Mineral equilibria at high PT-parameters

Ashchepkov I.V. Amphibole thermobarometer for mantle rocks (preliminary version). UDC 551.22- 552.11

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Abstract. Calibration of S-Al- K-Na-Ca distribution in the structure of the mantle amphiboles (Cr- hornblende , pargasite, kaersutite) using experimental data (Niida, Green, 1999 ;. Wallace Green, 1991, etc.) allow to obtain an equation for pressure estimates in 5 - 60 kbar interval. Regression calculated pressures with experimental values (R ~ 0.82) and precision~ 5 kbar allow to use barometer for a wide range of mantle rocks from peridotite to pyroxenites and megacrystals.

Keywords: mantle, experiment, amphibole, peridotite, pyroxenite, empirical barometer, thermometer

Calibration redistribution S-Al-K-Na-Ca according to experimental data

For mantle amphiboles (Cr-hornblende, pargasite, kaersutite, richterite) the calibrations of the S-Al-K-Na-Ca exchange was made using experimental data [Niida, Green, 1999; Wallace, Green, 1991; Medard et al, 2006, etc.] Used
KD =Si/(8-Al-2.2*Ti)*(Na+K))/Ca

It was obtained the preliminary equation for the pressure range of 5 - 32 kbar.
P(kbar)=0.035*(4+K/(Na+K))*2*Mg)/Fe + 3.75**(K+Na)/Ca)*)*KD**T*°*K**
*0.75/ (1+3.32*Fe) - ln(1273/*T*°*K**5*(8*Mg-Al*2 +3*Ti+8*Cr+3*K)

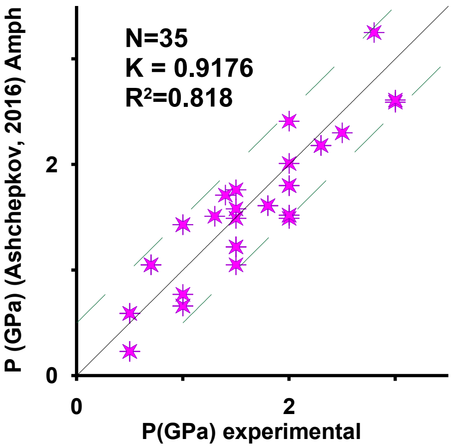

Fig. 1. Dependence between experimental and calculated pressures.

