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EXPERIMENTAL STUDIES OF MELTING IN THE MODEL FERRIFEROUS ECLOGITIC SYSTEM CLINOPYROXENE-GARNET AT 40 KBARS

(Figs. 9, Tab. 1)

Abstract: Melting relations were studied in the model ferriferous system clinopyroxene ($Di_{80}Hed_{20}$)—garnet ($Py_{80}Alm_{20}$) at 40 kbar. Unlike the analogous iron-free system orthopyroxene appearence on the liquidus and essential lowering (up to 150—200 °C) of solidus boundary temperatures were observed. The wide liquidus orthopyroxene field was detected at the liquidus diagram of the triple system clinopyroxene ($Di_{80}Hed_{20}$)--garnet($Py_{80}Alm_{20}$)-olivine($Fo_{80}Fa_{20}$). Fe-components maintain olivine and orthopyroxene to melt congruently that proves the stabilization of eclogitic thermal barrier. The study of melting at 40 kbar in the model eclogitic system clinopyroxene-garnet containing as great quantities of Fe and Na as the real minerals of mantle eclogites shows clinopyroxene and garnet to be liquidus as well as solid phases of subliquidus and subsolidus. This results from the prevalent effect of jadeite component reacting with enstatite. Fe- and Na- components may be suggested to affect concurrently the melting relations in the systems of mantle minerals.

Резюме: При 40 кбар изучены фазовые отношения при плавлении в модельной железосодержащей системе клинопироксен ($Di_{80}Hed_{20}$) — гранат ($Py_{80}Alm_{20}$). В отличие от аналогичной безжелезистой системы обнаружено появление ортопироксена на ликвидусе, а также существенное (на 150—200 °C) понижение температур солидусной границы. Существование обширного поля ортопироксена установлено и на диаграмме ликвидуса тройной системы ($Di_{80}Hed_{20}$)-гранат($Py_{80}Alm_{20}$)-оливин($Fo_{80}Fa_{20}$). Железистые компоненты способствуют сохранению конгруэнтного характера плавления оливина и ортопироксена, стабилизируя при этом эклогитовый термальный барьер. Исследованием при 40 кбар плавления в модельной эклогитовой системе клинопироксен-гранат, содержащей ка Fe-, так и Na- компоненты в количествах, отвечающих наблюдаемым в реальных минералах мантийных эклогитов, показано, что как ликвидусными фазами, так и твердыми фазами в субликвидусе и субсолидусе являются клинопироксен и гранат. Это связано с преобладающим влиянием жадеитового компонента, который находится в реакционных отношениях с энстатитом. При этом проявляется конкурирующее влияние Fe- и Na-компонентов на характер плавления систем мантийных минералов.

Symbols

Fo — forsterite	Fa — fayalite
Di — diopside	Hed — hedenbergite
Py — pyrope	Alm — almandine
En — enstatite	Fs — ferrosilite
Jd — jadeite	Akm — akmite
Gross — grossular	Ol — olivine

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Opx — orthopyroxene
Cpx — clinopyroxene
Gr — garnet
Sp — spinel
Cs — coesite

Knowledge on petrographical features of garnet-peridotite facies rocks and their mineral compositions was derived through the study of deep-seated nodulus that chiefly are to be found in kimberlites (Sobolev, 1974; Boyd — Danchin, 1980).

Mantle rocks are formed with olivine-bearing ultrabasites (garnet dunites and harzburgites, garnet lherzolites and pyroxenites) alongside basites of eclogitic composition, including coesite-bearing grospidites (Smyth — Hatton, 1977). The schematic diagram of the system CaO-MgO-Al_2O_3-SiO_2 (Fig. 1) reflects a relation between main mineral phases and types of garnet-peridotite facies rocks. The diagram also proves the system Ol(Fo)-Cpx(Di)-Gr(Py)-Cs to be of the prime importance to the theory of garnet-peridotite facies rocks in upper mantle. The plane Opx-Cpx-Gr divides this system into two bulks, namely: Ol-Opx-Cpx-Gr associated with olivine-bearing ultrabasite silica-poor rocks and Opx-Cpx-Gr-Cs one, which comprises basite silica-rich rocks, including coesite-bearing ones. In fact the system Na_2O-FeO-CaO-MgO-Al_2O_3-SiO_2 is considered (prevalent components in mineral composition of mantle rocks were taken into account), FeO being distributed in all Mg-bearing minerals and Na_2O being concentrated for the most part in clinopyroxenes. Therefore the diagram Ol-Cpx-Gr-Cs is also relevant in case Fe and Na components are present.

