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<sup>2</sup> Institute of Experimental Mineralogy RAS, Russia, Chernogolovka (t-shchekina@mail.ru; aleks7975@yandex.ru, yanaalf@yandex.ru, engramen@geol.msu.ru, kotelnik@iem.ac.ru, nzinov@mail.ru, andrewbychkov@rambler.ru, akhm@iem.ac.ru ).

**Abstract.** The distribution of rare-earth elements, Y, Sc and Li between aluminosilicate (L) and aluminofluoride (LF) melts in the granite system with limiting fluorine concentrations at 700 and 800°C, 1 and 2 kbar pressure was studied. The water content was from 2.5 to 50 wt.%. It is shown that all rare-earth elements, Y, Sc and Li are distributed in favor of the aluminofluoride salt melt, regardless of the experiment conditions. However, the partition coefficients of the elements  $Kd_{REE}^{(LF/L)}$  between these phases depend on the pressure, temperature and water content in the system. It is shown for the first time that an increase in pressure from 1 to 2 kbar at T = 700-800°C in the studied system causes a significant decrease in the  $Kd_{REE}^{(LF/L)}$ . An increase in the water concentration in the system usually causes an increase in  $Kd_{REE}^{(LF/L)}$ .

**Keywords:** distribution; partition; rare-earth elements; yttrium; scandium; lithium; aluminosilicate melt; aluminofluoride melt; liquid immiscibility process; pressure effect.

The aim of this work is to study the distribution of rare earth elements, scandium, yttrium and lithium among aluminosilicate (L) and aluminofluoride (LF) model melts in the granite system Si-Al-Na-K-Li-F-O-H with limiting concentrations of fluoride at the temperature of 700 and 800 °C, pressures of 1 and 2 kbar and the water content is from 2.5 to 50 wt.%. Two series of experiments with the same initial composition of the solid charge (table. 1): 1 series of experiments at T=700°C, P=1 and 2 kbar and different water content (5, 10, 30, 50 wt. %) and 2 series at T=800 °C and P=1 and 2 kbar with water concentration (2,5, 5, 10, 30, 50 wt. %) from the dry overhang of the original mixture.

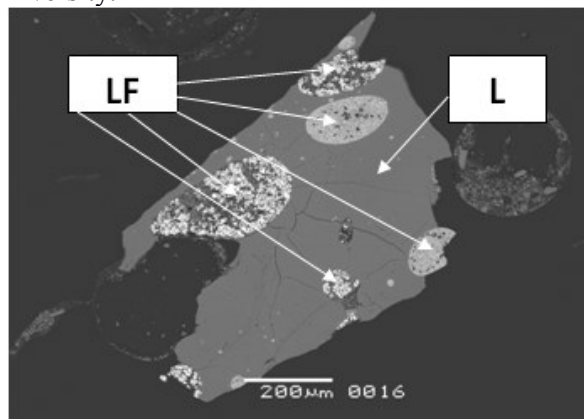
**Table 1. Initial composition of silicate-salt mixture for all experiments (at. %)**

Si	Al	Na	K	Li	F	O	Sum
17,24	6,92	5,07	3,84	4,46	21,82	40,65	100

The initial composition of the aluminosilicate part of the charge for experiments on the main components-Si, Al, Na, K was close to the composition of granite eutectic with 1% F at 1 kbar H<sub>2</sub>O (Manning, 1981). To it in equal weight ratios

with silicate salt component, corresponding in composition (Li, K, Na)- to aluminofluoride of cryolite stoichiometry was added. This composition of silicate-salt mixture was used as a reference composition for all experiments. The following reagents were used for preparation of initial compositions: LiF, K<sub>2</sub>SiF<sub>6</sub>, NaF, AlF<sub>3</sub>, Al<sub>2</sub>SiO<sub>5</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and distilled water. Rare earth elements (REE) La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu as well as yttrium and scandium were introduced as oxides of 0.5 wt. %. The ratios of the reagents were chosen so that the aluminum-silicate melt expected in the products of the experiments was close to the compositions of high-evolved Li-F and cryolite-containing granites.

The experiments were carried out at a high-pressure gas installation (the "gas bomb") at the Institute of Experimental Mineralogy of the Russian Academy of Sciences in Chernogolovka (IEM RAS) in platinum ampoules. The size of the ampoules in length was up to 25 mm and with an external diameter of 3 mm, the wall thickness was 0.2 mm. The accuracy of the control and temperature control was ± 5 °C; pressure ± 50 bar. For each ampoule, the mass was monitored before and after the experiment. The experiment was considered successful if the difference in mass was not more than 0.001g. The products of the experiment were examined on a Jeol JSM-6480LV scanning electron microscope (Japan) with an energy-dispersive INCA Energy-350 and crystal-diffractive INCA Wave-500 (Oxford Instrument Ltd., UK) spectrometer in the laboratory of local methods of substance research at the Department of Petrology of the Moscow State University. The accelerating voltage was 20 keV at a current of 0.7 nA. Concentrations of rare-earth elements and lithium were determined by mass spectrometry with inductively coupled plasma on an ICP MC instrument in the laboratory of the Department of Geochemistry of the Moscow State University.



**Fig. 1.** Aluminosilicate glass (L) and quenching products of a salt aluminofluoride melt (LF) experiment at 700 °C, 1 kbar with an initial water content of 10 wt. %. Image in back-scattered electrons (BSE).

