small oriented eskolaite intergrowths in enstatite.

Table 1.

Composition of enstatite in the samples obtained at 7 GPa (starting composition $\text{Knr}_{50}\text{En}_{50}$)

Analysis	T , $^\circ\text{C}$	MgO	SiO_2	Cr_2O_3	Total	Mg	Si	Cr	Total
12-02	1200	39.26	62.41	1.16	102.83	0.960	1.013	0.016	1.989
13-01	1500	37.44	59.07	1.44	97.95	0.955	1.009	0.020	1.984
04-01	1500	38.11	58.88	1.38	98.37	0.967	1.003	0.019	1.988
05-02	1600	37.40	59.62	1.57	98.59	0.945	1.012	0.021	1.978
08-01	1800	35.60	59.20	3.21	98.01	0.907	1.012	0.043	1.963

We should emphasize that liquidus enstatite obtained at a temperature $>1800^\circ\text{C}$ contains small (sometimes hardly visible even at the highest magnification) oriented eskolaite inclusions. Their shape and regular orientation allow us to interpret them as the texture of eutectic crystallization (Fig. 1b). The bulk analysis of such grains provided extremely high chromium concentrations in intergrowths reaching 7.23 wt % Cr_2O_3 . The correlation between the concentrations of Mg, Cr, and Si in synthetic pyroxenes confirms their aggregate nature and provides evidence for existence of the concentration barrier (between 3.2 and 5.7 wt %) of Cr_2O_3 incorporation in orthopyroxene.

Garnets of the majorite–knorringite composition were synthesized in multi-anvil experiments performed at 12–16 GPa and 1400–1600°C.

The starting compositions of $\text{Knr}_{100}\text{Maj}_0$ and $\text{Knr}_{50}\text{Maj}_{50}$ (mol %) were studied in the system $\text{MgO-SiO}_2\text{-Cr}_2\text{O}_3$ at 16 GPa and 1600°C. The main phases obtained in experiments are garnet of the majorite–knorringite composition and eskolaite (Fig. 2a). The synthesized garnets contain from 15 to 25 mol % majoritic component (Table 2). It is typical that even for the starting composition of pure knorringite $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$, we obtained the garnet solid solution containing 15 mol % $\text{Mg}_4\text{Si}_4\text{O}_{12}$, which reflects the more significant influence of pressure on the formation of majorite in comparison with knorringite.

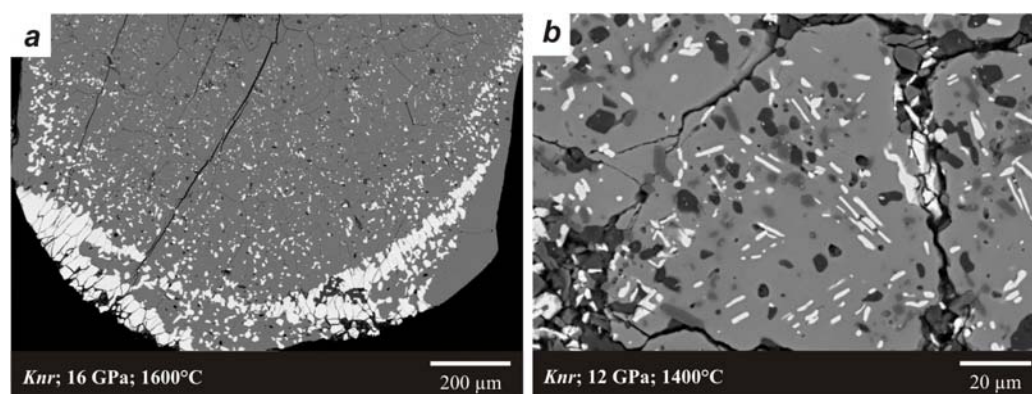


Fig. 2. Back-scattered images of textural features of experimental samples obtained in the system $\text{MgO-SiO}_2\text{-Cr}_2\text{O}_3$ at 16 GPa and 1600°C (a) and 12 GPa and 1400°C (b) for the starting composition $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$. (a) Relatively large knorringite grains (gray) and small grains of eskolaite (white) in the groundmass; (b) knorringite (gray) with small oriented intergrowths of eskolaite (white) in the central part of grain and with inclusions of stishovite (dark-gray) and periclase (black) in the marginal part of grain.

Table 2. Composition of garnet in samples obtained at 16 GPa

Composition	SiO ₂	MgO	Cr ₂ O ₃	Total	Si	Mg	Cr	Total
<i>Knr</i> ₁₀₀ <i>Maj</i> ₀	42.73	27.66	28.64	98.33	3.15	3.09	1.71	7.95
<i>Knr</i> ₅₀ <i>Maj</i> ₅₀	44.36	28.87	24.97	98.20	3.25	3.27	1.41	7.94