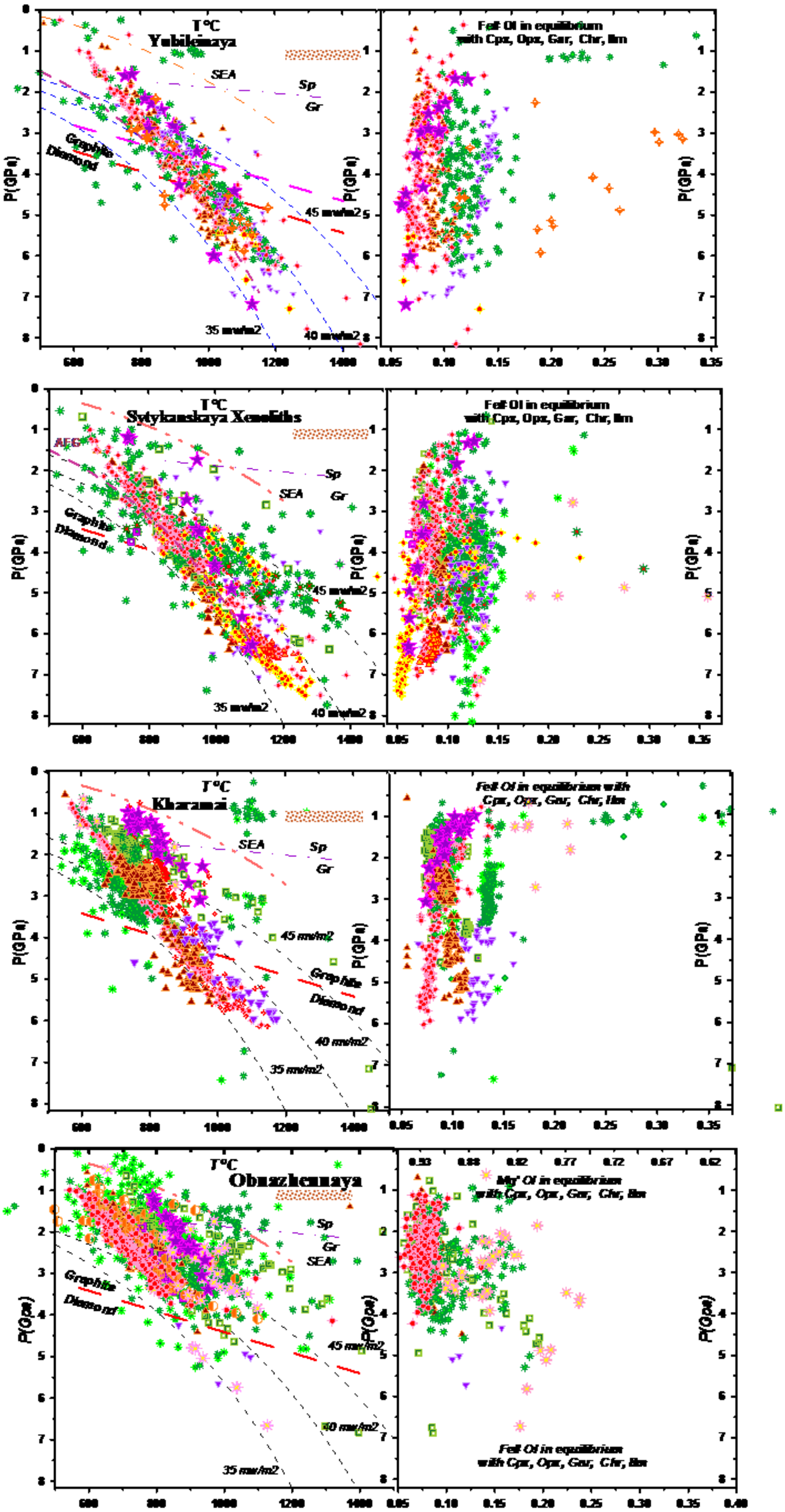

Fig. 2. ***PT parameters for the amphiboles*** **(asterisks, see legend) and other mantle minerals from kimberlite pipes [Ashchepkov et al., 2013] estimated using monomineral methods.** The sign are also from cited work.

For the higher pressures (Cr- pargasite richterite) calibration is carried cross- correlations with the estimates calculated for the natural associations obtained using clino- and orthopyroxene. I was used Fig.1.

Aplication of the mantle amphibole thermobarometry for the reconstruction of sections of the lithosphere

For the calculations of the PT parameters of the natural associations it was used monomineral version of Gar-Apmh termometer (Ravna et al., 2000) in combination with the received barometer.