## Interaction in the systems of fluid–melt–crystal

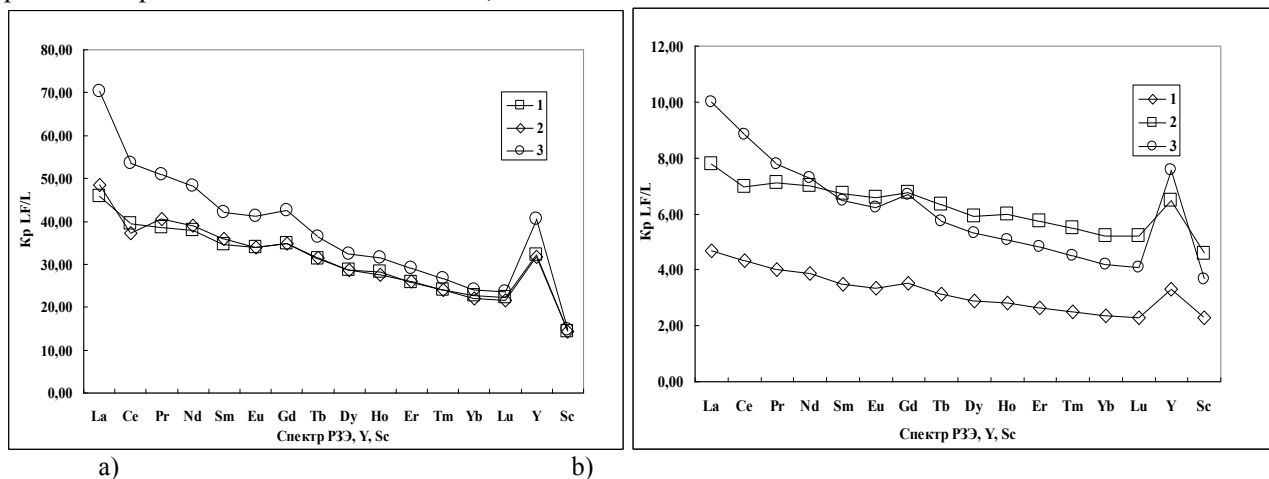
In the model granite system Si-Al-Na-K-Li-F-H-O with the limiting fluorine content (Alfereva et al., 2011) in the range of the studied temperatures and pressures, irrespective of the contents of the introduced water, the equilibrium phases are the aluminosilicate melt (L), aluminofluoride melt (LF), which are formed as a result of the liquid immiscibility process, and the fluid (Fl). The fluid phase was observed at the opening of ampoules at an initial water content of more than 10% by weight. At lower concentrations, it was completely dissolved in the melt.

The experimental products (Fig. 1) are represented by aluminosilicate glass with a small amount of quenching fluoride phases with a size of less than 5-10  $\mu\text{m}$ ; rounded and oval non-uniform globules of alkaline-aluminofluoride composition of 20 to 1000  $\mu\text{m}$  in cross section. They are composed of small quenching phases: the light gray sections of the globules are represented by the potassium-rich Na-K aluminofluoride, dark gray - poor K-Na potassium aluminum fluoride, and white -

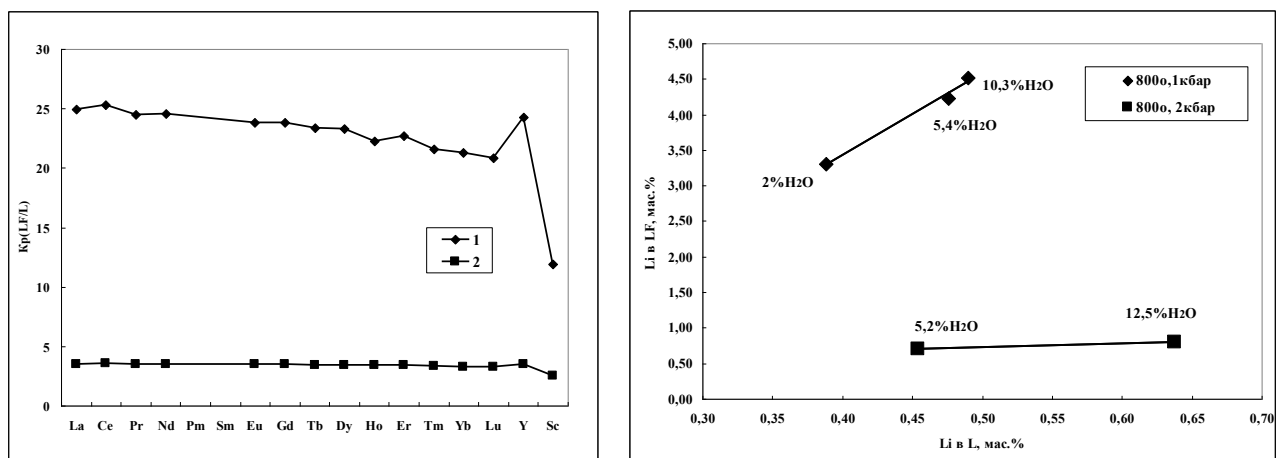
fluorides of rare-earth elements. All fluorides contain Li.

To determine the content of rare-earth elements in phases by the ICP MS method, silicate glasses with a minimal amount of quench phases and salt globules were selected from the samples. The weight of the salt phase was usually from 0.0005 to 0.0070 g.

As a result of the experiment, it was shown that all the rare-earth elements, yttrium, scandium and lithium are distributed in favor of the aluminofluoride melt salt, regardless of the experimental conditions specified. The fluid is the phase most depleted in all the above rare elements and yttrium. The coefficients of separation of the elements of the LF/L between the aluminofluoride and aluminosilicate melts depend on the pressure, temperature and water content, which is a new, first obtained result for the system under study. The partition coefficients are significantly reduced from light to heavy REE (Fig. 2).



**Fig. 2.** Separation coefficients of REE, Y and Sc Kr (LF / L) between aluminofluoride and aluminosilicate melts: a - 800 °C, 1 kbar, 1 - 2% H<sub>2</sub>O, 2 - 5.4% H<sub>2</sub>O, 3 - 10.3% H<sub>2</sub>O; b - 800 °C, 2 kbar, 1 - 2.5% H<sub>2</sub>O, 2 - 5.2% H<sub>2</sub>O, 3 - 12.5% H<sub>2</sub>O.



**Fig. 3.** Pressure dependence of the separation coefficients  $K_d(\text{LF} / \text{L})$  REE, Y and Sc between aluminofluoride and aluminosilicate melts at 700 °C (generalized data for different water contents): 1 - 1 kbar, 2 - 2 kbar. Sm was not entered into the system.

**Fig. 4.** Lithium distribution between aluminosilicate (L) and aluminofluoride (LF) melts at 800 °C, 1 and 2 kbar pressure and different water content in the system.

Significant increases in  $K_d$  are observed for Y, which behaves in experiments like Sm, Eu, Gd (Gramenitsky, Shchekina, 2005; Veksler, 2005). For scandium, on the contrary, the lowest separation coefficients are characteristic, close to those for heavy rare earths, especially for Lu. As was shown earlier (Schekina, Gramenitsky, 2008), Sc is always distributed in favor of the aluminofluoride melt, but its low values of  $K_d$  compared with the rare earths indicate a relatively higher affinity of Sc to the aluminosilicate melt, compared with most REE. In addition, the graphs (Fig. 2) indicate the effect of water on the value of the separation coefficients, which, as a rule, increases with increasing its concentration in the system.