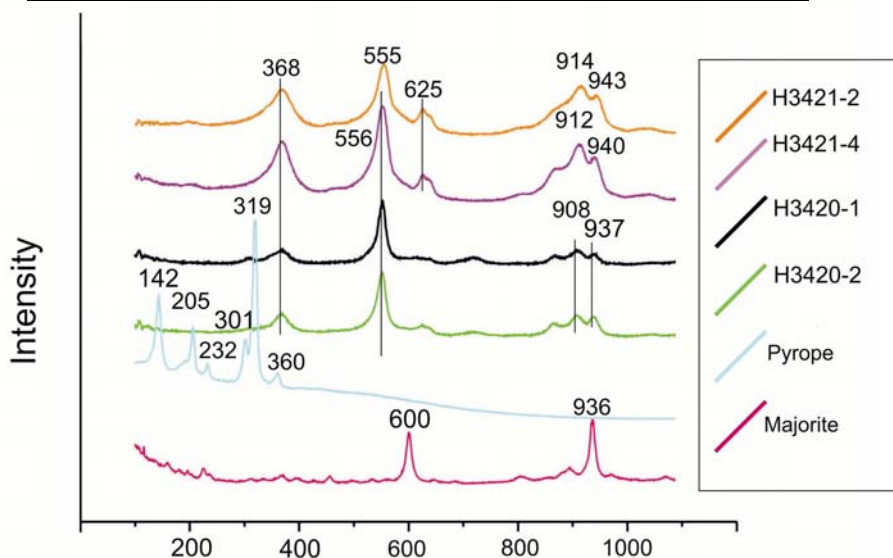
**Fig. 3.** Raman spectra of garnets of the majorite–knorringite composition synthesized at 12–16 GPa in comparison with the spectra of pyrope and majorite.

Fig. 3 demonstrates the Raman spectra of synthesized garnets in comparison with the data on pure pyrope and majorite. Since the data on Raman spectra are not available for pure knorringite, the morphology of spectra of garnets obtained from the starting compositions *Knr*₅₀*Maj*₅₀ (H3421) and *Knr*₁₀₀*Maj*₀ (H3420) may be analyzed by their mutual comparison, as well as by comparison with the spectra of pyrope and majorite. As garnet from Sample H3421 contains the higher portion of majoritic component (25 mol %) in comparison with garnet from Sample H3420 (15 mol %), we may suggest that the peaks at 625 cm⁻¹ for H3421 and 624 cm⁻¹ for H3420 correspond to the spectrum of majorite. The same is evident for the peaks in the range of 937–943 cm⁻¹. Garnets (H3420 and H3421) synthesized at 12–16 GPa are represented by the majorite–knorringite solid solution and consequently all other peaks correspond to knorringite.

It should be noted that garnet monocrystals with such a high portion of knorringite component were not previously synthesized in experiments, which did not allow to obtain reliable crystallochemical characteristics of knorringite. [Juhin *et al.*, 2010] determined the structural peculiarities of garnet of the similar composition by powder X-ray diffraction. In our study synthesized knorringite-rich garnet was studied by single-crystal X-ray diffraction for the first time. We established its cubic symmetry with a space group *Ia-3d* and cell parameters $a = 11.5718(1) \text{ \AA}$, $V = 1549.54(2) \text{ \AA}^3$.

To obtain garnet with the higher content of knorringite end-member, we studied the starting composition *Knr*₁₀₀*Maj*₀ at the lower *PT*-parameters (12 GPa and 1400°C). The phase associations also included garnet of the majorite–knorringite composition and eskolaite (Fig. 2b); inclusions of periclase (MgO) and stishovite (SiO₂) were registered in the marginal parts of garnet grains. According to the tabular shape and mutual orientation of eskolaite inclusions, we may suggest that they were formed as a result of decomposition of chromium-rich

garnet. The bulk analysis of garnet demonstrated that before decomposition this was pure knorringite.

Thus stable incorporation of majoritic component in knorringite garnets synthesized at high pressures (12–16 GPa) illustrates the concurring behavior of majorite and knorringite under the conditions of pressure increase. Being applied to natural garnets, this observation provides evidence for the fact that relative enrichment of garnet in knorringite may occur in the lithospheric mantle, whereas significant concentrations of majoritic component (>5–10 mol %) may be gained only in the

lowermost upper mantle and transition zone. The results of our experiments demonstrate that pure knorringite is unstable under the atmospheric conditions and should be studied *in situ* in experiments at high temperatures and pressures.

This study was supported by the Russian Foundation for Basic Research (project no. 12-05-00426) and by the Foundation of the President of the Russian Federation (grant MD-534.2011.5 for Young Doctors of Sciences and grant NSH-5877.2012.5 for Leading Scientific Schools).

References:

1. Malinovskii, I.Yu., A.M. Doroshev, E.N.Ran (1975). The stability of chromium-bearing garnets pyrope - knorringite series, *Experimental studies on the mineralogy (1974-1976)*, Institute of Geology and Geophysics of the Siberian Branch of AS USSR, Novosibirsk, 110-115.
2. Akaogi, M., A. Akimoto (1979). High pressure phase equilibria in a garnet ilherzolite, with special reference to Mg²⁺-Fe²⁺ partitioning among constituent minerals, *Phys. Earth. Planet. Inter.*, V. 19. P. 31-51.
3. Akaogi, M., A. Akimoto (1977). Pyroxene-garnet solid-solution equilibria in the system Mg₄Si₄O₁₂-Mg₃Al₂Si₂O₁₂ and Fe₄Si₄O₁₂-Fe₃Al₂Si₂O₁₂ at high pressures and temperatures, *Phys. Earth. Planet. Inter.*, V. 111. P. 90-106.
4. Berman, R.G., L.Y. Aranovich (1996). Optimized standard state and solution properties of minerals: I. Model calibration for olivine, orthopyroxene, cordierite, garnet, and ilmenite in the system FeO-MgO-CaO-Al₂O₃-TiO₂-SiO₂, *Contrib Mineral Petrol.*, 126: 1-24.
5. Irifune, T. (1987). An experimental investigation of the pyroxene-garnet transformation in a pyrolite composition and its bearing on the constitution of the mantle, *Physics of the Earth and Planetary Interiors*, V. 45. P. 324-336.
6. Juhin, A., G. Morin, E. Elkaim, D.J. Frost, M. Fialin, F. Juillot, G. Calas (2010). Structure refinement of a synthetic knorringite, Mg₃(Cr_{0.8}Mg_{0.1}Si_{0.1})₂(SiO₄)₃, *American Mineralogist*, V. 95. P. 59-63.
7. Ono, S., A. Yasuda (1996). Compositional change of majoritic garnet in a MORB composition from 7 to 17 GPa