Physical-chemical analysis of mantle magmatism processes is derived through the study subliquidus mineral equilibria in the system Ol-Cpx-Gr-Cs at 30—80 kbar and 1200—1600 °C (conditions analogous to those of continental mantle in the periods of stirring up the deep-seated magmatic activities). The mineral compositions of mantle origin reflect the complexity of chemical processes of deep-seated magmatism. The study of subliquidus mineral equilibria in the system CaO-MgO-Al_2O_3-SiO_2 is shown to apply to the extreme model situation because such important components as FeO and Na_2O are not kept in mind. FeO exceed CaO in content in all the minerals except clinopyroxenes. The Fe-component concentrations are as follows (in wt %): up to 10—16 of Fa in 01, 10—16 of Fs in Opx, 15—20 of Hed in Cpx, 50—65 of Alm in Gr. Na-component content (jadeite) reaches 50—65 wt % in Cpx of eclogites. Fe- and Na-components influence essentially upon the physical-chemical processes of mantle magmatism because they belong to relative easily fusible component of deep-seated rocks and show the degree of their exhaustion by "basalt" components.

Experimental study of melting in the system Ol-Opx-Cpx-Gr over the range 30—80 kbar are relevant to the following ironless systems: at 30 kbar to En-Di (Davis, 1963)), En-Py (Boyd — England, 1964) and Di-Py (O'Hara, 1963); at 40 kbar Fo-Di, Fo-Py, Di-Py (Davis, 1964), Fo-Di-Py (Davis — Schairer, 1965).

Present experiments deal with melting relations in ferriferous systems at 40 kbar. The model ferriferous system Cpx ($Di_{80}Hed_{20}$)-Gr($Py_{80}Alm_{20}$) is the first to be considered. It belongs to the join Opx-Cpx-Gr of the system Ol-Cpx-Gr-Cs bounding the Ol-bearing ultrabasic and Cs-bearing basic assemblages. The eclogitic thermal barrier (O'H a r a, 1968) conjugated with this boundary imposes a ban on the evolution of Ol-rich ultrabasic magmas towards silica-rich ones. Besides, clinopyroxenes and garnets being the minerals of variable composition isomorphically capacious to Fe-components are "through" minerals of ultrabasic and basic rocks of mantle origin. The experimental data for analogous ironless system at 30 kbar and 40 kbar allow to estimate and

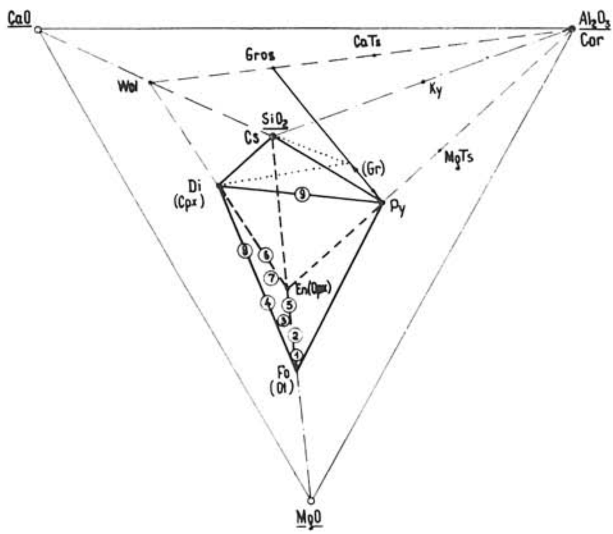

Fig. 1. Schematic diagram of the system $CaO—MgO—Al_2O_3—SiO_2$.
Explanations: The position of the system Ol—Cpx—Gr—Cs and the rock types of garnet-peridotite facies are observed: 1 — dunite; 2 — harzburgite; 3 — lherzolite; 4 — werhlite; 5 — olivine orthopyroxenite; 6 — websterite; 7 — olivine websterite; 8 — olivine clinopyroxenite; 9 — eclogite.

