MINERAL EQUILIBRIA AND FORMATION OF DIAMOND IN THE MANTLE ECLOGITES

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Phase relations of multicomponent system garnet-clinopyroxene (omphacite) are investigated at 7 GPa and 1200-1600°C, PT – conditions of diamond stability. The experimental data combined with published data for boundary components permit to construct a liquidus surface for the ternary omphacite – Mg-Ca-Grt –Fe-Ca-Grt system and to definite physical-chemical peculiarities of diamond-bearing eclogite formation. According to modern experimental [1] and mineralogical [2] researches there are two natural parent mediums: sulfide and carbonate-silicate, which take part in diamond formation. According to the experiments silicate melts can't be effective solvent for carbon, but it's necessary for spontaneous diamond nucleation.

Mineral composition of Diamond-bearing Ilmenite-rutile Mg-Fe eclogite (group 3) was taken from numerous types of eclogite (26 genetic groups of garnet after claster analyze [3]) for our experiment. The compositions were calculated as the most representative for the Maksutov Complex (Southern Urals) and reflect some key peculiarities of eclogite minerals from the mantle nodules in kimberlite pipes (table 1).

Table 1. Chemical analyzes of garnets and clinopyroxenes from mantle nodules in kimberlite pipes Ruslovaya and Obnazhennaya.*

№№	Mineral	Component, mol.%								Name of pipe
		SiO_2	TiO_2	Al_2O_3	FeO + Fe_2O_3	MnO	MgO	CaO	Na_2O	
4/15	Grt***	37.20	0.10	21.60	25.00	0.60	4.00	11.50	0.00	
4/15	Cpx	54.60	0.10	8.80	7.30	0.00	8.30	14.70	6.20	
AO-319	Grt	38.52	0.13	21.25	27.63	0.58	3.78	8.11	0.00	Obnazhennaya
AO-319	Cpx	54.55	0.10	7.60	9.11	0.00	7.76	15.00	5.89	
RSL-8	Grt	37.43	0.04	21.25	28.57	0.59	3.49	8.61	0.02	Ruslovaya
RSL-8	Cpx	55.60	0.22	7.81	8.98	0.00	8.14	14.86	4.39	
Claster group 3**	Grt	38.30÷ 42.93	0.00 ÷ 0.71	19.52÷ 23.60	11.59 ÷ 28.70	0.17 ÷ 0.84	7.50 ÷ 17.30	2.50 ÷ 14.28	0.00 ÷ 0.28	Different pipes, total 129 analyzes
Claster group 4**	Cpx	51.37 ÷ 56.57	0.00 ÷ 1.04	3.43 ÷ 12.91	1.56 ÷ 9.83	0.00 ÷ 0.45	7.92 ÷ 17.30	10.00 ÷ 20.30	2.81 ÷ 7.29	Different pipes, total 176 analyzes

* Data from [9].
**Data from [3]. Claster group №4 of clinopyroxene from: Mg, Mg-Fe, Al ± diamond-bearing eclogites.
***Used symbols: Grt – garnet, Cpx – clinopyroxene, Alm – almandine, Prp – pyrope, Grs – grossular, Jd – jadeite, Hd – hedenbergite, Di – diopside, L – melt.

Previous experiments in the eclogitic system [4] gave a possibility to specify the phase fields in the pseudo-binary system garnet-clinopyroxene, as well as to define the nature of the garnet-clinopyroxene equilibrium. The present experiment was performed using Pt-Rh and Pt ampoules, which were preliminarily equipped with tungsten foil of 0.02 mm in thickness. This foil was applied in order to prevent from the partial absorption of iron from a melt by the PtRh-alloy. As a result, during the partial oxidation of tungsten the buffer couple W/WO_2 was formed, which conditioned the stability of ferrous iron [5]. Pressure and temperature were regulated with an accuracy of ± 0.1 GPa and ± 10°C, respectively, in the range of 1500 – 1700°C, and ± 20°C at higher temperature. After runs samples were studied by electron microprobe CamScan equipped with EDS Link AN 10/85S (Department of Petrology, analysts E.V. Guseva and N.N. Korotaeva) and WDS Camebax (IEM RAS, analyst A.N. Nekrasov).

Run conditions and their results are shown in table 2. A phase diargam for the clinopyroxene-garnet system at 7 GPa is demonstrated in fig. 1. The garnet - omphacite join is an internal polythernmal cross section of the system (almandine + grossular) – (pyrope + grossular) – clinopyroxene (fig. 4), whose liquidus equilibria are very important for petrolgical constraints.

Table 2. Conditions and results of experiments in the pseudobinary system garnet-clinopyroxene at 7,0 GPa.