Abstracts

and 1400 to 1600 °C, *Physics of the Earth and Planetary Interiors*, V. 96. P. 171-179.

8. Taylor, L.A., M. Anand (2004). Diamonds: time capsules from the Siberian Mantle, *Chemie der Erde*, V. 64. P. 1-74.

Suk N. I. Distribution of REE, Nb, Ta, Ba and Sr between immiscible phases in silicate-carbonate systems (experiment)

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Liquid immiscibility and distribution of REE, Nb, Ta, Ba and Sr between immiscible phases in silicate-carbonate systems at 1100 and 1250°C and P=2 kbar has been experimentally studied. It has been shown that Ba and Sr enrich the carbonate melt, and Nb and Ta – silicate melt.

It has been shown that partition coefficients ($K = C_{\text{carb}}^{\text{REE}} / C_{\text{sil}}^{\text{REE}}$) of REE between immiscible silicate and carbonate phases depend on the initial magmatic melt composition and correlate with coexisting silicate melt composition: the magnification of K_{REE} with increase of $(\text{Al}+\text{Si})/(\text{Na}+\text{K}+\text{Ca})$ relation and decrease of $\text{Ca}/(\text{Na}+\text{K})$ and $\text{Ca}/(\text{Si}+\text{Al})$ relations in silicate melt is observed.

Key words: experiment, liquid immiscibility, silicate-carbonate systems, partition coefficients

Reference: Suk, N.I. (2012), Distribution of REE, Nb, Ta, Ba and Sr between immiscible phases in silicate-carbonate systems (experiment), *Vestnik ONZ RAS*, 4,

The possible role of liquid immiscibility for the formation of carbonatites and related rocks was pointed out by a number of authors [Koster van Groos, Wyllie, 1966, 1973; Wyllie, Tuttle, 1960; Kjarsgaard, Hamilton, 1988 and others]. These experimental investigations demonstrated the existence of a wide field of liquid immiscibility of carbonate and silicate melts at various temperatures and pressures [Koster van Groos, 1975; Wedlandt, Harrison, 1979; Freestone, Hamilton, 1980; Hamilton et al., 1989; Kjarsgaard, Hamilton, 1988 and others].

We have experimentally studied the silicate-carbonate melt layering at T=1100 and 1250°C and P=2 kbar which

corresponds to the superliquidus region of the systems considered. Special emphasize was placed on the character of some ore element (REE, Nb, Ta, Ba, Sr) distribution between immiscible phases.

The experiments were carried out in a high gas pressure vessel in sealed platinum capsules (3 mm in diameter) at a duration of 6 h with subsequent quenching. Dry systems were investigated. The initial mixtures consisted of natural minerals (albite, diopside, potassium feldspar, nepheline) in different with addition of sodium carbonate (Na_2CO_3) or its mixture with calcite ($\text{Na}_2\text{CO}_3 + \text{CaCO}_3$). Ore elements were introduced as oxides La_2O_3 , CeO_2 , Y_2O_3 , Nb_2O_5 , Ta_2O_5 and barium and strontium as carbonates BaCO_3 and SrCO_3 . The initial charge was 100 mg in weight and was preliminary dried at T=100°C for 18–20 h. The experimental samples were analyzed on a Camebax X-ray microanalyzer with an energy-dispersive system Link and on a digital scanning electron Tescan Vega TS5130MM microscope.

The experimental investigation of silicate-carbonate systems at T=1100 and 1250°C and P=2 kbar shows the wide field of liquid immiscibility with separation of starting silicate-carbonate melts into two liquids – silicate and carbonate [Suk, 2001, 2003]. Sharp phase boundaries between the melts are remarkable. These melts can form layers and drops of one liquid in another and fluidal textures (fig. 1). The relations between carbonate and silicate melts experimentally obtained model textural peculiarities observed in natural carbonatite complexes.

The heterogeneities of obtained carbonate liquids showed in the separation of carbonate phase into alkaline (mainly, sodic) and calc-alkaline (mainly, calcic) fractions is observed.

Comparison of previous experimental data with our results shows a good agreement and confirms that pressure increase and temperature decrease promotes the extension of immiscibility field.