compare the results obtained. In the course of experimental study of silicate systems with ferriferous melts we encountered the problem of ampule for the materials under investigation. Sealed Pt ampules protected the samples chemically but extracted Fe from melts resulting in Pt-Fe alloys formation and changing the composition of the studied system that is inadmissible. Moreover Pt ampules may be used in solid medium (MgO and BN mixture) in the temperature range limited by 1450 °C. That is why the $Pt_{60}Rh_{40}$ ampules providing the temperature rise up to 1800 °C were used. But the study of a ferriferous melt of andesite composition (7.4 wt % of FeO) shows $Pt_{60}Rh_{40}$ to extract Fe from silicate melts although to a lesser degree than Pt too. The study of ferriferous melts was succeeded by the use of sealed Pt and $Pt_{60}Rh_{40}$ ampules lined with tungsten foil (Fig. 2) (L i t v i n, 1981) of 0.02—0.03 mm thickness. Experiments show tungsten not to react with ferriferous silicate melts. Fig. 3 illustrates the data in Fe loss by andesite melt in Pt, $Pt_{60}Rh_{40}$ and W ampules. Moreover, W appears to oxidize partially to $WO-WO_3$ during a run resulting in

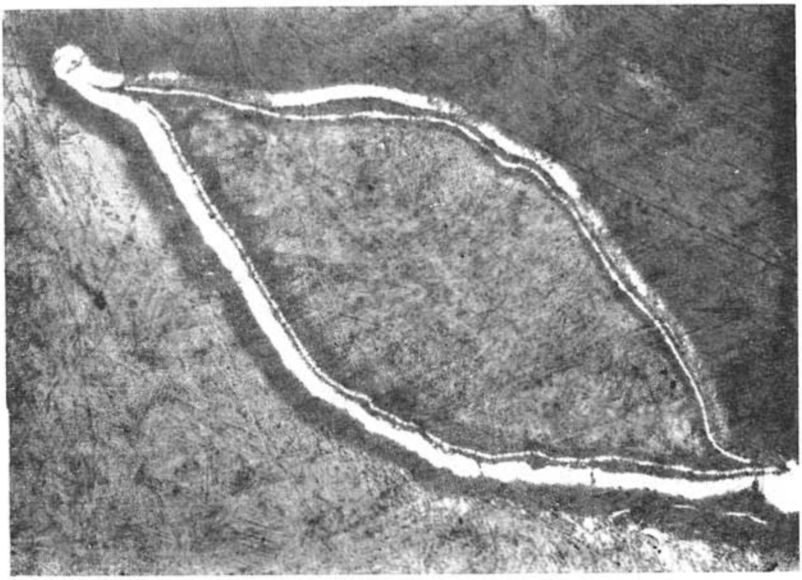

Fig. 2. Sealed Pt ampule lined by tungsten (thin open layer) in section. Glass (quenched andesite melt) is observed on the inside after a run at 1450 °C and 40 kbar.

buffered pair W/WO formation that maintaines oxygen fugacity in an ampule providing two valency Fe stability.

Phase equilibria in ferriferous systems at melting were studied in high pressure anvil-with-hole apparatus with large useful bulk (Fig. 4), the quenching method being used. Pressure in every run was estimated by Bi-Tl transducer, temperature up to 1700 °C was determined by $Pt_{70}Rh_{20}$-$Pt_{94}Rh_{06}$ thermocouple inserted to the ampule with studied sample or to the cluster of such ampules (2—8). Isobar-isothermal zone occupy not less ∅12×h 10 mm in the center of a cell. The mixtures of fine-crystalline phases such as diopside--hedenbergite clinopyroxene $Di_{80}Hed_{20}$ and pyrope-almandine garnet $Py_{80}Alm_{20}$ were studied. They were synthetized from gel mixtures in the same apparatus at 30—35 kbar and 1300—1400 °C for 8 hours, platinum ampules of ∅10××h 10 mm also lined with tungsten foil being used. The mixtures of starting composition were prepared as usual using 3-valency Fe compounds converted into two-valency form by special treatment of mixtures in hydrogen flow at 700 °C. Fe valency in these mixtures and in crystalline materials after the synthesis was controled by the Mössbauer spectroscopy.