#	Grt-Cpx	ımpoule	t, min	T, C	phases	components, mol.%						
						SiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O
begin. comp.					Grt	37,20	21,60	25,00	0,60	4,00	11,50	
					Cpx	54,60	8,80	7,30	0,00	8,30	14,70	6,20
722	50-50	PtRh	60	1200	e.a.* Cpx+Grt							
					Cpx	56,26	12,35	9,96	0,03	4,34	8,12	8,83
					Cpx	55,41	12,00	7,31	0,03	6,63	11,34	7,17
					Grt	38,02	20,75	22,08	0,71	6,49	11,96	
					Grt	39,24	20,81	24,16	0,47	4,55	10,42	
748	50-50	PtRh	155	1300	e.a. Cpx+Grt							
					Cpx	54,15	16,77	4,75	0,14	6,87	11,67	5,55
					Grt	40,98	22,66	12,66	0,80	10,88	12,03	
719	50-50	PtRh	60	1400	e.a. Cpx+Grt							
					Cpx	55,65	11,13	10,66	0,01	5,34	10,07	7,11
					Cpx	55,70	12,35	8,02	0,02	5,71	11,28	6,81
					Cpx	55,08	11,96	7,13	0,17	6,69	11,88	7,05
					Grt	40,58	19,95	19,04	0,46	8,87	11,01	
					Grt	38,98	20,31	23,51	0,00	6,17	11,03	
908	50-50	PtRh, W	50	1450	e.a. Cpx+Grt+L							
					L	50,74	15,94	13,61	0,00	6,55	10,58	2,60
					Grt	40,71	21,91	20,27	0,56	6,81	9,74	
					Grt	41,21	22,07	18,34	0,46	8,66	9,26	
					Cpx	55,22	14,09	6,74	0,00	6,85	10,08	7,03
					Cpx	55,14	15,55	5,83	0,00	6,77	9,49	7,22
916	50-50	PtRh, W	10	1500	e.a. Cpx+Grt+L							
					L(calc.)**	47,42	15,70	16,68	0,31	6,35	13,53	3,20
					Grt	40,55	21,63	23,24	0,39	5,39	8,80	
					Grt	39,67	21,41	23,07	0,44	6,25	9,15	
					Grt	39,87	21,12	22,38	0,27	7,01	9,35	
					Cpx	55,74	11,70	7,41	0,23	6,86	11,30	6,75
					Cpx	55,69	10,21	7,06	0,00	8,21	12,00	6,84
909	50-50	PtRh, W	75	1550	e.a. L							
					L(calc.)	47,42	15,70	16,68	0,31	6,35	13,53	3,20
					L	41,46	12,19	14,20	0,59	10,52	14,01	7,04
					L	45,27	14,70	17,93	0,43	5,04	14,49	2,13
					L	50,74	14,41	12,23	0,00	4,18	16,67	1,77

*e.a.- assosiacion of equilibria in the definite field of phase diagram; **composition of melt calculated for cotectic temperature (1500C).

Firstly, consider the phase relations in the pseudo-binary system omphacite – garnet (fig. 1). Its subsolidus involves two fields: (1) Cpx_{ss} and (2) Cpx_{ss} + Grt_{ss}. Cinopyroxene is a solid solution of diopside, hedenbergite, jadeite and Ca-Eskola and low Ca-Tschermak molecules. A boundary between mono-phase and binary fields is a curve of thermal dependence for composition of clinopyroxene solid solution. Melting of the binary assemblage omphacite + garnet starts at 1400 ^{o}C and is eutectic. A presence of the Cpx+Grt+L field corresponds to the monovariant cotectic in the ternary system. As temperature is drown higher, compositions of all cotectic phases change. In samples corresponding to the cotectic region, glass was homogeneous, without dendritic textures. Glasses in the samples 910 and 916 were not analyzed, whereas their compositions were estimated from the bulk composition in the point of complete melting at 1500 ^{o}C ($Cpx_{50}Grt_{50}$, mol. %), that is the minimum temperature of liquidus. Clinopyroxene and garnet are liquidus phases. As a rule, melts were homogeneously quenched. Locally, dendrite-like quenching textures form (fig. 2). Fig.3 shows a sample of ternary cotectic assemblage Cpx+Grt+L, whose compositions are presented in Table 2. Slight increase of pyrope component in garnet occurs with the increasing of temperature in subsolidus and the decrease of temperature in liquidus.

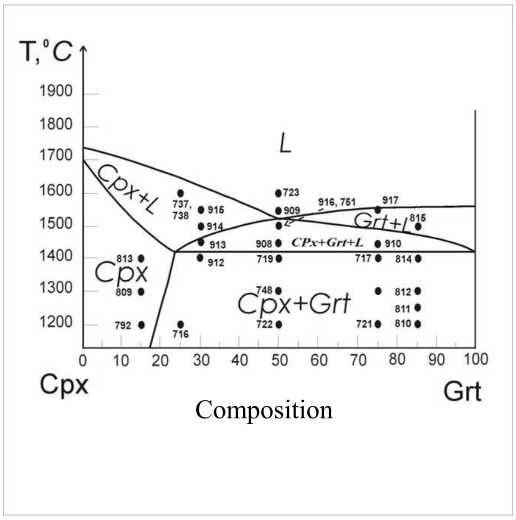

Fig.1. Diagram of pseudobinary system on clinopyroxene-garnet join at 7,0 GPa.