But the main feature of the behavior of REE is the dependence of the separation coefficients  $K_d^{(LF/L)}$  on pressure (Fig. 2), revealed in this system, which sharply decrease with increasing pressure from 1 (Fig. 2a) to 2 kbar (Fig. 2b).

When the temperature falls from 800 to 700° C, the REE separation coefficients also decrease (Fig. 3). But the nature of their dependence on pressure persists. In Fig. 3 shows a sharp decrease in  $K_d^{(LF/L)}$  with increasing pressure.

The distribution of lithium between the aluminofluoride and aluminosilicate melts at 800 and 700° C and 1 and 2 kbar pressure was studied by ICP MS (Fig. 4).

It is shown that the lithium content in aluminosilicate glass is almost an order of magnitude lower than in the salt phase in the experiments carried out at 1 kbar. At the same time, the concentration of Li increased with a higher water content in the system. In experiments carried out at 2 kbar, the Li content was substantially lowered in the salt melt and increased slightly in the silicate melt. It was found that the separation coefficients of lithium  $K_d^{(LF/L)}$  decrease significantly with increasing pressure, just as it does for REE. Obviously, the behavior of rare-earth elements in the system is inextricably linked with the properties of lithium, which along with fluorine, is a segregation factor in this system, and which probably forms complex groupings with fluorine, aluminum and rare earths in both melts (L and LF). Undoubtedly, such factors as the solubility of water, lithium and rare elements in melts and coexisting fluid, their tendency to complex formation, cause the properties of both silicate and fluoride melts to vary depending on the experimental conditions and lead to a change in the coefficients of separation of elements between phases.

As a result of the studies, the following conclusions were obtained:

1) Regardless of the given experimental conditions, all rare-earth elements and lithium with large separation coefficients (several times) are distributed into a salt aluminofluoride melt.

2) The coefficients of separation of REE between salt and aluminosilicate melts depend on the temperature, pressure and content of volatile (water) in the system.

3) Data were first obtained showing that an increase in pressure from 1 to 2 kbar, both at 700 and at 800 ° C, leads to a decrease in the separation coefficients of rare-earth elements, lithium, yttrium, and scandium between salt and aluminosilicate melts.

4) An increase in the water content in the system leads to an increase in the separation coefficients between aluminosilicate (L) and aluminofluoride (LF) melts.

The work was supported by the Russian Foundation for Basic Research, Grant No. 16-05-00859.

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### Bataleva Y. V., Palyanov Y.N., Borzdov Y.M. Experimental modeling of interaction of iron carbide with sulfides, oxides and silicates under lithospheric mantle conditions.

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**Abstract.** Iron carbide is one of the potential carbon sources in the natural diamond-forming processes. Experimental modeling of carbon-producing reactions involving cohenite, sulfides, oxides and silicates was carried out on the BARS equipment (6.3 GPa, 900-1600 °C, 18-40 h). During the interaction of cohenite with sulfide melt, carbon and iron are extracted from the carbide and metal-sulphide melt with dissolved carbon ( $\sim\text{Fe}_{78}\text{Ni}_6\text{S}_{11}\text{S}_5$ ) is formed, which is the medium for the crystallization of the carbon phases. It was demonstrated that the interaction of the cohenite with minerals of the silicate mantle is most likely realized with the participation of the oxidized fluid and leads to the formation of graphite (diamond growth) in association with Fe-silicates, Fe-oxides and Fe-C-O melt. The results obtained allow us to consider interaction of iron carbide with sulphides, oxides and silicates, during which carbon extraction is realized as one of the possible processes of the global carbon cycle.

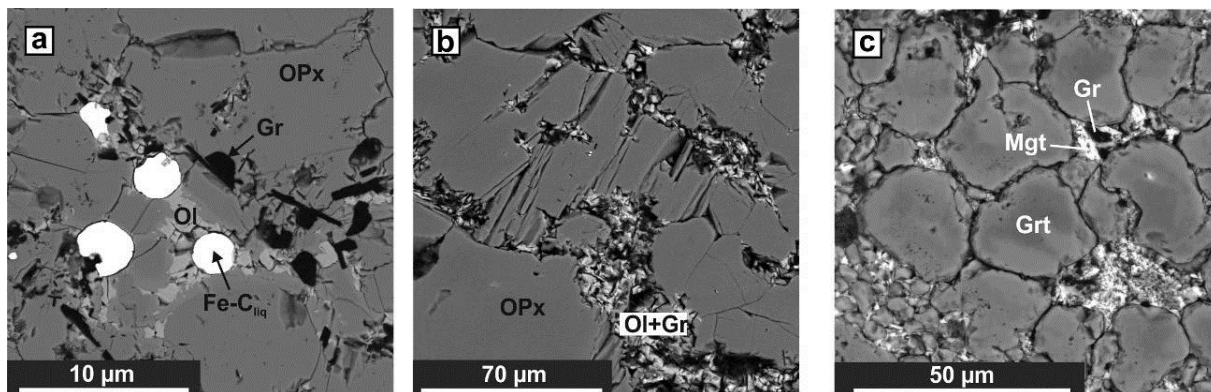
**Keywords:** *cohenite, graphite, diamond, mantle sulfides, high-pressure experiment, lithospheric mantle*

According to the results of experimental modeling, at depths over 250 km the mantle acquires a reduced character and becomes metal-saturated, with bulk concentrations of metallic iron of about 1400 ppm (Rohrbach et al., 2007). Under these conditions, the most likely mineral-concentrator of carbon is iron carbide (cohenite,  $\text{Fe}_3\text{C}$ ). A number of studies have shown that iron carbide can be formed by subduction of crustal carbonates to great depths, into a metal-bearing mantle (Rohrbach, Schmidt, 2011; Palyanov et al., 2013). Direct evidence of the presence of iron carbide in mantle rocks is the discovery of this mineral in inclusions in diamonds (Bulanova, 1995). In addition, these findings confirm the potential genetic relationship of carbide and diamond, as well as the possibility that under reduced mantle conditions, iron carbide is one of the potential sources of carbon in the processes of natural diamond formation. Taking into account the heterogeneity of the mantle redox conditions, justified by the data on inclusions in diamonds, it seems relevant to study the behavior of iron carbide in various redox environments. Analysis of the current state of the problem shows that there is a lack of experimental studies on the stability of carbide in various redox environments, and the mechanisms of its interaction with mantle minerals, melts and fluids have not yet been studied. The main goal of this study is experimental modeling of the behavior of iron carbide in the oxidized, moderately oxidized and