Studied mixtures were welded up in the sealed way into Pt or $Pt_{60}Rh_{40}$ disk ampules (∅ = 5.5 mm) lined by tungsten. The experiments were performed at 1300—1400 °C for 7—8 hours, at 1450—1500 °C for 2—4 hours, at 1550 °C for 1—2 hours, at 1600 °C for 30—60 min, at 1650 °C for 10—20 min. Temperatures were measured by thermocouple within an accuracy ± 5 °C, pressure at room temperature was estimated within an accuracy ± — 0.5 kbar. At high temperatures pressure was determined to be 40 kbar in all the runs. Pressure values were calibrated (Litvin, 1979) at 1000—1700 °C by using quartz-coesite transition. The boundary assigned as the basic one was plotted with account of phase compresibility (Holm et al., 1967). It is displaced 2.5 kbar nearer to lower pressures region relative to the boundary determined by X-ray analysis under pressure in situ (Böhler — Arndt, 1974).

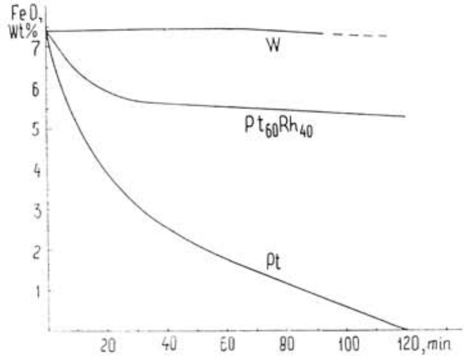

Fig. 3. Kinetic curves showing Fe loss by andesite melt in Pt, $Pt_{60}Rh_{40}$ ampules and when tungsten lining used (at 1450 °C and 40 kbar).

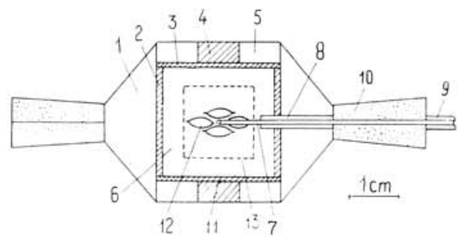

Fig. 4. Solid-media cell of anvil-with-hole apparatus.
Explanations: 1 — container (lithographic stone) 2—4 — details of isothermal heater (graphite); 5 — insulator of electroinlet (lithographic stone); 6 — sample holder (MgO: BN = 3 : 1 mixture); 7 — thermocouple $Pt_{70}Rh_{30}/Pt_{94}Rh_{06}$; 8—9 — thermocouple insulation (alundum, polychlorvinyle); 10 — gasket (pyrophillite); 11 — pressure transducer (Bi, Tl); 12 — ampule for the phase-equilibria study; 13 — contours of the ampule for isothermal synthesis of starting crystalline phases.

The diagram of the system clinopyroxene $Di_{80}Hed_{20}$-garnet $Py_{80}Alm_{20}$ (Fig. 5) is based upon experimental results. It is pseudobinary, complicated by orthopyroxene appearing on the liquidus and among subliquidus and subsolidus phases. Solid solutions containing clinopyroxenes and garnets alongside diopside, hedenbergite, pyrope, almandine and enstatite, ferrosilite, aluminoferous, grossular components, whose compositions do not belong to the studied join, also complicate the diagram. Melts appearing below the temperature range of three phase assemblage Cpx-Opx-Gr solidus proves that phase relations between mineral phases and melts where peritectic reactions take place are complicated. Topologically the diagram of the ferriferous system $Di_{80}Hed_{20}$-$Py_{80}Alm_{20}$ for 40 kbar is close to that of the system Di-Py for 30 kbar (Fig. 6a) but differs essentially from the diagram of an iron-free system at 40 kbar (Fig. 6b). The solidus boundary in the ferriferous system clinopyroxene-garnet at 40 kbar is observed at the temperatures 150—200 °C lower than in the iron-free system at 40 kbar and at 30 kbar (by 90—120 °C) primarily due to ferriferous compo-

