

Phase equilibria (transformations) under high P-T parameters

#Bulatov V.K.¹, Girnis A.V.², and Ryabchikov I.D.² Na Partitioning between clinopyroxene and orthopyroxene at high pressure

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key words [clinopyroxene orthopyroxene partitioning experiment]

Compositions of clinopyroxene and orthopyroxene have been studied experimentally at 20-50 kbar and 1100-1500°C in the systems Na₂O-CaO-MgO-Al₂O₃-SiO₂ and Na₂O-CaO-MgO-Al₂O₃-SiO₂-Cr₂O₃ with variable Na/Ca ratio in the presence of carbonate-silicate melts. Oxide mixtures or synthetic end-members of pyroxene solid solutions were used as starting materials. Carbon dioxide was introduced with sodium carbonate. The material was loaded into platinum capsules, which were then welded. Experiments were carried out on piston cylinder and belt apparatuses using solid cell assemblies of natural polycrystalline CaF₂. The duration of experiments varied from one to fourteen days. The experimental products were studied on a JEOL 8900 electron microprobe. All the investigations were performed at the Institute of Mineralogy, J.-W. Goethe University, Frankfurt am Main, Germany.

The content of Na₂O varied considerably in both clinopyroxene (from 0.1 to 6.0 wt %) and orthopyroxene (from 0 to 1 wt %). The investigation of concentration profiles of contacting clino- and orthopyroxenes on the basis of the reversal experiment approach allowed us to conclude that the partition coefficient of Na₂O between clinopyroxene and orthopyroxene was sensitive to temperature and changed from about 2 at 1500°C to 7.5 at 1100°C. No pressure or compositional dependence of the partition coefficient was established.

The results can be used at the analysis of physicochemical conditions of natural mineral formation. For instance, coexisting inclusions of clinopyroxene and orthopyroxene in diamond crystals sometimes yield unusually high apparent partition coefficient of Na₂O, up to 40 [1-4]. Such a discrepancy can indicate that these minerals were not in equilibrium and were trapped under

different physicochemical conditions by a single diamond crystal. This suggests a complicated crystallization history of some diamonds accompanied by changes in physicochemical conditions and, probably, gain or loss of alkali-rich material, i.e., mantle metasomatism.

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Yakovlev O.I.¹ Dikov Yu.P.², Gerasimov M.V.³ Experimental data on impact-vapor differentiation

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The impact experiments (5.0-6.5 km/s) which were carried out using the two stage hypervelocity launch facility (the experimental technique is described in [1]) showed that the impact vaporization (IMPVAP) is selective, that is the impact melt and vapor have different compositions. Some typical data of the impact vapor (≡ condensate) and initial rock compositions are presented in the **Table**.

This work has been supported by the RFBR

wt. %	Ultramafic target		Mafic target		Acid target		
	harzburgite	condensate	basalt	condensate	granite	condensate	
SiO ₂	45.2	52.6	51.8	61.7	70.2	50.8	
Al ₂ O ₃	1.7	2.7	15.4	16.7	16.0	19.2	
FeO	7.8	9.6	9.9	1.7	2.3	1.1	
MgO	43.6	25.1	8.2	3.7			
CaO	1.5	4.3	11.7	8.2	1.1	3.5	
Na ₂ O	0.1	3.8(?)	2.8	7.0	3.8	22.7	
K ₂ O	0.1	1.9(?)	0.2	1.0	6.6	2.7	

At least 5 conclusions follow from the experiments: 1) The IMPVAP of ultramafic rocks tends to more SiO₂ and less

MgO contents in the vapor. A comparison between target rocks and vapors shows that the SiO₂/MgO ratio is as a

rule 1.5-2 times higher in a vapor phase; 2) The IMPVAP of a basalt gives rise to more silica- and alkalis-rich vapors. The total apobasaltic vapor compositions are formally similar to granodiorite ones; 3) The IMPVAP of acid rocks tends to silica decrease in the vapor. The total apogranitic vapor compositions are formally similar to nepheline-syenite ones; 4) The systematic increase of a number low volatile lithophile elements (U,Th,Hf,REE) in the vapor phase was detected; 5) It was measured and estimated that at the impact velocity ~6 km/s the total mass of silicate vapor reached amounts comparable to ~10% of the projectile mass.