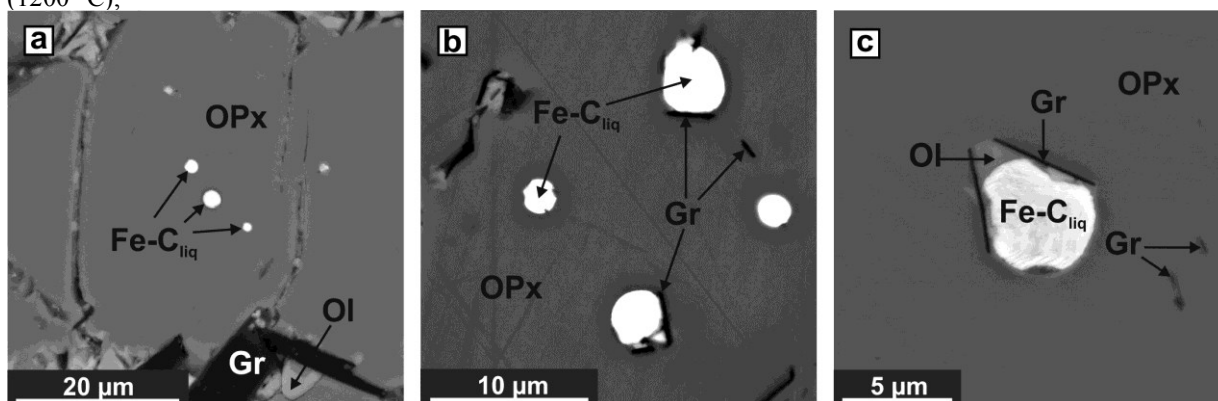
reduced domains of the lithospheric mantle, on the base of carbide-carbonate-oxide, carbide-oxide, carbide-sulfur and carbide-sulphide systems, respectively.

Experimental studies were performed using a multi-anvil high-pressure apparatus of a "split-sphere" type, at a pressure of 6.3 GPa, in the temperature range of 1100-1500 °C and durations of 20 hours. The main methods of analytical studies of the obtained samples were optical and electron microscopy, microprobe analysis, energy dispersive spectroscopy, Raman and Mössbauer spectroscopy.

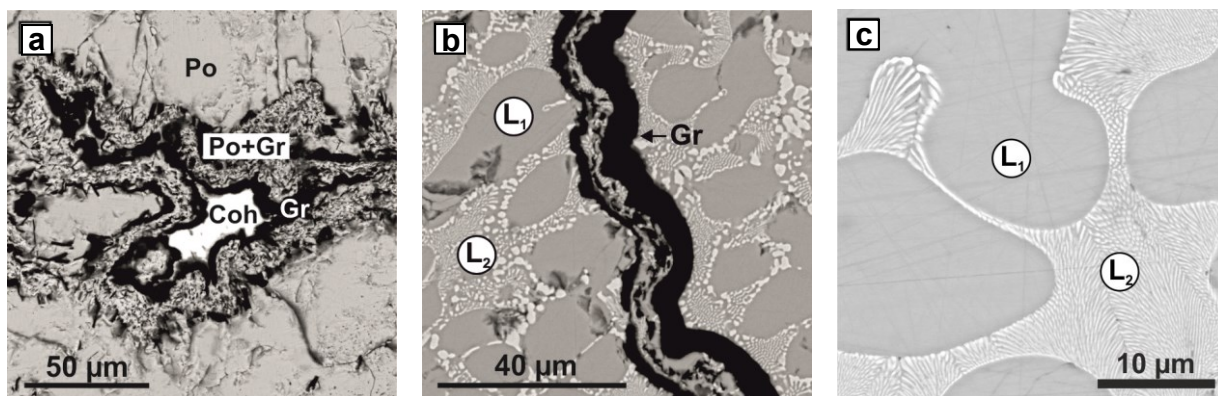
In experiments on the modeling the behavior of iron carbide in the oxidized domains of the upper mantle, we created conditions for the formation of mantle silicates and  $\text{CO}_2$ -fluid, which plays a role of an agent of oxidizing mantle metasomatism, and further interaction of carbide with the fluid, as well as with silicates. It has been established that as a result of the carbide-oxide-carbonate interaction, the formation of polycrystalline aggregates of ferrous orthopyroxene or garnet occurs (Figure 1a-c), in the interstices of which graphite in association with fayalite or ferrosilite, as well as single microspheres of Fe-C melt are formed. The cohenite is completely consumed in the redox reactions with the  $\text{CO}_2$ -fluid. As the main processes of phase formation occurring in the system, decarbonation with the formation of Mg-silicates and  $\text{CO}_2$ -fluid, the redox interaction of cohenite and  $\text{CO}_2$ -fluid by the reaction of  $3\text{Fe}_3\text{C} + 3\text{CO}_2 \rightarrow 6\text{FeO}_{\text{in silicates}} + 3\text{Fe-C}_{\text{melt}} + 5\text{C}^0$ , leading to cohenite oxidation, crystallization of ferrous silicates and the formation of graphite are established. At the temperatures above 1300 °C, the formation of iron-carbon melt, as well as the crystallization of graphite and the growth of diamond on seed crystals by the reaction of  $3\text{Fe-C}_{\text{melt}} + 3\text{CO}_2 \rightarrow 6\text{FeO}_{\text{in silicates}} + 4\text{C}^0$  were established. It should be separately emphasized that in the graphite- and diamond-forming redox reactions of the cohenite and  $\text{CO}_2$ -fluid, carbide and carbonate are both sources of carbon. One of the most important results obtained in this study is the synthesis of orthopyroxene and garnet crystals with inclusions of iron-carbon melt, graphite, fayalite and ferrosilite (Figure 2a-c). Our bulk analysis of the composition of inclusions demonstrated the fact of selective capture of the metal-carbon melt and graphite by silicates. It is established that the presence of  $\text{CO}_2$ -fluid in the interstices does not affect the preservation of metallic and graphite inclusions in silicates. Such a selective capture of inclusions is one of the potential scenarios for the conservation of metallic phases in mantle domains exposed to the effect of agents of mantle oxidative metasomatism.