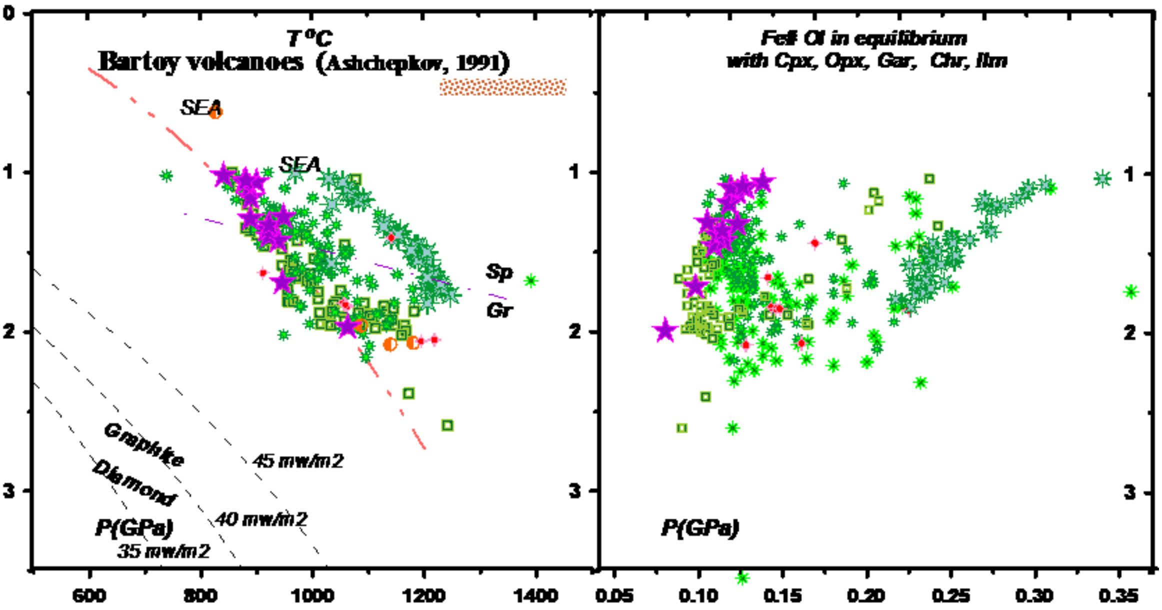

Fig. 3. PT estimates for amphibole and other minerals from mantle xenoliths Bartoy volcanoes [Ashepkov 1991]

The PT parameters were calculated for the richterite and pargasite from kimberlite Sytykanskaya, Yubileinaya and Cr- hornblende - pargasite Kharamai field and tr. Nude (Ashchepkov et al., 2013). In addition, assessments were conducted for the mantle amphiboles Bartoyskih volcanoes (Aschepkov, 1991)

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Marchenko E.I., Eremin N.N. Computer modeling of Ca- and Mg- perovskites containing al atoms under Earth's mantle thermodynamic conditions.

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Abstract. Current paper presents semi-empirical theoretical investigation of energy, phase densities and elastic properties for some phases with simple $CaSiO_3$ and $MgSiO_3$ composition containing Al atoms. The calculation was performed by using two interatomic potential models at pressure up to 180 GPa. Reproduced and refined the phase diagram of $CaSiO_3$. Two mechanisms of aluminum atoms incorporation into perovskite structures were investigated. Calculations of defect energies were performed both by Mott-Littleton model and supercell calculations. The results of the calculation show that aluminum is preferably included in the $MgSiO_3$ than $CaSiO_3$.

Keywords: computer modeling, defects in perovskites, Al containing perovskites, CaSiO3.

In spite of increased activity in the study of the Earth's mantle composition many questions about mineralogy, phase stability of minerals and geochemistry of deep Earth layers of the Earth are still actual. In particular up to date the geochemical role of Ca in the mantle is not defined exactly. There are ambivalent data about $CaSiO_3$ high-pressure phases stability at the thermodynamic conditions of Earth's mantle.

The aim of this study was computer modeling of Al atoms incorporation into Mg- and Ca- perovskites structures using atomistic methods and $CaSiO_3$ phase diagram elaboration. Calculations were performed using semi-empirical approach with the help of GULP 4.0 code [Gale J.D., 2005] at 0-180 GPa pressures. Two independent models of the interatomic potentials were used in the calculations [Urusov V.S. and Eremin N.N., 2012; Pedone A. et al, 2006]. Three most possible modifications for $CaSiO_3$ were investigated: cubic (Pm-3m), tetragonal (I4 / mcm) and orthorhombic (Pnma) (Table 1.).

Table. 1 $CaSiO_3$ modifications of [Caracas et al., 2007].

Space group	Atomic sites	Cell parameters, Å
Pnma	Ca 4 c 0.5106 0.25 0.0022 Si 4 a 0 0 0 O1 8 d 0.2656 0.0214 0.2344 O2 4 c 0.9983 0.25 0.9584	a=5.0083 b=7.0858 c=5.0243
I4/mcm	Ca 4 b 0 0.5 0.25 Si 4 c 0 0 0 O1 4 a 0 0 0.25 O2 8 h 0.2124 0.7124 0	a= 4.6368 c=6.7240
P m-3m	Ca 1b 0.5 0.5 0.5 Si 1 a 0 0 0 O 3 d 0.5 0 0	a=3.2221

As a result of calculations the phase diagram for $CaSiO_3$ phases was reproduced (Fig. 1). It should be noted that the difference between calculated Gibbs free energies for tetragonal and cubic modifications is less than 1 eV; this fact make it difficult to define exactly the stability boundaries for these modifications in the phase diagram.