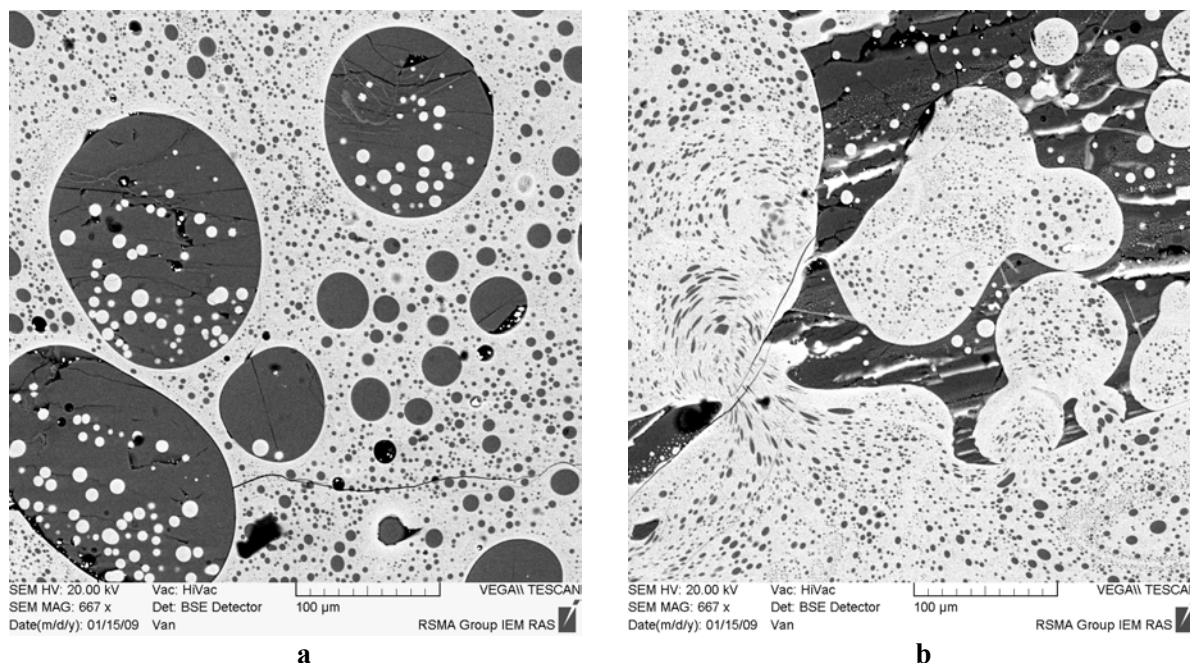


Fig. 1. Liquid immiscibility of silicate-carbonate melts at T=1100°C and P=2 kbar: a – with structure “drop in drop”, b – with fluidal texture (light – silicate melt, dark – carbonate melt). BSE images