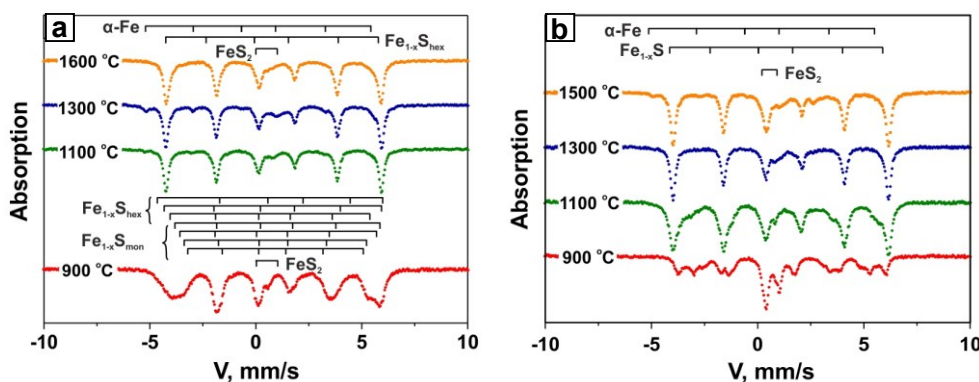
**Figure 1.** SEM micrographs of polished samples from experiments in the system  $\text{Fe}_3\text{C-SiO}_2\text{-(Mg,Ca)CO}_3$  (a-b),  $\text{Fe}_3\text{C-SiO}_2\text{-Al}_2\text{O}_3\text{-(Mg,Ca)CO}_3$  (c): (a) Polycrystalline aggregate of orthopyroxene with ferrous olivine, graphite and microspheres of quenched Fe-C melt in interstices (1300 °C); (b) Polycrystalline aggregate of orthopyroxene with ferrous olivine and graphite in interstices (1400 °C); (c) Aggregate of garnet crystals with magnetite and graphite in interstices (1200 °C);



**Figure 2.** SEM micrographs of ground samples from experiments in the  $\text{Fe}_3\text{C-SiO}_2\text{-(Mg,Ca)CO}_3$  system: incorporation of Fe-C melt, graphite and olivine in orthopyroxene.



**Figure 3.** SEM micrographs of fragments of ampoules: (a) - reaction zones from graphite around the initial crystals of cohenite (1100 °C); (b) - a reaction zone of graphite in Fe-S and Fe-S-C melts (1400 °C); (c) - structure of quenched Fe-S and Fe-S-C melts (1400 °C);



**Figure 4.** Mössbauer spectra of samples obtained in the carbide-sulfur (a) and carbide-sulphide systems (b).

## Mineral equilibria at high PT-parameters

In the experiments on modeling of the behavior of iron carbide in moderately oxidized domains of the upper mantle, we created conditions for studying the interaction of iron carbide with mantle oxides, silicates, and oxygen-bearing intergranular fluid. It has been established that the carbide-oxide interaction is a carbon-producing process, as a result of which graphite is formed in association with Fe-orthopyroxene, wüstite and cohenite, or with a Fe-C-O melt (1300-1500 °C). The main processes realized at relatively low temperatures are the oxidation of cohenite, the extraction of carbon from the carbide and the crystallization of metastable graphite, as well as the formation of ferrous silicates. At  $T \geq 1300$  °C, not only crystallization of graphite, but also diamond growth, resulting from the redox interaction of predominantly metallic melt (Fe-C-O) with oxides and silicates, as well as disproportionation of iron in this process is established in the system. The main reactions of carbide-oxide interactions are  $\text{Fe}_3\text{C} + 2\text{SiO}_2 + \text{MgO} + 1.5\text{O}_2 \rightarrow (\text{Fe,Mg})_2\text{Si}_2\text{O}_6 + 2\text{FeO} + \text{C}^0$  ( $T=1100-1200$  °C) and  $\text{Fe}_3\text{C} + \text{SiO}_2 + \text{MgO} + \text{O}_2 \rightarrow (\text{Fe,Mg})_2\text{Si}_2\text{O}_6 + \text{F-C-O}_{\text{melt}} + \text{C}^0$  ( $T=1300-1500$  °C). It has been experimentally demonstrated that this interaction can be considered as one of the potential scenarios for graphite crystallization and diamond growth from carbon of iron carbide at oxygen fugacity values near the iron-wüstite buffer.

Experiments carried out in a more complex carbide-oxide system, where associations of garnet with cohenite or Fe-C-O melt are obtained, show similar results. However, we should dwell on one fundamental point. The Mössbauer spectroscopy established the formation of a pyrope-almandine garnet coexisting with a predominantly metallic melt and containing trivalent iron at a level of 0.1 formula units. In the study of Rohrbach co-authors (2007) it has been experimentally shown that at pressures of 7 GPa metallic iron can coexist with garnet enriched in ferric iron, due to disproportionation processes. The data obtained by us show that these processes can also be realized at the pressures of 6.3 GPa.

Experiments on modeling the behavior of iron carbide in the reduced domains of the upper mantle, performed at the base of the interaction of carbide and sulfur-enriched reduced fluid. At relatively low temperatures this interaction occurs according to the reaction scheme  $2\text{Fe}_3\text{C} + 3\text{S}_2 \rightarrow 6\text{FeS} + 2\text{C}^0_{\text{graphite}}$  ( $T=900-1100$  °C), with the formation of the association of pyrrhotite and graphite (Figure 3, 4). At higher temperatures, the crystallization of graphite is accompanied by the generation of sulfide and metal-sulfide melts, according to the reaction  $2\text{Fe}_3\text{C} + 3\text{S}_2 \rightarrow 6\text{Fe-S}_{\text{melt}} + 6\text{Fe-S-C}_{\text{melt}} + 2\text{C}^0_{\text{graphite}}$  ( $T=1200-1400$  °C). As a result of the carbon-producing reactions, not only graphite crystallizes in metal-sulfide melt, but diamond growth also occurs

at relatively high temperatures:  $2\text{Fe}_3\text{C} + 3\text{S}_2 \rightarrow 6\text{Fe-S}_{\text{melt}} + 2\text{C}^0_{\text{graphite, diamond}}$  ( $T=500-1600$  °).