The behaviour of the elements during IMPVAP does not obey the classic row of volatility. This is the result of specific cluster mechanism of IMPVAP under the conditions of impulse high temperature heating. Molecular cluster can join together elements with different individual volatility that is responsible for joint vaporization, transport and condensation. The main detected clusters are of enstatite (Mg:Si=1:1) [2] and nepheline (Na:Al:Si=1:1:1) [3] type.

If we take into account that all the planet mass is just a sum of former projectiles, the portion of the planet material which was involved in IMPVAP and possible differentiation is $\geq 10\%$. Hence, the obtained data permit to suggest that the impact protoEarth accretion was accompanied by profound changes of the planetary substance as a result of IMPVAP and later vapor condensation. Through all accretionary time the main petrochemical tendency of the surface rocks was an increase of silica contents due to the cyclic impact vaporization-condensation process and increasingly more admixture of condensate materials into surface regolith. It is not difficult to imagine that the impact differentiation could lead to the formation of primary basalt crust and even zones with primitive granitic-like rocks.

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Khicsina N.R.¹, Wirth R.,² Andrut M.³, Ukhanov A.V.¹ OH-bearing crystalline microinclusions in mantle olivine: the first finding of the "10A-Phase" (dense hydrous magnesian silicate) in nature

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Olivine is a nominally unhydrous mineral; however FTIR data give an evidence that olivines contain some amounts of water (or hydroxyl) [1,2]. The highest water content is found to be $^{97}\text{H}/^{106}\text{Si}$ in olivines from kimberlites [1,2]. A mode of H incorporation into olivines as either intrinsic or extrinsic is discussed up to date. OH-

absorption bands in IR-spectra of olivines can be referred to either OH incorporated into olivine structure (intrinsic OH) or to inclusions of hydrous minerals in olivine such as HMS - hydrous magnesian silicates (extrinsic OH). The interpretation of an IR spectrum can be unambiguous only if both IR spectroscopic measurements and TEM examination of one and the same sample are combined. A modern transmission electron microscopy (TEM) allows to obtain local chemical and crystal structure information (including qualitative determination of hydroxyl and water [3]) from such a small square of the sample as 4 nm.

It is important to know how H is incorporated in olivine to understand the behaviour of water in the mantle, its transport and storage at great depths of the Earth. During the last years many high-pressure - high-temperature experiments were carried out to synthesize so called DHMS - dense hydrous magnesian silicates. DHMS-phases are considered to be possible mineral phases in the upper mantle [4], however, except humite-group minerals no other DHMS-phases were found in natural material till now.

FTIR and TEM examination of olivines from two mantle nodules (pipes "Udachnaya" and "Obnazennaya", Yakutiya) was carried out.

OH-absorption bands are observed in the IR spectra. TEM investigation show that olivines under study contain OH-bearing crystalline inclusions of different morphology.

(1) "Large" inclusions (up to several hundred nm in size) are isolated and incoherent. They are composed by hydrous magnesian silicates (HMS). HMS such as talc+serpentine and talc+"10A-Phase" intergrowth were identified. "10A-Phase" $\text{Mg}_3\text{Si}_4(\text{OH})_2n\text{H}_2\text{O}$ is known as the DHMS phase experimentally synthesized at high pressures (above 32 kb) and temperatures 300-700 C [5]. This phase, considered as a possible mineral of the mantle, was not found in nature till now. Our observations of "10A-Phase" as nanometer-scale inclusions in mantle olivines is the first finding of "10A-Phase" in nature.

(2) "Small" hydroxyle-bearing inclusions (up to several tens nm in size) are coherent; they are observed along either dislocations or planar features in the olivine grains. The inclusions are depleted in Mg compared to the olivine matrix. It was found that the inclusions have the olivine-like crystal structure with superperiodicity along certain directions. The superperiodicity is interpreted as resulted from the ordered OH-bearing point defects associated with Mg-vacancies in the olivine structure. We consider the "small" inclusions as hydrous olivine with cation-deficient crystal structure. It should be mentioned that although the "small" inclusions have olivine-like crystal structure, they have a stoichiometry of dense hydrous magnesian silicates, namely wadsleyite $\text{Mg}_{1.75}\text{SiH}_{0.5}\text{O}_4$ [6] and phase "D" $\text{Mg}(\text{OH})_2\text{SiO}_2$ [7]. Therefore we can consider the "small" inclusions as intermediate metastable form of DHMS exsolution from the olivine structure.