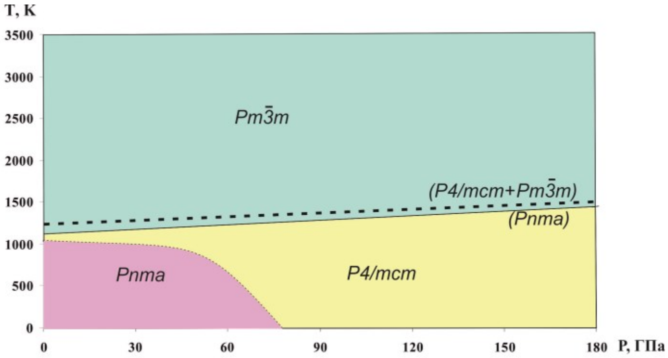

Fig. 1 Phase diagram for $CaSiO_3$ by atomistic calculation.

Colors shows simulation results using the potential model [Urusov V.S. and Erremin N.N., 2012], The dashed line - [Pedone A. et al, 2006].

The energy of Al incorporation into perovskites structures was calculated by two schemes:

1) Mg+Si →Al+Al
2) Si+Si+O→Al+Al+V, where V-vacancy of O atom

Incorporation energies were calculated for $CaSiO_3$ and $MgSiO_3$ isolated defects at different thermodynamic parameters. For correctness confirmation of the Mott-Littleton method calculations we also carried out the calculations in supercells. For methodical purposes the effect of a supercell size on the energies of defects. was determined The calculation results showed that scheme 1) is the most energetically favorable for $MgSiO_3$ which is in qualitative agreement with the results of quantum chemical calculations [2], and scheme 2) for $CaSiO_3$. Energy of impurities occurrences of Al calculated by Mott-Littleton and supercell methods are in a good agreement with each other and differs no more than 1 eV.

The difference in the Al incorporation energies into Mg- and Ca- perovskites at studied pressure range reaches 39-40 eV. This fact demonstrates the dramatic preference of Al incorporation into $MgSiO_3$ as compared with $CaSiO_3$. In the future we plan to calculate the $CaSiO_3$ and $MgSiO_3$ isomorphic capacity in relation to Al at different pressures by quantum chemical methods and the semi-empirical modeling.

This work was supported by RFBR Grant number 15-05-04575

Some computer calculations carried out on the MSU supercomputer "Lomonosov"

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Khodorevskaya L.I., Varlamov D.A. Experimental study of amphibole's interaction with NaCl-KCl-H_2O fluids: applications to high-temperature alkaline metasomatism of basic rocks.

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Abstract. Experimental results of interaction of an amphibole, one of the most important minerals of rocks with medium and basic composition, which are involved in the processes of high temperature metamorphism, metasomatism and melting in the lower and middle crust, with fluids NaCl-KCl-H_2O at various ratios of fluid components, T = 750°C and P = 7 kbar are presented.

The sequence of formation of newly formed mafic minerals is established with a growth of a ratio of $X_{KCl}/(X_{KCl} + X_{NaCl})$ in the fluid, which in general can be expressed as *Hbl*±Na-*Phl* → *Cpx*+*Bt*+*Kfs*±*Hbl* → *Grt*+*Cpx*+*Bt*. The ratio of K/Na in such minerals as the amphibole, nepheline, feldspar is dependent on this relationship in the fluid.

Keywords: amphibole, Na-K chlorides, fluid interaction, experimental modeling, metasomatism

The processes of high-temperature metamorphism, magmatism and metasomatism often occur with the participation of the fluid in which the chlorides (Na-K-Cl) are the main components. The evidence of participation of such fluids in these processes are water-salt fluid inclusions. The experimental studies of systems "mineral – fluid" (water – salt) consist substantially in studying of solubility in similar fluids of a number of rock-forming minerals, such as quartz, albite, grossular, wollastonite, etc. The experimental data on the interaction of mafic rock-forming minerals, especially rocks, with water and chloride solutions is much smaller.