In the experiments on the carbide-sulfide interaction, it was established that during the interaction of iron carbide with Fe<sub>3</sub>Ni-sulfide melt, carbide recrystallization in the sulfide melt, extraction of carbon and iron from carbide, and the formation of predominantly metal-sulfide melt with dissolved carbon (~ Fe<sub>78</sub>Ni<sub>6</sub>S<sub>11</sub>C<sub>5</sub>), which is the medium of crystallization of carbon phases, occur.

As a summary, it is established, that the stability of iron carbide in the upper mantle depends directly on the oxidation-reduction conditions, the composition of the minerals interacting with it, and also on the temperature. At the pressures of the upper mantle, in the presence of agents of oxidizing (CO<sub>2</sub>-fluid) or reducing (S-rich fluid) metasomatism, the cohenite is unstable even at relatively low temperatures. Experimental results allow us to consider a cohenite as a potential source of carbon in the processes of diamond and graphite genesis in nature. The interactions of iron carbide with mantle fluids, silicates, oxides and sulfides, during which carbon extraction is realized, can be considered as possible processes of the global carbon cycle.

This work was supported by the Russian Foundation for Basic Research (project No. 16-35-60024) and by a State Assignment (project no. 0330-2016-0007).

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### Novoselov I.D.<sup>1,2</sup>, Bataleva Yu.V.<sup>1</sup>, Palyanov Yu.N.<sup>1</sup>. Experimental study of the interactions in the ankerite-pyrite and ankerite-olivine-pyrite systems under upper mantle PT-parameters.

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**Abstract.** Experimental modeling of ankerite-pyrite and ankerite-olivine-pyrite interactions was carried out on a multi-anvil high-pressure apparatus of a "split sphere" type (6.3 GPa, 1050-1550 °C, 20-60 h). In the ankerite-pyrite system at  $T \leq 1250$  °C, the formation of pyrrhotite, dolomite and pyrite ( $\pm$  magnesite) was established, and at higher temperatures formation of carbonate and sulphide melts occurred. The decrease of iron concentration in silicates and carbonates takes place by extraction of iron in sulfide and leads to the formation of pyrrhotite or sulphide melt. Interaction of ankerite-olivine-pyrite at  $T \leq 1250$  °C leads to the formation of pyrrhotite in association with diopside,

Ca,Mg-carbonates, olivine, graphite and pyrite. At  $T \geq 1350$  °C, the formation of carbonate and sulphide melts coexisting with olivine and graphite was established. The main processes of interactions investigated are generation of sulfide and carbonate melts, the extraction of iron from silicates and carbonates by sulfide phases, and the formation of elemental carbon.

**Keywords:** ankerite, olivine, pyrite, sulphidation, mantle sulfides, high-pressure experiment, lithospheric mantle

The subduction is the key process of the recycling of crustal material into the mantle. According to the modern researches, large volumes of sulphur, carbon and iron are recycled this way. The quantity of recycled sulphur, iron and carbon was estimated; it was calculated, that input of carbon is about  $4,6 \pm 4,0 \times 10^{12}$  moles per year, one of sulphur -  $2,5 \pm 1,5 \times 10^{12}$  mol/year and one of iron -  $55 \pm 13 \times 10^{12}$  mol/year (Evans, 2012).

It is evident that main containers of carbon in crustal rocks are carbonates, and the essential container of sulphur is sulphides. According to modern researches, carbonates can be thermodynamically stable under PT-conditions of lower mantle (Shatskiy et al., 2014) and can be subducted up to 600 km (Shirey et al., 2013). The main evidences of existence of carbonates in mantle rocks are the carbonate inclusions in the diamonds (Sobolev et al., 1997). Sulphides are also stable under PT-conditions of mantle (Sharp, 1969, Boehler, 1992) and are found as inclusions in the diamonds very often. Fe in crustal rocks can be beared by both sulphides (pyrite, pyrrhotite, etc) and carbonates (siderite, ankerite).

In this paper results of experimental modeling of C-, S- and Fe-bearing phases behavior of in PT-

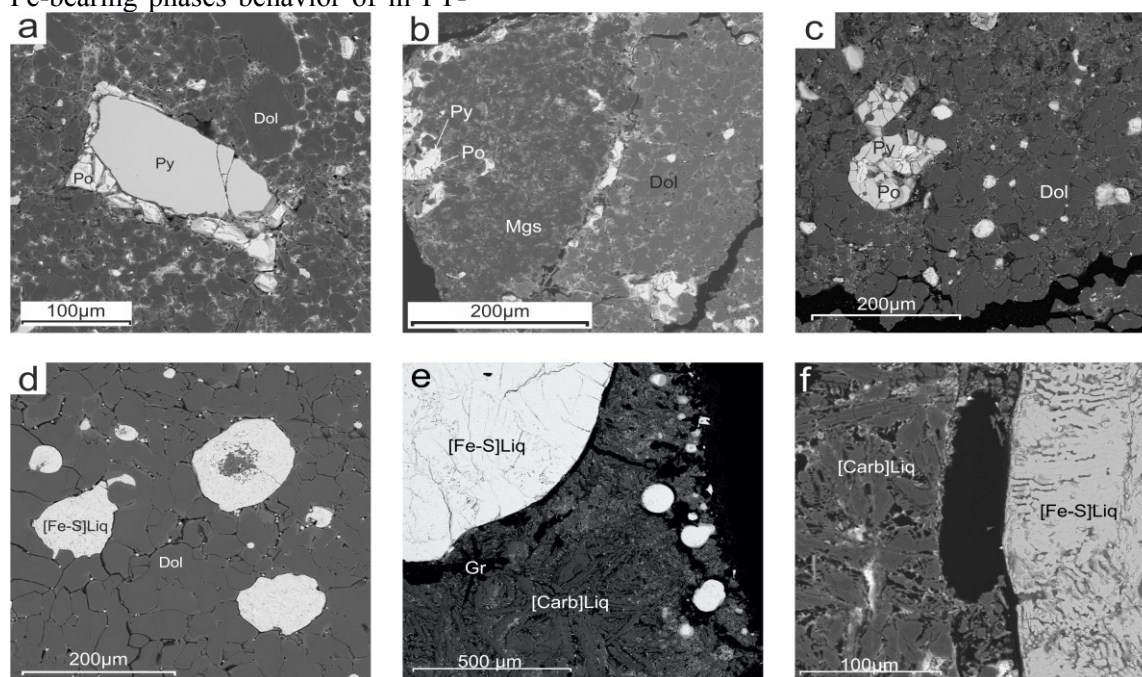
conditions of upper mantle are presented: crustal minerals interaction that is modeled by ankerite-pyrite system ( $\text{Ca}(\text{Mg,Fe,Mn})[\text{CO}_3]_2 - \text{FeS}_2$ ) and interaction between crustal and mantle minerals that is modeled by ankerite-olivine-pyrite system ( $\text{Ca}(\text{Mg,Fe,Mn})[\text{CO}_3]_2 - (\text{Mg,Fe,Ni})\text{SiO}_4 - \text{FeS}_2$ ) (table 1).