Thus, two different modes of OH occurrence in olivine are estimated, intrinsic ("small" inclusions) and extrinsic ("large" inclusions).

The origin of the "large" and "small" inclusions seems to be different. The "small" inclusions are evidently exsolved from olivine by a solid state reaction at the post-crystallization stage. The origin of "large" incusions is not

clear. We supposed that the “large” inclusions represent the recrystallized fluid (or melt) inclusions. 10A-Phase is considered to be a primary crystalline phase of inclusions substituted later by talc and serpentine during the decompression and cooling process.

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Reutskii V.N. and Borzdov Yu.M. Carbon isotope fractionation in the model system Fe-Ni-C at high PT-parameters

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key words: [carbon, isotopes, fractionation, high temperatures and pressures, diamond, graphite]

Carbon forms numerous compounds in the wide range of thermodynamic parameters. Partitioning of carbon isotopes at normal Pt parameters is studied experimentally and theoretically relatively well. Theoretical calculation of the fractionation of carbon isotopes at high temperatures and pressures are weakly maintained by experimental data. Since this problem is one of the most important in the isotope geochemistry related to the problems of (1) diamond formation, (2) early evolution of the Earth substance, (3) origin of meteoritic carbon, new experimental data on the behavior of carbon isotopes at high pressures and temperatures are very actual. One way to solve the problem is to study the carbon fractionation in model systems, which are used for growth of artificial diamonds.

Metal-carbon systems, which are a particular case of the system carbon-solvent, are most investigated diamond-forming systems. First studies on the isotope fractionation at durable recrystallization of carbon in the system Fe-Ni-C allowed to find, that isotope partitioning between carbon phases could be very significant, up to 4.5‰ (see Table 1).

In order to study peculiarities of the behavior of carbon isotopes during diamond crystallization, a series of runs on diamond growth was performed using the method of thermal gradient [2]. The press-free multi-anvil split-sphere apparatus was applied for diamond growth. A metal of composition 70% Ni-30% Fe was used as a solvent. Graphite MG-1 was used as a carbon source. In order to preserve a gaseous phase, a reaction volume was hermetically sealed into a platinum ampoule. The metal and graphite were isolated from platinum by MgO-bush

and ZrO-washers. The ampoule was isolated from a heater by MgO-bush. The experiments were conducted at $T=1400^{\circ}\text{C}$ and $P=5.5\text{-}6.0$ GPa. Duration of each run was 40 hours. Chromatographic analysis of a gas emitted from one ampoule showed, that it contained CH_4 exclusively. The gas was analyzed in the laboratory of the Institute of Mineralogy and Petrology of the Siberian Branch of RAS with using the well-known procedure [3]. In order to study an isotopic composition of the gaseous constituent, the ampoule was cut in the special assembly under the conditions of high vacuum. The gas escaped in 24 hours was oxidized to CO_2 and sealed into glass ampoule. Addition of CO_2 into the system did not exceed 0.005 cm^3 per day, that is appreciably lower than a quantity of the produced gas (0.1 cm^3). The following phases were observed after dissolution of the metal in acids: (1) remnants of carbon source, transformed in diamond aggregate; (2) fine-grained carbon (FGC); (3) diamond crystals. Table 1 shows the values of $\delta^{13}\text{C}$ of the phases. Carbon dissolved in the Pt ampoule was disregarded. An isotopic analysis was performed using the method and apparatus described earlier [4].

Table. . Carbon isotope composition of the produced phases.

Sample	$\delta^{13}\text{C}$, ‰ PDB	
	1 [1]	2
Carbon source	-28,0±0,2	-27,2±0,2
Gas component	?	-30,3±1,0
FCC	-31,3±0,3	-30,5±0,2
Graphite crystals	-26,6±0,2	----
Diamond crystals	-28,1±0,2	-27,1±0,2
Initial graphite MG-1	-27,8 ±0,4	

According to the obtained isotopic data, all studied compounds can be divided into two groups. The first group includes carbon compounds relatively enriched in ^{13}C (remnants of the carbon source, diamonds, and graphite). Their isotopic composition is very close to that of the starting graphite MG-1. The compounds of the second group (gaseous phase and FGC) are appreciably poor in ^{13}C in comparison to the initial graphite (Table 1).