Amphibole - one of the major minerals involved in the formation and melting of rocks with medium or basic composition in the lower and middle crust. The interaction of amphibole with NaCl solutions experimentally was investigated earlier at 500 MPa, 900°C [1].

However in nature the composition of fluid phase differs in more complicate salt component (NaCl+KCl, NaCl+$CaCl_2$ etc.), at the same time the ratio K/Na/H_2O in a fluid substantially determines process of formation of this or that type of rocks. For example, the observed processes of a granitization or charnokitization which are especially often confined to the Precambrian shields are determined by specifics of a fluid concerning to ratio potassium-sodium. Variations of formation of alkaline magmatic rocks from the leucite to nepheline phonolites also depend on K/Na ratios in a magmatic fluid.

This study presents the results of experiments on the interaction of natural amphiboles with fluids NaCl-KCl-H_2O at T = 750°C, P = 7 kbar. Experiments were carried out on standard apparatus of high gas pressure with internal heating in gold ampoules (to avoid losses of iron in walls of ampoules) without external monitoring of oxygen fugacity f_{O_2}.

The natural amphibole (Hbl) was used as the starting material – chermakite from metasomatic veins on Kii island (White Sea). The composition of a fluid phase was set by various ratio of NaCl/KCl/H_2O. Ampoules were welded and maintained in the experimental mode during 7-14 days. After the experiments ampoules were opened, the solid body was taken from an ampoule, then was located in a container, then was filled in with epoxy glue, polished and analyzed. The compositions of mineral phases have been studied by method of a local X-ray spectral microanalysis with application of the scanning electronic microscopes Camscan/Tescan with INCA Energy EDS unit. More in details the technique and features of carrying out for experiments and the analysis of phases after experiments are presented in [1].

In system "amphibole – (Na,K)Cl – H_2O" at the given T-P parameters formation of these or that mineral associations is defined both by activity of water a_{H_2O}, (X_{H_2O}), and a ratio of $X_{KCl}/(X_{KCl}+X_{NaCl})$ in a fluid. Fig.1 shows the newly formed association of minerals depending on the composition of the fluid.

At X_{H2O} = 0.3-0.4 and absence of a potassium (i.e. $X_{KCl}/(X_{KCl}+X_{NaCl})=0$) after experiments primary amphibole (Hbl) remains and are formed nepheline (*Ne*) + sodalite (*Sdl*) + a plagioclase (*Pl*) + a Na-phlogopite (Na-*Phl*). These are well expressed squares and hexagons of nepheline, or large individual crystals of sodalite $Na_4(Al,SiO_4)_3Cl$ with the content of Cl to 7.3 wt.%. However, even small additives of potassium (KCl) in composition of the initial solutions lead to the appearance of clinopyroxene (*Cpx*) and biotite (*Bt*), along with *Nf*, *Sdl* and *Pl*. In the range of $X_{KCl}/(X_{KCl}+X_{NaCl}) \approx 0.05$ - 0.4 at the same X_{H2O} the association *Cpx+Hbl+Bt+Nf+Sdl±Pl±Kfs* is stable.

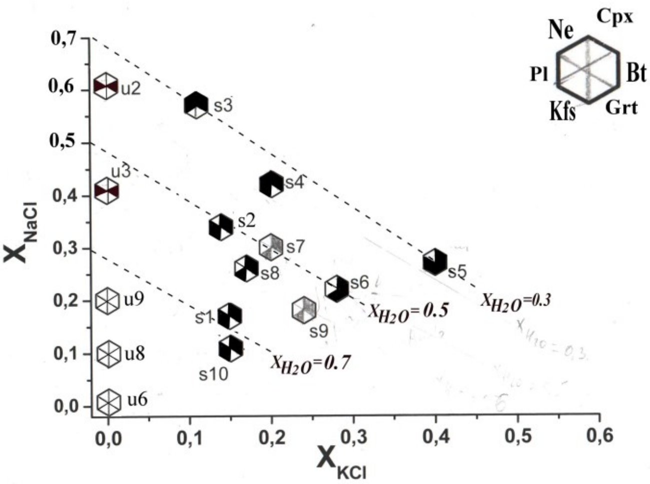

Fig.1. Mineral association after the experiments with different ratios of NaCl-KCl at given XH_2O (dashed lines)