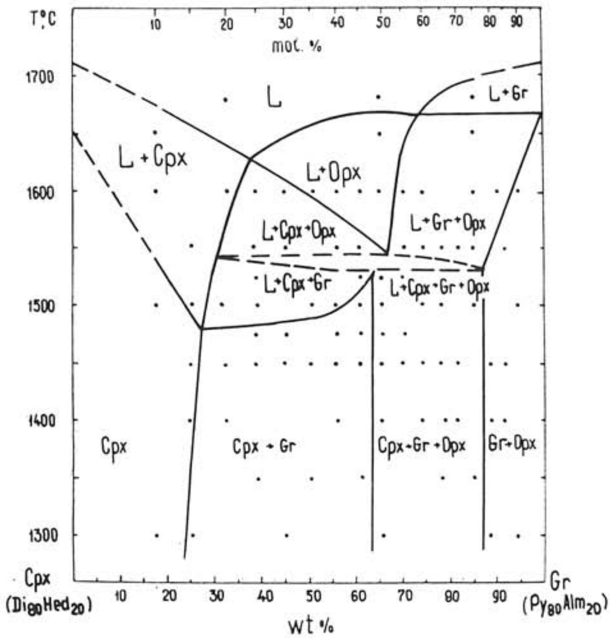

Fig. 5. Melting diagram of the system Cpx($Di_{80}Hed_{20}$)-Gr($Py_{80}Alm_{20}$) at 40 kbar. Experimental points are shown.

nents melting, all the runs being performed in different manners: Di-Py compositions were held at 40 kbar in graphite ampules for 5—30 min, at 30 kbar — in opened Pt ampules for 5—20 min; $Di_{80}Hed_{20}$-Py_{80} compositions welded up in the sealed way in Pt and $Pt_{60}Rh_{40}$ ampules lined by tungsten were held at 40 kbar for 0.5—8 hours.

Opx occurs on the liquidus at 40 kbar in the system $Di_{80}Hed_{20}$-$Py_{80}Alm_{20}$ (as well as in the system Di-Py at 30 kbar) alongside Cpx and Gr, whereas it was not detected in an iron-free system at 40 kbar. This effect is an evidence of eclogitic thermal barrier existence across the range of studied compositions. In case of the system $Di_{80}Hed_{20}$-$Py_{80}Alm_{20}$ at 40 kb the point of the cotectic line Cpx-Opx-L intersecting the diagram plane is essentially shift towards Cpx. That is why the crystallization of Opx-rich cotectic melts as two-phase assemblage Cpx-Gr is believed possible (in an iron-free system at 30 kbar it results in Cpx-Opx-Gr crystallization). When two-phase field Cpx-Gr expanded, the one-phase field of solid Cpx solutions is noted to be reduced essentially in the subsolidus of a ferriferous system (about 27 wt % of garnet component as against 42—43 wt % for iron-free systems at 30 kbar and at 40 kbar), the boundary between Cpx+Opx+Gr and Cr+Opx fields is shifted towards two-phase assemblage. Fig. 7 clarifies the difference between possible configurations of the liquidus plane. The field of the four-phase assemblage Cpx+

+Opx+Gr+L was not detected in the region of near solidus temperatures by experimets. Fig. 7 illustrates evolution expectancy of melting relations in the system Cpx-Gr-Opx within the Opx-Wol-Al_2O_3 plane. This plane involves iron-free minals of mineral compositions and melts of the studied system. But iron-rich minals make the indicated join shift to FeO-Opx-Wol-

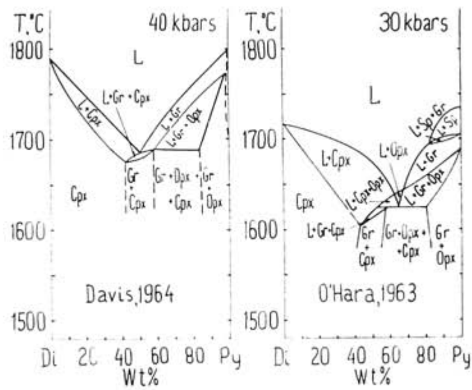

Fig. 6. Melting diagram of the system Di-Py; a) at 30 kbar (O' H a r a, 1963); b) at 40 kbar (D a v i s, 1934).