A comparison of the obtained data with the published results for the same system [1] shows a definite relationship between a number of carbon phases participating in reactions and an absolute value of fractionation of carbon isotopes in the system. In the presence of 6 phases, the isotope fractionation reached for 4.5‰. The absence of one phase led to the change of the value down to 3.4‰ (Table 1).

Consider some processes, taking place in the volume restricted by the Pt-ampoule. Transformation of graphite source into polycrystalline diamond aggregate (catalytic synthesis) occurs after reaching PT parameters of the experiments. The presence of H_2 and O_2 additions causes formation of Mg-wüstite (interaction of the metal melt with MgO-bush [2]) and CH_4 equilibrated with the Fe/FeO buffer. The thermal gradient causes a dissolution of the source by the metal melt and carbon transportation towards the crystallization zone. Depending on PT conditions, graphite or diamond crystallizes in this zone.

It was experimentally demonstrated, that the catalytic synthesis of diamond from graphite and carbon dissolution was not accompanied by notable fractionation [5, 6]. Methane formation is known to cause an enrichment of CH₄ in ¹³C [7]. Crystallization from the melt under conditions close to the isotopic equilibrium would be accompanied by the enrichment of the solid phase in ¹³C [7].

According to our calculations, the coefficient of isotope fractionation (α) between FGC and diamond was 0.9965. This value was constant in all the experiments. The coefficient α for the FGC-graphite pair was 0.9952. Reproduction of the coefficient from one experiment to another can be considered as an evidence of the regular isotope fractionation between carbon dissolved in the metal melt and growing solid phases. It is well known, that dissipated carbon from igneous rocks, as well as from stony and iron meteorites, is enriched in ¹²C [8]. It is in agreement with the experimental results. It was proposed earlier, that the dissipated carbon could be represented by atomically dissipated zero-valent forms. That corresponds to its lighter isotopic composition (β -factor of such form is 1) [9]. The β -factor for diamond at T=1400°C and P=6 GPa is 1.0083. Calculation of the β -factor for carbon dissolved in the metal melt using the obtained data shows the value 1.0048. Thus, in this case, it is not the atomically dissipated zero-valent form.

Natural systems are more complex, and some their parameters are not considered or artificially fixed in the experiment. However, the obtained data allow to suggest a significant isotope fractionation during multiphase carbon crystallization in the diamond stability region. It is reflected in $\delta^{13}\text{C}$ value of diamond.

The following major conclusions can be formulated on the basis of the experiments:

(1) the range of fractionation of carbon isotopes in the system Fe-Ni-C in the diamond stability region depends on a number of carbon phases participating in reactions;

(2) in the case of carbon crystallization from the Fe-Ni melt, crystalline phases are enriched in ¹³C, whereas the melt and equilibrium methane are enriched in ¹²C

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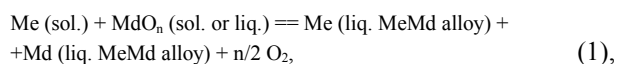
Borisov A. Anomalous behavior of noble metals under reducing conditions: theoretical and experimental investigations and application to the geochemical and cosmochemical problems.

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key words [noble metals thermodynamics oxygen fugacity refractory metal nuggets Ca-Al-rich inclusions carbonaceous chondrites solar nebula]

It is well known that noble metals at high temperatures can easily react with certain substances (sulfur, selenium, tellurium, phosphorus, arsenic, antimony, molten lead, zinc, tin, bismuth, etc.). At low oxygen fugacity noble metals can react not only with such “exotic” substances, but even with silica, the main component of silicate melts. For example, Borisov with coworkers, during experiments performed by a loop technique to determine Pd and Au solubilities in silicate melts [1, 2] revealed that slightly below IW buffer conditions all experiments failed because of the destruction of the Pd- and PdAu loops. The reason was Pd alloying with silica of the melt [1]. Indeed, the eutectic temperature in Pd-Si binary is only 760°C and the eutectic composition is about 16 at.% Si. It is obvious, that at “normal working” temperatures (1300°C or higher) a much smaller fraction of silicon would be enough to destroy a capsule or a loop.