At $X_{KCl}/(X_{KCl}+X_{NaCl}) > 0{,}4$ amphibole disappears and there is a garnet of a andradite-grossular series; Cpx, Bt and Kfs are stable; Ne and Sdl are not marked

The clinopyroxenes arising in experiments on composition answer an aegirine-augite, similar in composition to [2], there is a direct correlation between the content of Na in Cpx and NaCl content in the fluid: $X_{NaCpx} = 0.0326 + 0.5938(X_{NaCl/fl}) - 0.0185(X_{NaCl/fl})^2$.

The ratio of K/(K+Na) in feldspars well correlates with the same ratio in a fluid. Good compliance of our data and [3] demonstrates that T-P parameters in the range of T = 750-900°C, P = 7.5 – 10 Kbar do not influence on distribution of alkalis between a fluid and feldspar.

K/Na relation in nepheline and amphibole also depends on a ratio of $X_{KCl}/(X_{KCl}+X_{NaCl})$ in a fluid. For nepheline this dependence is expressed as $X_{K(Ne)} = 0{,}00478+0{,}85288\, X_{K(fluide)} - 0{,}71293\, [X_{K(fluide)}]^2$, for amphibole

$(K/K+Na)Hbl = 0{,}04+1{,}67(X_{KCl}/(X_{KCl}+X_{NaCl})fl - [X_{KCl}/(X_{KCl}+X_{NaCl})fl]^2$.

Conclusions

KCl/NaCl ratio at constant and low activity of water a_{H2O} define type of mineral associations: at $X_{KCl}=0$ in a paragenesis amphibole and a Na-phlogopite are observed. Even at small KCl additives ($X_{KCl}<0.1$) formed biotite and clinopyroxene begin to replace amphibole; at $X_{KCl}>0.1$ potassium feldspar appears, at $X_{KCl}>0.27$ garnet of an andradite-grossular series is steady. In general, the sequence of changes of mafic minerals with increasing $X_{KCl}/(X_{KCl}+X_{NaCl})$ in the fluid can be expressed as *Hbl→ Cpx+Bt±Hbl→ Grt+Cpx+Bt.* The ratio of K/Na in such minerals as the amphibole, nepheline, feldspar is dependent on this relationship in the fluid.

Thus, the interaction of amphibole with NaCl-KCl-H_2O fluid at low a_{H2O}, T = 750°C, P = 700 MPa leads to the formation of mineral associations, which typical for alkaline metasomatism of amphibole-bearing rocks with basic or medium composition. Compositions of such minerals as nepheline, feldspars, clinopyroxene and amphibole allow to define a ratio $X_{KCl}/(X_{KCl}+X_{NaCl})$ in a fluid. Similar alkaline metasomatism can occur in various geological situations. For example, it can be interaction of alkaline intrusions with the host rocks.

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Limanov E.V.[1,2], Kuzyura A.V.[1], Bovkun A.V.[2], Litvin Yu.A. Genetic classification of primary growth inclusions in upper mantle diamonds (according to the physico-chemical experiments).

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Abstract. The paper presents a genetic classification of primary mineral inclusions in diamonds of the upper mantle. The minerals of syngenetic inclusions are classified as (1) primary ones, paragenetic with diamonds ones, (2) accessory paragenetic ones (soluble in parental melts), (3) accessory xenogenetic ones (insoluble in parental melts). This genetic classification is developed based on the results of physico-chemical experiments.

Keywords: diamond, peridotite, eclogite, primary inclusions, paragenesis, genetic classification, mantle-carbonatite concept.

Minerals of primary inclusions in the upper mantle diamond belong to peridotite and eclogite paraginesises that almost doesn't occur combined in the same crystal of diamond. Variable peridotite/eclogite-carbonatite-carbon compositions of diamond-forming melts are fundamental basis of mantle-carbonatite concept of the genesis of diamonds and associated minerals. Experimentally analyzed melting diagrams of syngenesis of diamond and primary inclusions characterize the conditions of nucleation and growth of diamonds, and capture of paragenetic and xenogenetic minerals by them. (fig. 1).