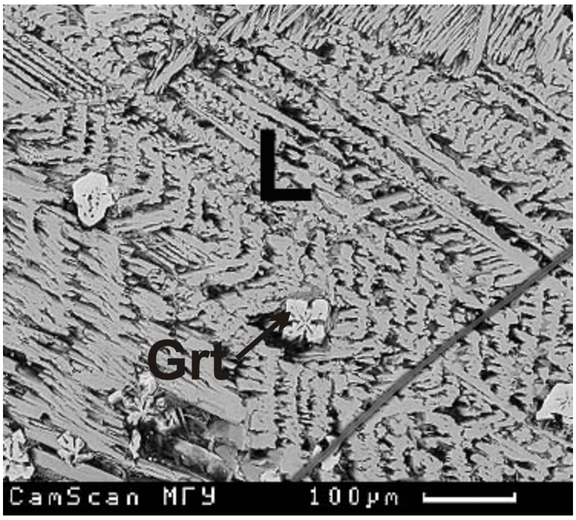

Fig 2. Dendritic quenching textures of phases. ($Cpx_{50}Grt_{50}$, # 723, 7 ГПа, 1600 ^{o}C, 30 min).

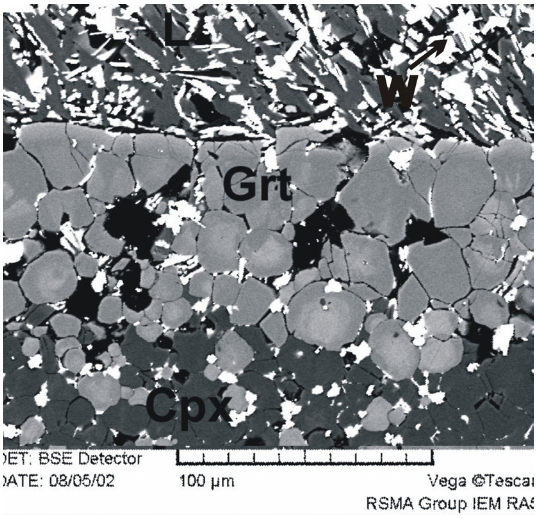

Fig.3. Equilibrium cotectic assemblege clinopyroxene+garnet+L (# 908, 7 GPa, 1450 ^{o}C, 50 min).

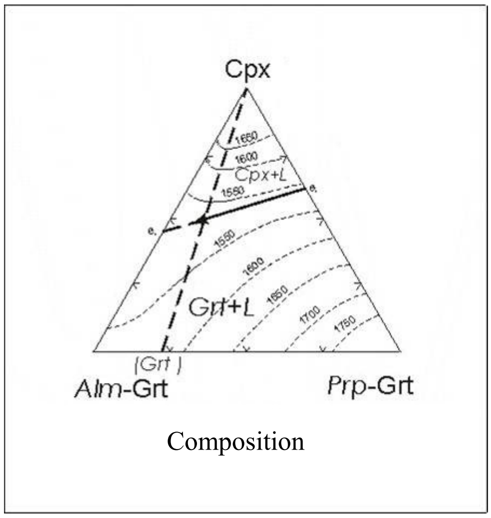

Fig.4. Liquidus surfice of the ternary eclogitic system clinopyroxene-garnet at 7 GPa; studied pseudobinary join (fig.1) is shown by thick dashed line; figures at isotherms (thin dashed lines) correspond to temperatures in ^{o}C.

Fig. 4 shows the liquidus surface of pseudo-ternary system (almandine + grossular) – (pyrope + grossular) – omphacite at 7.0 GPa, that is constructed using the above experimental data for the pseudo-binary join omphacite – garnet (dashed-dotted line in fig. 4). Temperatures of melting of the boundary phases was estimated using the known data on end-members of the Cpx_{ss} и Grt_{ss} solid solutions. The system almandine – pyrope is studied previously at 6.5 GPa [6]. It is characterized by wide solubility of components both in solids and liquids. Low concentrations of grossular do not significantly change this pattern, since grossular is an end-member of the garnet solid solution. The system almandine(±grossular) – clinopyroxene. Temperature 1450 ^{o}C at $Cpx_{40}Alm_{60}$ of the eutectic is estimated from special runs in the system almandine-clinopyroxene. These data allowed reconstruction of the mono-variant cotectic in the ternary system. The join pyrope-clinopyroxene is the third boundary system. The temperature (1520 ^{o}C) and composition of eutectic in this join were evaluated from published data on diopside, pyrope, and jadeite [7,8].

According to the ternary diagram there is no reason for the formation of inverse Mg/Fe zonation in garnets at constant pressure. Since the composition of garnet is controlled by the boundary pyrope-almandine join, the thermal evolution can result in direct zonation only, i.e. Mg-number of garnet must decrease toward rims of individual grains. The inverse zonation, shown in [6], could appear as a result of abrupt decompression.

Problem of diamond formation in eclogites cannot be solved in silicate-carbon system only. Preliminary experiments on eclogite-carbonatite-sulfide-carbon system at 6-8 GPa established immiscibility of silicate and sulfide melts in UHP environments and demonstrated leading role of carbonatite-silicate-carbon and sulfide-carbon melts in diamond formation in the Earth's mantle.

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