Two series of experiments (one series for each system) at the pressure of 6.3 GPa, in the temperature range of 1050-1550 °C were performed. Experiments were divided to temperature ranges -low-temperature (1050-1250 °C) and high-temperature (1350-1550 °C); ranges were singled out according to the expected appearance of sulphide melt. Duration of low-temperature experiments was 60 hours, one of high-temperature experiments was 20 hours. Experiments were performed on a multi-anvil high-pressure apparatus of a "split sphere" type (Palyanov et al., 2010).

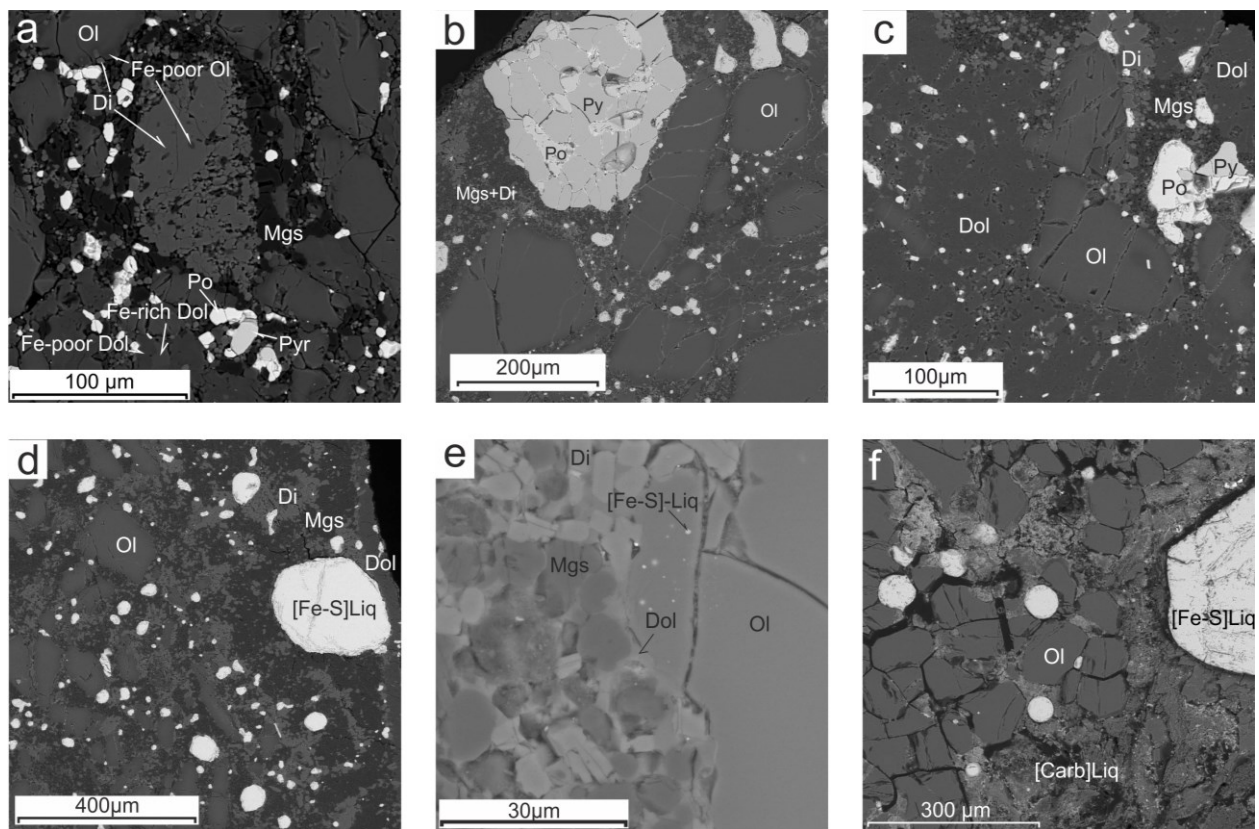
In ankerite-pyrite system in low-temperature range pyrrhotite, dolomite, magnesite, graphite and recrystallized pyrite were formed. Samples are massive polycrystalline aggregates of dolomite, magnesite, pyrrhotite, pyrite and graphite (Figure 1a-c).

**Table 1. Data on initial system components.**

Reagent	Composition	Mass, mg		Source
		Ank+Py system	Ank+Ol+Py system	
Ank	$\text{CaFe}_{0.49}\text{Mg}_{0.49}\text{Mn}_{0.02}(\text{CO}_3)_2$	56.7	33	Kyshtym deposit
Py	$\text{FeS}_2$	10.5	10.5	Astafievskoe deposit
Ol	$\text{Mg}_{1.77}\text{Fe}_{0.19}\text{Ni}_{0.01}\text{SiO}_4$	-	33.2	Lerzolite xenolite from Udachnaya pipe



**Image 1.** SEM-microphotographs of polished fragments of samples received by the ankerite-pyrite interactions in pressure of 6.3 GPa and temperatures of 1150°C (a, b), 1250°C (c), 1350°C (d) and 1550°C (e, f).



**Image 2.** SEM SEM-microphotographs of polished fragments of simples received by the ankerite-olivine-pyrite interactions in pressure of 6.3 GPa and temperatures of 1050°C (a), 1350°C (b, c), 1350°C (d, e) и 1550°C (f).

The size of dolomite crystals is 10-100 μm, content of FeO in dolomite varies from 0 to 10 wt.%. The smallest grains of carbonates and rims of its large crystals are characterized by the lowest iron content, whereas cores of medium (about 50 μm) crystals show the highest content of iron.

Magnesite is mostly interstitial fine crystalline (grain size up to 10 μm) phase, but occasionally it forms rather large aggregates (Figure 1b). Magnesite has calcium impurity up to 6 wt.% CaO.