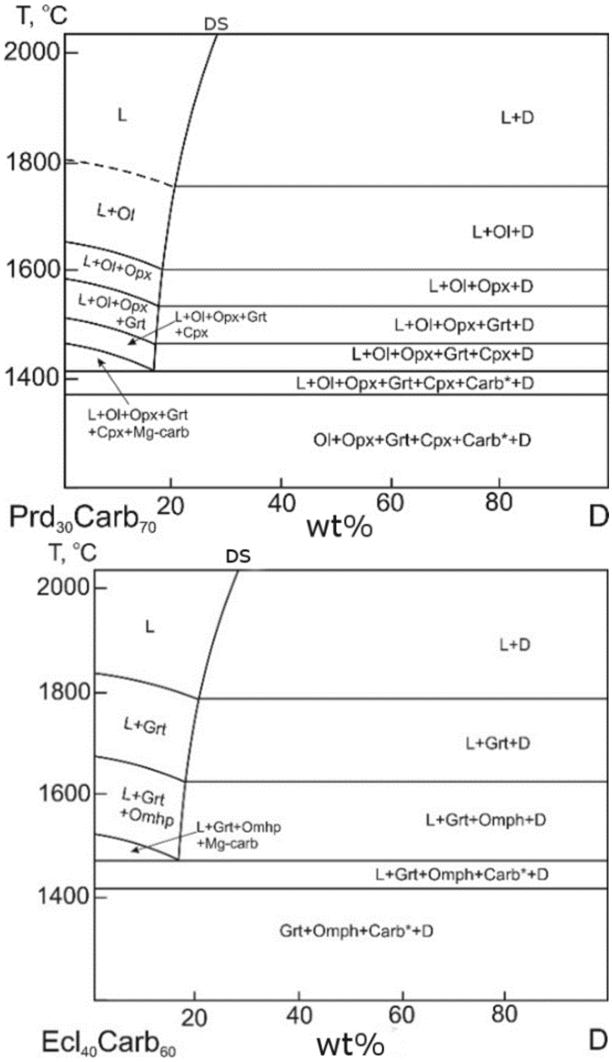

Fig.1. Phase diagrams of syngenesis of diamond and mineral phases of peridotite and eclogite paragenesis (polythermal sections). a) peridotite$_{30}$ carbonatite$_{70}$ – carbon ($Prd_{30}Carb_{70}$ - D);
b) eclogite$_{40}$carbonatite$_{60}$ - carbon ($Ecl_{40}Carb_{60}$ - D); *L* – melt, *D* -diamond, *Ol* - olivine, *Opx* -orthopyroxene, *Cpx* - clinopyroxene, *Grt* - garnet; *Omph* - omphacite, *Mg-Carb* – magnesia carbonate, *Carb** - carbonates of various compositions.