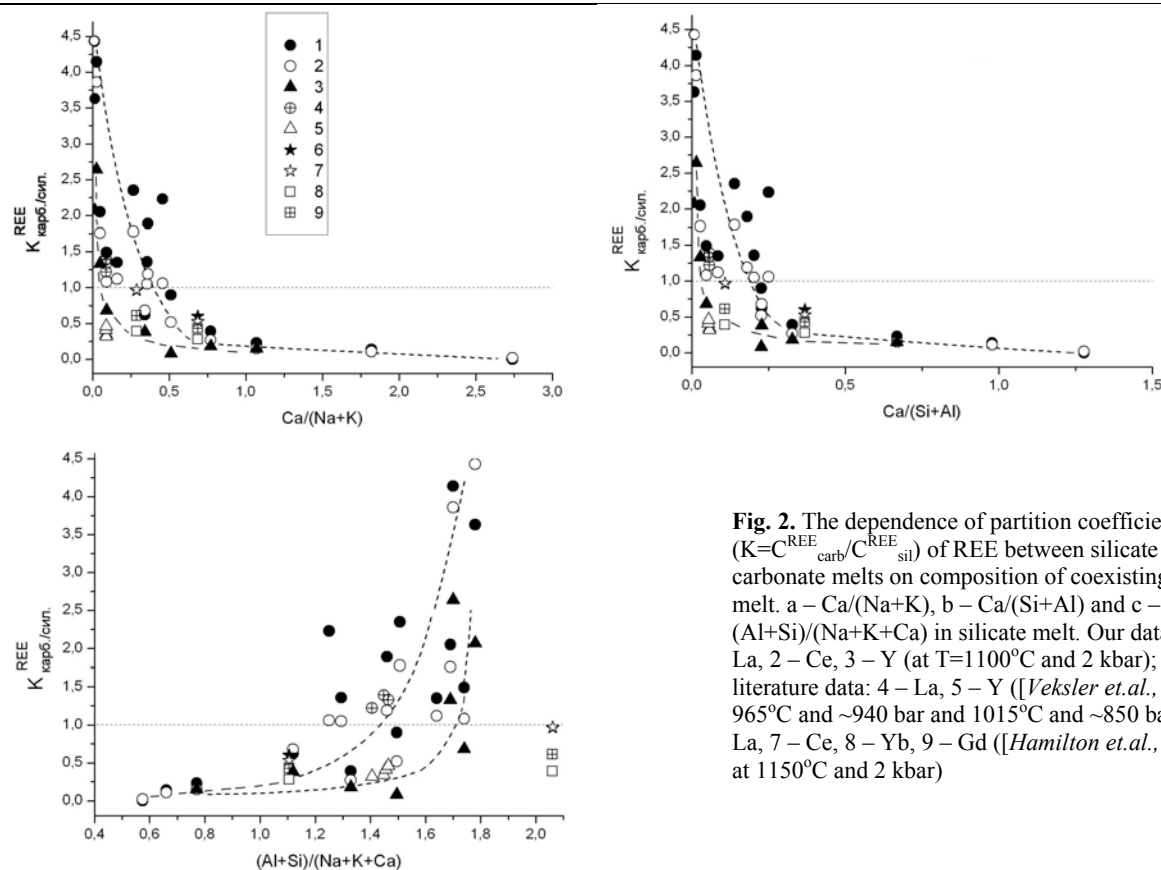


Fig. 2. The dependence of partition coefficients ($K = C_{\text{carb}}^{\text{REE}} / C_{\text{sil}}^{\text{REE}}$) of REE between silicate and carbonate melts on composition of coexisting silicate melt. a – $\text{Ca}/(\text{Na}+\text{K})$, b – $\text{Ca}/(\text{Si}+\text{Al})$ and c – $(\text{Al}+\text{Si})/(\text{Na}+\text{K}+\text{Ca})$ in silicate melt. Our data: 1 – La, 2 – Ce, 3 – Y (at $T=1100^\circ\text{C}$ and 2 kbar); literature data: 4 – La, 5 – Y ([Veksler et al., 1998] at 965°C and ~ 940 bar and 1015°C and ~ 850 bar); 6 – La, 7 – Ce, 8 – Yb, 9 – Gd ([Hamilton et al., 1989]; at 1150°C and 2 kbar)

Previous experimental investigations [Koster van Groos, 1975; Veksler et al., 1998] show that Ba and Sr concentrate in carbonate melt, and some rare elements, such Nb, Ta, Zr, Hf, enrich silicate melt with respect to carbonate melt [Veksler et al., 1998]. It has been shown that REE enrich carbonate melt with temperature decrease [Hamilton et al., 1989], pressure increase [Hamilton et al., 1989; Jones et al., 1995] and increase of coexisting silicate melt polymerization [Hamilton et al., 1989]. But distribution of rare and rare earth elements was studied in local field of more alkaline compositions. We studied the distribution of some ore elements in wide composition diapason involving the whole immiscibility field.

Our experimental study reveals the dependence of the character of rare earth partitioning on the temperature, too. At $T=1250^\circ\text{C}$ and $P=2$ kbar REE concentrate in silicate melt. At $T=1100^\circ\text{C}$ and $P=2$ kbar the character of their distribution depends on the initial melt composition.

Because the compositions of coexisting carbonate and silicate melts are connected we can consider the dependence of REE partition coefficients ($K = C_{\text{carb}}^{\text{REE}} / C_{\text{sil}}^{\text{REE}}$) on the compositions of silicate melt coexisting with carbonate melt and correlating with initial composition of the system. So we have made some diagrams. At 1100°C the magnification of K_{REE} with increase of $(\text{Al}+\text{Si})/(\text{Na}+\text{K}+\text{Ca})$ relation (Fig. 2c) is observed. This relation is likely to reflect the balance of net work cation and modifying cation [Galakhov, Varshal, 1969] in the melt and the polymerization degree pointed by Hamilton [Hamilton et al., 1989]. But we can observed more strong dependence of K_{REE} on the $\text{Ca}/(\text{Na}+\text{K})$ and $\text{Ca}/(\text{Si}+\text{Al})$ relations in coexisting silicate melt (Fig. 2 a, b). At $T=1100^\circ\text{C}$ and $P=2$ kbar in alkaline silicate-carbonate systems (where in silicate melt $\text{Ca}/(\text{Na}+\text{K}) < 0.5$ and $\text{Ca}/(\text{Si}+\text{Al}) < 0.25$) the light REE (La, Ce) accumulate

in carbonate phases: their partition coefficients (K_{REE}) are more 1. Thereby it is observed their predominant concentration in the calcium-rich fractions of carbonate phases as compared with sodium ones which don't content REE. In the lime silicate-carbonate systems (where in silicate melt $\text{Ca}/(\text{Na}+\text{K}) > 0.5$ and $\text{Ca}/(\text{Si}+\text{Al}) > 0.25$) inverse regularity is observed: rare earth elements are accumulated in the silicate melt (fig. 2). For Y (which is considered as a model of hard (HREE) rare earth elements) partition coefficients become more 1 only in the systems where $\text{Ca}/(\text{Na}+\text{K}) < 0.05$ and $\text{Ca}/(\text{Si}+\text{Al}) > \sim 0.03$ (Fig. 2 b, c). For comparison of obtained data of REE distribution between silicate and carbonate melts the experimental data of Hamilton et al [Hamilton et al., 1989] for La, Ce, Yb and Gd (1150°C , 2 kbar) and data of Veksler et al [Veksler et al., 1998] for La and Y (for 965°C and ~ 940 bar and 1015°C and ~ 850 bar) were plotted. These data are in a good agreement.

At $T=1250^\circ\text{C}$ and $P=2$ kbar the predominant concentration of REE in silicate melt is observed: the partition coefficients ($K = C_{\text{carb}}^{\text{REE}} / C_{\text{sil}}^{\text{REE}}$) are lower than 1. But for the light REE (LREE) the analogical dependence (K_{REE}) on $\text{Ca}/(\text{Na}+\text{K})$ and $\text{Ca}/(\text{Si}+\text{Al})$ is estimated. For Y the dependence of partition coefficient on these relations practically does not observe.