In the following discussion I will designate a noble metal as *metal* (Me) and the alloying partner, that is usually stable as oxide under redox conditions at which the noble metal is stable in metallic state, as *metalloid* (Md). The latter could be Si, Ge, As, Bi and other nonmetals, but also Fe, Co, Ni or other metals. By definition, the Me/Md oxide equilibrium line in the T-fO₂ field lies in a much more oxidizing region, than Md/Md oxide one. The reaction of Me with Md oxide can be described as:



with the reaction constant:

$$K_1 = (f\text{O}_2)^{n/2} \times a_{\text{Me}}^{\text{alloy}} \times a_{\text{Md}}^{\text{alloy}} / a_{\text{MdO}_n} \times a_{\text{Me}}, \quad (2)$$

where a_i is the activity of the component i . For pure Me the equation (2) can be rewritten as:

$$\log f\text{O}_2 = 2/n \log(K_1 \times a_{\text{MdO}_n}) + 2/n \log(a_{\text{Me}}^{\text{alloy}} \times a_{\text{Md}}^{\text{alloy}}), \quad (3)$$

At constant activity of Md oxide, the oxygen fugacity, at which solid Me converts into liquid MeMd alloy is a strong function of temperature. There are two ways to

construct such T-fO₂ diagrams: by calculation, if thermodynamic data are known [3] or by experiments [4].

On Fig. 1 I showed the calculated melting diagram of Pt-Fe alloy in silicate melt with constant concentration (10 mol. %) of FeO (see [3] for details). Trend A-B clearly demonstrates that even at decreasing temperature one could imagine the situation with melting of an initially solid alloy. It could be a spike of very reducing H₂-containing deep fluid, or quick decompression of carbon-containing melts or any other process with temporal sharp decrease of fO₂. I would propose a term “*redox melting*” to emphasize the process, when it is not temperature but oxygen fugacity, which is responsible for solid phase melting. If these Pt-Fe alloy droplets are small enough, they will easily reequilibrate after fO₂ “normalization” to have a composition relevant to T-fO₂ conditions in point B (see Fig. 1). An attempt to reconstruct the maximum temperature for such alloy composition by simply using solidus of Pt-Fe binary diagram will thus result in ironically high overestimation.

On Fig. 2 I gave an example of the construction of Pd-Si melting diagram by experiment [4]. The experiments were conducted in one-atmosphere furnace with controlled fO₂ (±0.1 log unit). Short pieces of Pd wire (99.9% purity, 0.025 mm in diameter) were placed in small quartz crucible filled with SiO₂ powder (99.99% purity). This silica was first heated for about one hour at high temperature to be converted into cristobalite. The crucible was suspended in the hot zone of the furnace at given temperature and fO₂ for 30-60 minutes. The reaction of Pd with silica (melting of wire) was determined visually after removing the crucible from the furnace. At 1300°C, for example, initially solid Pd react with pure solid SiO₂ and melts at fO₂ = 10^{-12.2} atm, which is only 1.6 log unit below IW buffer. Remember, 1300°C is about 250°C below the melting point of pure Pd!

Refractory metal nuggets in Ca-Al rich inclusions of carbonaceous chondrites are known to contain practically no Pd [5, 6] and this fact I would explain the next way. By recalculating experimental data it is possible to show that an alloy with a few ppm of Pd may react with a silicate phase at fO₂ assumed for a canonical solar nebula. It does not exactly mean (but it is possible) that Pd would be melted out from alloy *after* condensation of the first silicate phase. It rather means that primary RMN composition must not be calculated without taking into account silicides of PGE (as solid, liquid or vapor phase). Indeed, the experiments on equilibrium of model PGE alloys with silicate melt of CAI composition [7] demonstrated that not only Pd-Si, but perhaps, even Pt-Si alloys should be normal phases at very reducing conditions.