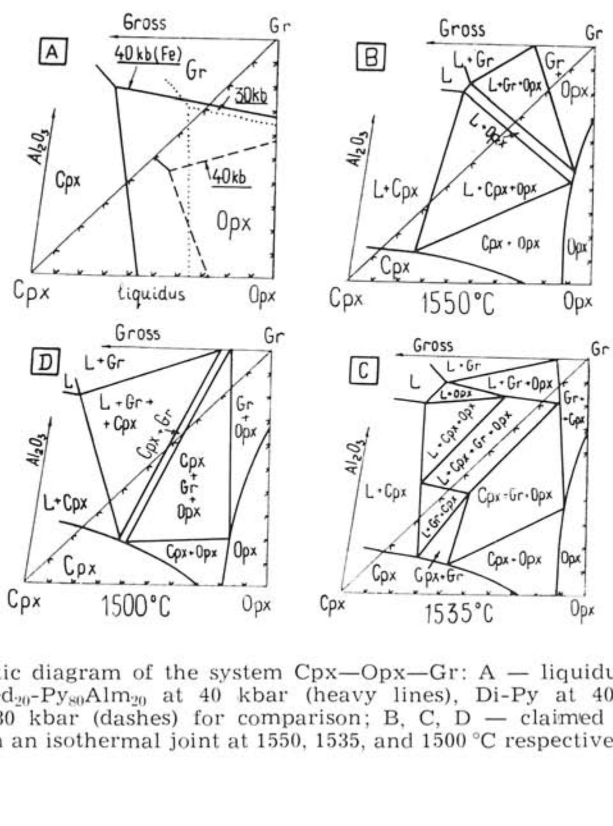

Fig .7. Schematic diagram of the system Cpx—Opx—Gr: A — liquidus planes in the systems $Di_{80}Hed_{20}$-$Py_{80}Alm_{20}$ at 40 kbar (heavy lines), Di-Py at 40 kbar (points), and Di-Py at 30 kbar (dashes) for comparison; B, C, D — claimed phase relations in an isothermal joint at 1550, 1535, and 1500 °C respectively.

-Al_2O_3 that may result in melt crystallization in a different manner. The ferriferous assemblage Gr-Cpx-Opx is to melt at temperature rise resulting in the four-phase assemblage Gr+Cpx+Opx+L formation. The Gr+Cpx+L assemblage converts first into the four-phase assemblage Gr+Cpx+Opx+L and then into the three-phase one Cpx+Opx+L by the peritectic reaction. The transition line in the studied join is confined by the non-variant point Cpx+ +Opx+Gr+L ($Cpx_{33}Cr_{67}$ wt %, 1545 °C) and the field Cpx+L. In this connection the four-phase field Cpx+Gr+Opx+L is designated at the diagram of the system $Di_{80}Hed_{20}$-$Py_{80}Alm_{20}$.

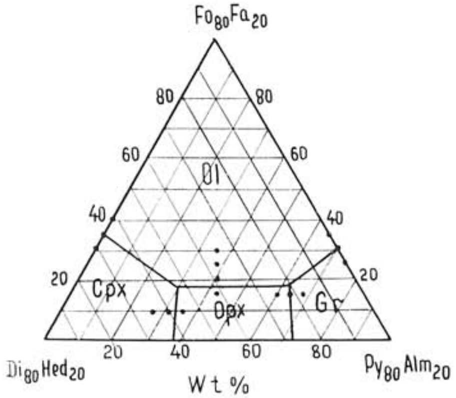

Fig. 8. Liquidus diagram of the system $Di_{80}Hed_{20}$-$Py_{80}Alm_{20}$-Fo_{80}-Fa_{20} at 40 kbar. Experimental points are shown.