Our experimental investigation have shown that Nb and Ta in the systems studied at $T=1100$ and 1250°C are concentrated in silicate melt and Ba and Sr at $T=1250^\circ\text{C}$ and $P=2$ kbar are accumulated in carbonate phases. [Suk, 2001, 2003]. This is in a good agreement with previous experimental investigations [Koster van Groos, 1975; Veksler et al., 1998]. But the dependence of partition coefficients of Nb and Ta on the initial system composition is in contemplation as aforesaid for REE.

Abstracts

Our experimental results on REE partitioning between immiscible liquids in alkalic systems at T=1100°C and P=2 kbar demonstrated the extraction of these elements by carbonate melts allow us to conclude that the carbonatite deposits of rare earth elements could be formed in connection with alkalic (agpaitic) magmatism only.

References :

- Galakhov, F. Ya., B. G. Varshal (1969). About causes of liquation in simple silicate systems, *Liquation phenomena in glass*. Nauka, pp. 6–11.
- Suk, N. I. (2001). Experimental study of immiscibility of silicate-carbonate systems, *Petrologiya*, v. 9. N 5, pp. 547–558.
- Suk, N. I. (2003). Experimental study of carbonate-silicate immiscibility with the connection of barium-strontium carbonatites, *Petrologiya*, v. 11. N 4, pp. 443–448.
- Freestone, J. C., D. L. Hamilton (1980). The role of liquid immiscibility in the genesis of carbonatites – An experimental study, *Contrib. Mineral. Petrol.*, V. 73. N 3. pp. 105–117.
- Jones, J. H., et al. (1995). Experimental investigations of Nb, Mo, Ba, Ce, Pb, Ra, Th, Pa and U between immiscible carbonate and silicate liquids, *Geochim. Cosmochim. Acta*. V. 59. N 7, pp. 1307–1320.
- Hamilton, D. L., et al. (1989). The behaviour of trace elements in the evolution of carbonatites, *Carbonatites. Genesis and evolution* Bell K., Ed., London: Unwyn Hyman, pp. 405–427.
- Kjarsgaard, B. A., D. L. Hamilton (1988). Liquid immiscibility and the origin of alkali-poor carbonatites, *Miner. Magaz.*, V. 52. pp. 43–55.
- Koster van Groos, A. F., P.J. Wyllie (1966). Liquid immiscibility in the system Na₂O–Al₂O₃–SiO₂–CO₂ at pressures up to 1 kilobar, *Amer. Jour. Sci.*, V. 264, pp. 234–255.
- Koster van Groos, A. F. (1975). The distribution of strontium between coexisting silicate and carbonate liquids at elevated pressures and temperatures, *Geochim. Cosmochim. Acta*, V. 39, pp. 27–34.
- Veksler, I. V. et al. (1998). Trace Element Partitioning in Immiscible Silicate-Carbonate Liquid Systems: an Initial Experimental Study Using a Centrifuge Autoclave, *Journal of Petrology*, V. 39. N 11&12, pp. 2095–2104.
- Wendlandt, R. F., W. J. Harrison (1979). Rare earth partitioning between immiscible carbonate and silicate liquids and CO₂ vapor: results and implications for the formation of light rare earth-enriched rocks, *Contrib. M. Petrol.*, V. 69, pp. 409–419.
- Wyllie, P. J., O. F. Tuttle (1960). The system CaO–CO₂–H₂O and origin of carbonatites, *Jour. Petrol.*, V. 1, pp. 1–46.

Zharkova E.V., Kadik A.A., Senin V.G.
“Memory” of the minerals of deep origin. The experimental determination of intrinsic oxygen fugacity

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The aim of this study is the experimental determination of the intrinsic oxygen fugacity of the minerals of deep origin and check up has the minerals “memory” or not.

Key words: *intrinsic oxygen fugacity of the minerals, “memory”, olivine, orthopyroxene, spinel*

Reference: Zharkova, E. V., A. A. Kadik, V. G. Senin (2012), “Memory” of the minerals of deep origin. The experimental determination of intrinsic oxygen fugacity, *Vestnik ONZ RAS*, 4, (doi:)

We choose for the experiments olivines (Ol) from India without inclusions and olivines (Ol ShTs 3-1), orthopyroxenes (Opx ShTs 3-1) and spinels (Spl ShTs 3-1) from xenolith of spinel lherzolite from alkaline basalts of volcano Shavarin-Tsaram (Mongolia).

The experiments were carried out on high temperature furnace based on two solid electrolyte cells. They manufactured from zirconium dioxide and stabilized by yttrium oxide in order to make the cubic structure of the electrolyte. The temperature interval is 750–1100°C. The precision of determination is $\pm 0.2 \log fO_2$.

In order to clearing up the question about the possibility of measuring crystals to keep the information of the intrinsic oxygen fugacity which is correspond with its growth were carried out the following experiments: crystals of Ol from India and Ol, Opx and Spl from xenoliths of spinel lherzolites of Mongolia which intrinsic oxygen fugacity lies in the field between of buffer equilibrium wustite–magnetite (WM) and iron–wustite (IW) (table 1, fig. 1-4) were put into gas atmosphere which correspond with intrinsic oxygen fugacity to the buffers QFM-2 log units fO_2 , QFM-3 log units fO_2 , nickel–nickel oxide (Ni–NiO) and quartz–fayalite–magnetite (QFM) at the temperature 900–1100°C during 8–25 hours (table 2). Then we measured the intrinsic oxygen fugacity of the crystals again. The intrinsic oxygen fugacity begin to correspond to fO_2 buffers: QFM-2 log units fO_2 , QFM-3 log units fO_2 , Ni–NiO and QFM buffers (fig. 1–4).