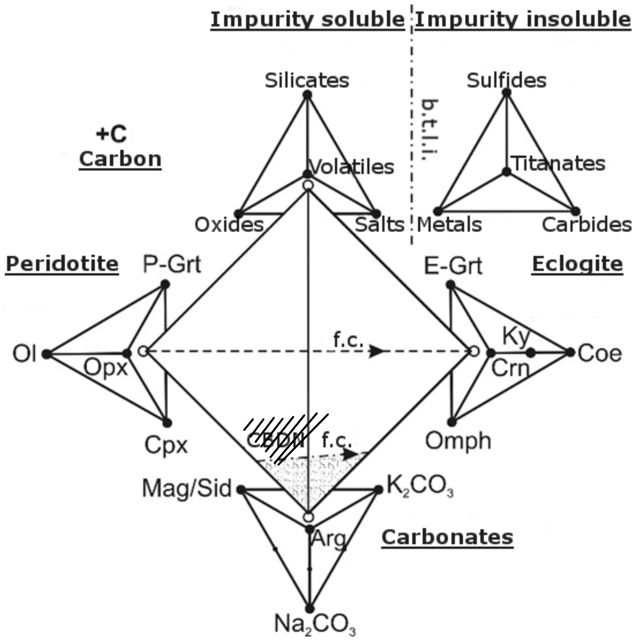

Fig.2. Diagram of compositions of upper mantle melts (shaded field). *Ol* - olivine, *Opx* - orthopyroxene, *Cpx* - clinopyroxene, *P-Grt* – garnet of peridotite paragenesis; *Omph* - omphacite, *E-Grt* – garnet of eclogite paragenesis, *Crn* - corundum, *Ky* – kyanite, *Coe* – coesite; *Mag* – magnesite, *Arg* – aragonite, *Sid* – siderite, CBDN – concentration boundary of diamond nucleation, b.t.l.i. – the boundary of total liquid immiscibility, f.c. – fractional crystallization.

Completely miscible peridotite-carbonatite and eclogite-carbonatite melts saturated with dissolved carbon in relation to diamond are characterized with solubility curve of diamond. Relatively fusible carbonate minerals formed at near solidus temperatures, so their rare occurrence in inclusions of upper mantle diamonds is explained by the fact. The bulk of diamonds crystallize at higher temperatures, so silicate minerals occur more often in inclusions in diamonds than carbonates. Peridotite-carbonatite-carbon melts of diamond-forming systems are undergone to ultrabasic-basic evolution with transition to eclogite-carbonatite-carbon melts. Such paragenetic transition from peridotite system Ol-Opx-Cpx-Grt to eclogite system Cpx-Grt is possible at fractional crystallization at rocks partial melting and disappearance of both, olivine and orthopyroxene.

A generalized diagram of parental melts of diamonds and minerals-inclusions (fig. 2) is used to be as physico-chemical basis of genetic classification of primary inclusions in diamonds of the upper mantle. The minerals of syngenetic inclusions are classified as (1) primary ones, paragenetic with diamonds one, (2) accessory paragenetic ones (soluble in parental melts), (3) accessory xenogenetic ones (insoluble in parental melts) (fig. 2).

The figurative points of the boundary compositions can move on surfaces and within the respective boundary tetrahedra, which corresponds to the variability of natural growth compositions. According to the experimental data of carbonate-peridotite and eclogite-carbonate systems, CBDN values (fig.2) are shifted to carbonatite structures and have content of 30 wt% of peridotite and 35 - 40 wt% of eclogite [BobrovA.V, 2011]. The developed genetic classification is based on results of physical and chemical experiments and presented in the table 1.

Table 1. Genetic classification of primary growth inclusions in upper mantle diamonds

Main (forming parental melts)	
Ultrabasic association	*Basic association*
Olivine (Ol)	Omphacite (Omph)
Orthopyroxene (Opx)	Mg-Fe-garnet (Prp-Alm-Grt)
Clinopyroxene (Cpx)	Diamond (Dia)
Chrome-garnet (Cr-Grt)	Corundum (Crn)
K-Na-Mg-Fe-Ca carbonates	Kyanite (Ky)
	Coesite / quartz (Coe/Qtz))
Diamond (Dia)	

Secondary (accessory)	
Soluble (paragenetic)	*Insoluble (xenogenetic)*
Sanidine (*Sa*)	Pentlandite (*Pn*)
Graphite (*Gr*)	Pyrrhotite (*Po*)
Chromospinel (*Cr-Spl*)	Pyrite (*Py*)
Xenotime (*Xtm*)	Chalcopyrite (*Ccp*)
Zircon (*Zrn*)	Dzherfisherit (*Jrf*)
Apatite (*Ap*)	Rutile (*R*t)
Magnetite (*Mag*)	Imenite (*Ilm*)
Chromite (*Chr*)	Perovskite (*Prv*)
Phlogopite (*Phl*)	Gold (*Au*)
C-O-H-N-volatile	Iron- nickel alloys
	Silicon carbide (?)
	Iron carbide (?)

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Reference:

Bobrov A.V., Litvin Yu.A. 2011. Mineral equilibria of diamond-forming carbonate-silicate systems. Geochemistry International. 49 (13), 1267-1363.