As it was pointed out above, oxides of some other nonmetals (As, Sb, Bi, Ge, etc.) react much more easily with PGE than silica. Borisov and Palme [8] suggested such reactions to be the main reason for the formation of submicron sized nuggets (so called “nugget problem” in experimental petrology) in melts, equilibrated with noble metals. El Goresy et al. [9] demonstrated alloying of Zn, Ga, Ge, Sn and As with noble metals in “Fremdlinge”, the complex assemblages of metal grains and sulfides, found in CAI along with RMNs. So, not only silicides, but also arsenides, bismuthides, etc. should be involved in

calculations of condensate composition at fO₂ as low as usually assumed for the solar nebula.

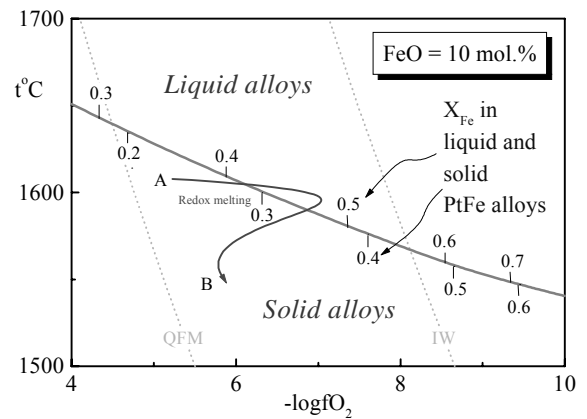


Fig.1. A melting diagram of Pt-Fe binary alloys in equilibrium with basaltic melt (10 % mol. FeO).

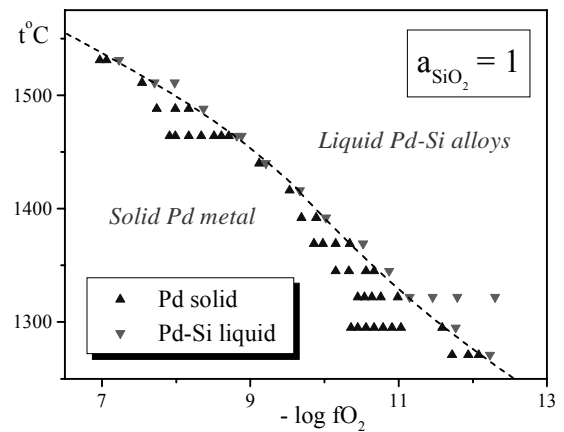


Fig. 2. A melting curve of pure Pd metal in pure silica

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Surkov N.V. Mineralogical composition of deep-seated paragenesis and phase diagrams of model alumina-silica systems..

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The problems of genesis of deep rocks and their classifications have a common basis. The solution of these problems needs experimental researches. The system CaO-MgO-Al₂O₃-SiO₂ is the most popular model for the experimental researches of the genesis of deep rocks. The system was chosen as an experimental model because its composition is fairly similar to deep paragenesis.

It is possible to arbitrarily divide the compositions of the system CaO-MgO-Al₂O₃-SiO₂ into three parts of compositions: forsterite, quartz and alumina. The forsterite part of the system CaO-MgO-Al₂O₃-SiO₂ is of the greatest petrological interest [1]. A basic component of this section of the phase diagram is a nonvariant equilibrium (Cpx, Opx, Gr, Fo, An, Sp). The paths of three monovariant reactions go out of this equilibrium point: An+Fo=Cpx+Opx+Sp, Opx+An+Sp=Cpx+Gr, Sp+Opx+Cpx=Gr+Fo, [1, 2, 3].

In the region of low pressure the association An+Fo is stable. Its phase composition corresponds to the paragenesis of low pressure facies rocks of basic and ultrabasic composition (gabbro type, etc.). At higher pressure from the reaction An+Fo=Cpx+Opx+Sp up to the reaction Sp+Opx+Cpx=Gr+Fo, the associations Sp+Opx+Cpx+Fo, Sp+Opx+Cpx+An are stable. In phase composition they correspond to the paragenesis of spinel lherzolite and spinel-feldspatoid pyroxenite. The formation of the pair clinopyroxene garnet becomes possible at pressure above the reaction Opx+An+Sp=Cpx+Gr and a series of clinopyroxene-garnet associations appropriate to the deep paragenesis becomes steady. Let us mark, that there is no direct transition of gabbro into eclogite. Of special interest is the association Opx+Cpx+Gr. In the system CaO-MgO-Al₂O₃-SiO₂ it is divariant. Either spinel, forsterite, quartz (coesite) or kyanite (sillimanite) can coexist with these three phases. Each four phases form extensive volume of compositions, which can be compared to some types of deep paragenesis. So the association Opx+Cpx+Gr+Sp corresponds to spinel-garnet pyroxenites, no analogs of natural paragenesis have been found for the associations Opx+Cpx+Gr+Qz(Co) and Opx+Cpx+Gr+Ky, and the association Opx+Cpx+Gr+Fo corresponds to the paragenesis of garnet lherzolites, and different types of garnet pyroxenites. The latter paragenesis are conventionally divided according to the amount of minerals, in particular olivine. However, this division makes no physical-chemical sense. It is one type of rocks. Calcium content in garnet which remains practically constant throughout the whole stability interval and is 12-16 mol. % of grossular component is a typomorphic feature of this type of paragenesis [4].