Thus, at the result of the experiments, we revealed, that the crystals of olivine, orthopyroxenes and spinels remember the information about redox conditions at which they were formed. This is mean that the crystals has the “memory” and the quenching isn’t influence on the “memory” of the minerals.

It should be mention, that before we measured the “memory” of the minerals of deep origin we determined the intrinsic oxygen fugacity of this crystals (table 1). We carried our the microprobe analyses as before the experiments and also after the experiments. Thus, we show that the chemical composition isn’t change during the experiments.

Table 1. The values of the coefficients “A” and “B” in the empirical equation $\log fO_2 = A - B/T, ^\circ K$ for olivines, orthopyroxene and spinel

Mineral	A	B	*r	**n
Ol (India)	9.034	28888	0.998	9
Ol (India) at QFM-2 log unite fO_2	6.116	24412	0.093	8
Ol (India) at QFM-3 log unite fO_2	6.789	26759	0.982	9
ShTs 3-1 Ol	11.039	31435	0.992	11
ShTs 3-1 Ol at QFM	8.326	24480	1	5

Mineral	Magmatic systems			
	A	B	*r	**n
ShTs 3-1 Ol at Ni–NiO	9.354	24920	1	7
ShTs 3-1 Opx	13.421	33982	0.996	11
ShTs 3-1 Opx at QFM	8.326	24480	1	9
ShTs 3-1 Spl	12.468	32913	0.998	11
ShTs 3-1 Spl at QFM	8.326	24380	1	8

*r – coefficient of correlation, **n – the number of experimental points.

Table 2. The values of log fO₂ for olivines, orthopyroxene and spinel at fix temperature and atmosphere

Mineral	Temperature, °C	log fO ₂	Time exposure
Ol at QFM-2 log unite fO ₂	1100	-11.664	25 hours
Ol at QFM-3 log unite fO ₂	1100	-12.7	16 hours
ShTs 3-1 Ol (Ni–NiO)	900	-11.890	17 hours
ShTs 3-1 Ol (QFM)	900	-12.541	8 hours
ShTs 3-1 Opx (QFM)	900	-12.625	15 hours
ShTs 3-1 Spl (QFM)	1000	-10.904	14–16 hours
QFM*	900	-12.55	
QFM*	1000	-10.91	
Ni–NiO**	900	-11.89	

*log fO₂ (QFM) = 8.29 – 24441.9/T°K, **log fO₂ (Ni–NiO) = 9.36 – 24930/T°K

Table 3. Microprobe analyses for the olivines (India) before and after the experiment of determine the “memory” of the minerals

Oxides	Ol		Ol (QFM-2)		Ol (QFM-3)	
	Before the experiment	After the experiment	Before the experiment	After the experiment	Before the experiment	After the experiment
MgO	50.51	50.34	49.83	49.8	50.48	49.59
SiO ₂	40.82	40.59	40.92	41.41	40.87	41.22
TiO ₂	0	0	0.03	0.02	0.01	0.01
V ₂ O ₅	0	0	0	0.2	0	0.08
Cr ₂ O ₃	0	0.02	0.01	0.03	0.07	0
FeO	8.38	8.68	8.84	8.68	8.48	8.46
NiO	0.45	0.16	0.45	0.57	0.48	0.44
Sum	100.16	99.79	100.08	100.39	100.37	99.1

Table 3a. Microprobe analyses for the olivine, orthopyroxene and spinel before and after the experiment of determine the “memory” of the minerals (Shavarin-Tsaram, ShTs 3-1, Mongolia)

Oxides	Olivine		Orthopyroxene		Spynel	
	Before the experiment	After the experiment	Before the experiment	After the experiment	Before the experiment	After the experiment
SiO ₂	41.01	41.2	54.55	55.61	0.051	0.028
MgO	49	48.15	31.85	30.73	21.014	21.578
CaO	0.06	0.04	0.89	0.9	-	-
TiO ₂	0	0	0.16	0.19	0.15	0.127
FeO+Fe ₂ O ₃	11	10.74	7.08	7	-	-
FeO	-	-	-	-	10.882	10.522
MnO	0.16	0.11	0.11	0.14	0.15	0.062
Cr ₂ O ₃	0	0	0.3	0.35	7.202	6.675
V ₂ O ₅	0	0.02	-	-	0.15	0.064
NiO	0.28	0.37	-	-	0.403	0.406
Na ₂ O	-	-	0.16	0.17	-	-
Al ₂ O ₃	-	-	5.45	5.35	60.707	61.025
Sum	101.51	100.63	100.54	100.45	100.709	100.487
FM	11.34	11.23	11.24	11.54	-	-
Fo	88.42	88.44	-	-	-	-
Fa	11.58	11.56	-	-	-	-
Wo	-	-	1.75	1.83	-	-
En	-	-	87.2	88.84	-	-
Fs	-	-	11.05	11.33	-	-