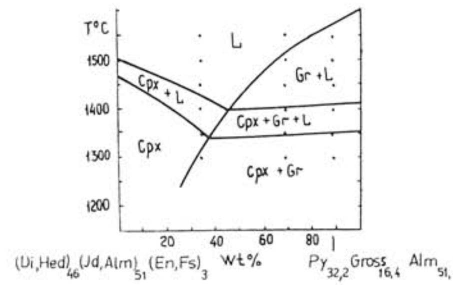

Fig. 9. Melting diagram of the eclogitic system Cpx-Gr at 40 kb. Experimental points are shown.

The inspection of the liquidus diagram indicates that unlike the iron-free system Di-Py-Fo (Davis — Schairer, 1965) there is an extensive liquidus Opx field in the three-phase system $Di_{80}Hed_{20}$-$Py_{80}Alm_{20}$-$Fo_{80}Fa_{20}$ at 40 Kbar (Fig. 8). The appearence of subliquidus mineral equilibria and temperatures of mineral assemblages primary melting at high pressures are dictated by Fe-components participating in melting processes. Moreover, Fe-components maintain Fo and melting congruently that contributes to the conservation of mantle minerals in ferriferous model systems and eclogitic thermal barrier in iron-free (magnesial) systems. In this connection the model eclogitic system Cpx-Gr containing as many both Fe and Na components as there are in real minerals of mantle eclogites is of interest.

Melting diagram of the system $Cpx(Ca_{0.46}Mg_{0.45}Fe_{0.19}Na_{0.5}Al_{0.39}Si_2O_6)$-Gr $(Mg_{0.97}Ca_{0.49}Fe_{1.54}Al_2Si_3O_{12})$ is given in Fig. 9. The component compositions of given systems are models of compositions of real Cpx and Gr bimineral eclogites from kimberlites (Tab. 1). Only Cpx and Gr are crystallized on the liquidus of this system. They are observed at subliquidus (being equilibrated with melts) and subsolidus assemblages. In this case we encounter prevalent influence of jadeite component. The study of the system Jd-En at 40 kb proves the jadeite component to react with En. Opx appears in subliquidus and sub-

Table 1
Real and model compositions of mantle minerals (wt %)

	Eclogite assemblage				Peridotite assemblage			
	Cpx		Gr		Cpx		Gr	
Oxides	real	model	real	model	real	model	real	model
1	2	3	4	5	6	7	8	9
SiO_2	55.3	55.74	19.2	40.44	5.1	55.9	41.7	42.66
TiO_2	0.52		0.44		0.20		0.68	
Al_2O_3	9.07	9.12	21.1	21.54	3.83	4.40	21.0	22.24
Gr_2O_3	0.07		0.06		0.50		1.10	
FeO	6.15	6.21	22.7	23.48	4.13	4.27	8.24	9.23
MnO	0.07		0.40		0.12		0.32	
MgO	8.93	8.91	8.32	8.52	17.1	17.32	21.0	21.14
CaO	12.7	12.67	5.81	6.02	15.1	15.32	4.68	4.73
Na_2O	7.29	7.35	0.20		2.77	2.79	0.11	
K_2O	0.07							
Total	100.24	100.0	98.13	100.0	98.9	100.0	99.4	100.0

solidus assemblages when the system Cpx($Ca_{0.60}Mg_{0.90}Fe_{0.14}Na_{0.18}Al_{0.18}Si_2O_6$)--Gr($Mg_{2.20}Ca_{0.30}Fe_{0.50}Al_2Si_3O_{12}$) melting, the component composition of this system modeling real Cpx and Gr compositions of peridotites from kimberlites.

Fe and Na components are claimed to affect the melting relations of mantle minerals, first of all Opx. Further experimental and theoretical research is needful to determine conclusively this effect. This research should be directed to the possible ways of magmatic differentiation at high pressures in the system Ol-Cpx-Gr-Cs, whose phase composition is the most realistic and is in full accord with the physical-chemical nature of mantle magmatism processes.

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