At pressure above the path of the reaction Sp+Opx+Cpx=Gr+Fo the divariant association Sp+Cpx+Gr+Fo is stable, it can be considered as a simple analog of the paragenesis of garnet verlite. The peculiarity of this association is the growth of the content of grossularite component in garnet with pressure [3], which corresponds to the specific of garnet composition in the paragenesis of garnet verlites.

In the liquidus of the forsterite part of the system CaO-MgO-Al₂O₃-SiO₂ two series of monovariant eutectic melting reactions are present. The first series is described by the reactions: L=Fo+Opx+Cpx+An, L=Cpx+Opx+An+Sp, L=Cpx+Gr+An+Sp and L=Cpx+Gr+An+Cor, where the liquid has essentially silicon and aluminum composition. The second series of eutectic reactions is described by one reaction: L=Fo+Opx+Cpx+Gr, whose path leaves upwards on pressure from the singular point (L, Fo, Opx, Cpx, Gr). The presence of this eutectics excludes the possibility of differentiation of liquids through the plane Mg₂Si₂O₆-Ca₂Si₂O₆-Al₂O₃ for the compositions containing normative forsterite. This eutectics is of fundamental character, and keeps the influence with thickening composition with additional components, such as FeO, Na₂O and etc.

In quartz area the phase mutual relations are investigated less explicitly. It is established, that at a pressure of 15 kbar and temperature about 900 °C there exists the nonvariant point (An, Opx, Ky, Gr, Qz, Cpx) [5, 6]. The paths of some monovariant reactions: An+Opx+Ky=Gr+Qz, An+Opx=Cpx+Gr+Qz, Qz+Gr+An=Cpx+Ky and Gr+Qz=Opx+Cpx+Ky go out of this point.

To establish the phase relations in the liquidus area a series of experiments in the join anortite-enstatite has been carried out. Based on the results of this experiments the phase diagram of this join was plotted at 16 kar. The melting in this join proceeds by the reaction An+Opx=Cpx+Gr+L [7].

The stability field of the association Gr+Qz in solidus is limited by the reactions An+Opx+Ky=Gr+Qz and Gr+Qz=Opx+Cpx+Ky. That is to say, coesite(quartz) eclogites represent a high-temperature paragenesis existing at moderate pressures. At high pressures it is substituted by kyanite eclogites.

At the pressure higher than 30-40 kbar no essential changes in phase relations of the system CaO-MgO-Al₂O₃-SiO₂ were observed. The basic changes are connected to the stability of solid solutions. As a result of the formation of a continuous series of garnet solid solutions in the join pyrope-grossular there occurs the transformation of the plane enstatite-wollastonite-alumina into autonomous three component system, which divides the volume of compositions of the system CaO-MgO-Al₂O₃-SiO₂ into two independent systems. With the further increase of pressure (up to 100 kbar) solid solutions of orthopyroxenes and clinopyroxenes, apparently, are reduced almost up to pure enstatite and diopside. But the area of compositions of solid solutions of garnets are extended, because the content of a majorite component increases [8].

Thus, the phase relations in the model system CaO-MgO-Al₂O₃-SiO₂ as compared to the known natural deep paragenesis allow to order essential indications describing deep rocks. The phase volumes enable to classify deep paragenesis without coming in conflict with the possible genesis of these rocks. The knowledge of phase relations in the model system allows to select paragenetic indications for deep paragenesis on a physical-chemical basis, instead of a casual set of empirical material.

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