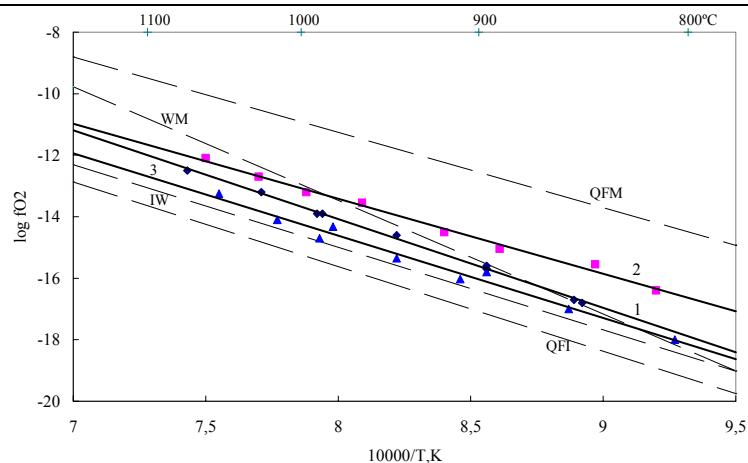


Fig. 1. The experimental determination of dependence of $\log fO_2 - 10^4/T^\circ K$ for the olivine (1), India. Control the “memory” of the olivine at QFM-2 log unite, fO_2 (2) and at QFM-3 log unite, fO_2 (3).

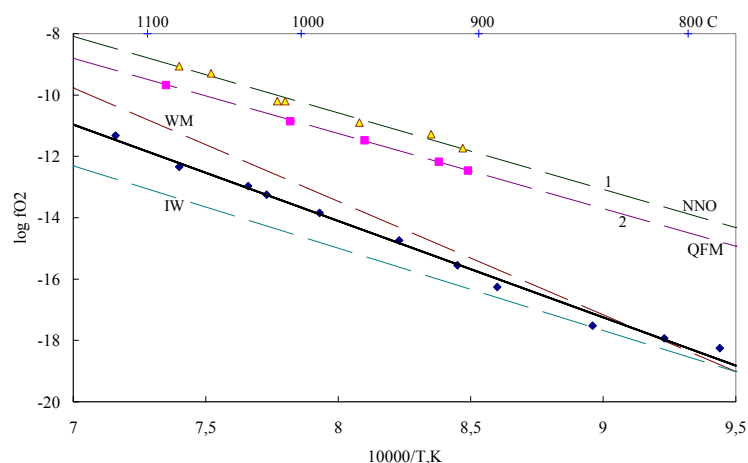


Fig. 2. The experimental determination of dependence of $\log fO_2 - 10^4/T^\circ K$ for the olivine from the spinel lherzolite of volcano Shavarin-Tsaram (ShTs 3-1 Ol). Control the “memory” of the olivine at Ni-NiO (1) and at QFM (2).

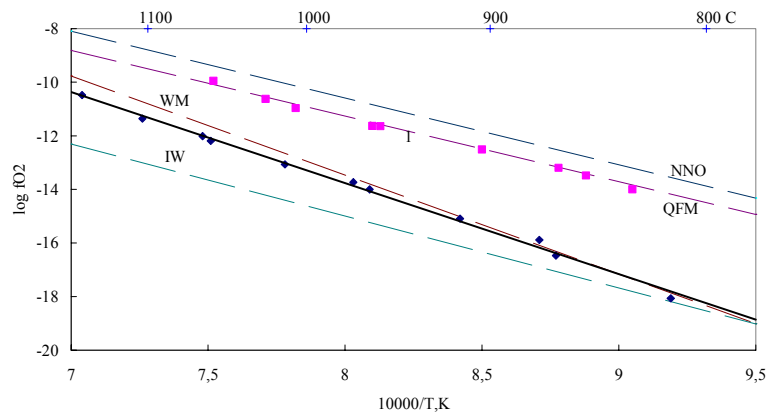


Fig. 3. The experimental determination of dependence of $\log fO_2 - 10^4/T^\circ K$ for the orthopyroxene from the spinel lherzolite of volcano Shavarin-Tsaram (ShTs 3-1 Opxl). Control the “memory” of the orthopyroxene at QFM (1).

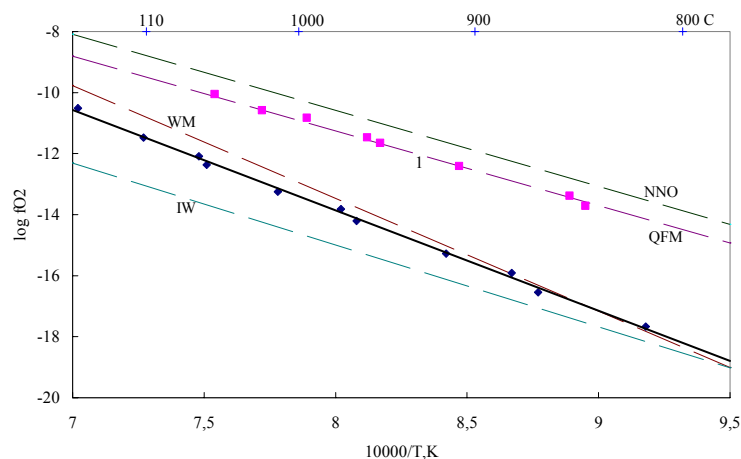


Fig. 4. The experimental determination of dependence of $\log fO_2 - 10^4/T^\circ K$ for the spinel from the spinel lherzolite of volcano Shavarin-Tsaram (ShTs 3-1 Spl). Control the “memory” of the olivine at Ni-NiO (1) and at QFM (2).

The investigation was carried out under support of RFFI 11-05-00926.