Pyrite and pyrrhotite form grains with size from 5 to 300 μm and in most cases are in intergrowths, in which pyrrhotite constitutes reaction rims (Figure 1a) or exists as drops inside of pyrite grains and aggregates (Figure 1c). It worth noting, however, that pyrrhotite can form also monomineral aggregates.

In ankerite-pyrite system in high-temperature range dolomite or carbonate melt, sulphide melt and graphite were formed; growth of diamond on seed crystals was also observed. Samples are massive polycrystalline aggregates of dolomite and graphite with sulphide melt (Figure 1d) or quenched aggregate of two immiscible melts (carbonate and sulphide) with graphite (Figure 1e, f).

Sulphide melt forms drops with size from first micrometers to one millimeter (Figure 1d, e) and has pyrrhotite-like composition with Fe:S ratio about 0.99-1.1.

Dolomite from the experiment at 1350 °C is characterized by grain size 20-50 μm (Figure 1d) and

shows more constant compositions than in low-temperature experiments in the same system, with average FeO content about 2.7 wt. %.

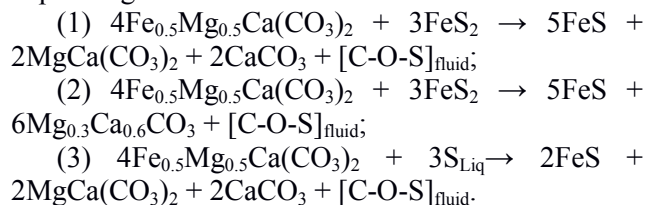
Magnesium aragonite is found as very fine crystalline aggregates in central parts of some sulphide melt drops at 1350 °C (Figure 1d) and more likely represents first portions of carbonate melt; MgO content in it is about 13 wt. %.

Carbonate quenched melt in 1550 °C experiment has dolomite-like composition and demonstrates spinifex texture.

In the experiment at 1550 °C graphite forms distinct (up to 100 μm) flake crystals or rosettes (Figure 1e).

Thus it is experimentally established that in the course of ankerite-pyrite interaction at the pressure of 6.3 GPa and temperatures of 1050-1550 °C sulphide phase extracts iron from carbonate phase, and, as a result, low-ferrous carbonates (1050-1350°C) and pyrrhotite (1050-1250°C) or carbonate (1550 °C) and sulphide (1350-1550°C) melts as well as graphite (1050-1550°C) are formed.

We can suggest following reactions for explaining of observed results:





In the ankerite-olivine-pyrite system in the low-temperature range pyrrhotite, dolomite, magnesite, low-ferrous olivine, diopside, graphite and recrystallized pyrite were formed. Samples are massive polycrystalline silicate-carbonate aggregates with very fine crystalline graphite (Figure 2a-c).

Textures of dolomite and sulphide aggregates and their compositions are identical to those in ankerite-pyrite system.

Magnesite in experimental samples is situated in interstices and also forms rims around diopside and sulphide grains (Figure 2a-c); calcium impurity in magnesite is up to 9 wt. % CaO.

Size of olivine crystals varies from 10 to 300  $\mu\text{m}$  (Figure 2a-c) and has variable iron content – from 0 to 9.3 wt. % FeO. Fine interstitial crystals and rims of large olivine grains have the lowest iron content, whereas cores of large crystals have the highest ferruginosity.

Diopside is found to present in mixed fine crystalline aggregates with magnesite and dolomite filling interstitial space (Figure 2b, c) and also sporadically forms large aggregations (Figure 2a).

In the ankerite-olivine-pyrite system in the high-temperature range sulphide melt, dolomite and magnesite or carbonate melt, low-ferrous olivine, diopside and graphite were formed; diamond growth on seed crystals was also observed. Samples are massive polycrystalline aggregates of dolomite, silicates and graphite with sulphide melt (Figure 2d, e) or quenched aggregate of two immiscible melts (carbonate and sulphide) with olivine and graphite (Figure 2f).

Sulphide melt forms drops with the size up to first millimeters (Figure 2d, f) and rounded inclusions in olivine (Figure 2e); it has pyrrhotite-like composition.

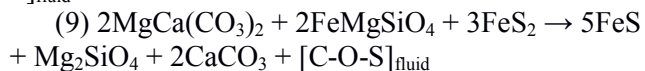
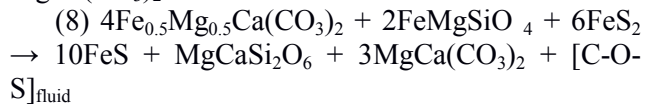
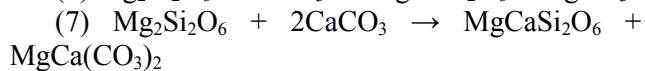
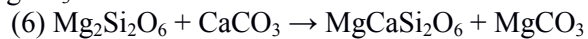
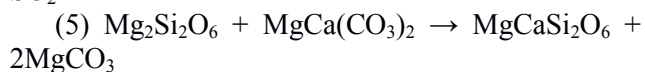
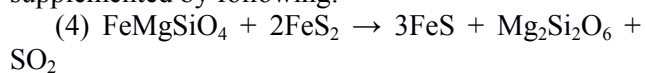
Carbonate melt is almost identical to that in ankerite-pyrite system texturally and compositionally.

At 1350 °C diopside, magnesite and dolomite form mixed fine crystalline aggregates filling interstitial space (Figure 2d, e).

Olivine forms large (up to 300  $\mu\text{m}$ ) crystals with iron content of 6 wt. % FeO at 1550 °C and of 1.5-8 wt.% at 1350 °C.

Thus it is experimentally established that in an ankerite-olivine-pyrite interaction at the pressure of 6.3 GPa and temperatures 1050-1550 °C sulphide phase extracts iron from carbonate and silicate phases, owing to which low-ferrous carbonates (1050-1350 °C), low-ferrous olivine (1050-1550 °C), diopside (1050-1350 °C) and pyrrhotite (1050-1250 °C) or low-ferrous olivine and carbonate (1550 °C) and sulphide (1350-1550 °C) melts as well as graphite (1050-1550 °C) are formed.

Suggested reactions that are realized in this system duplicate reactions (1), (2) and (3) and are supplemented by following:



As a summary, the main processes in ankerite-pyrite and ankerite-olivine-pyrite systems are total melting of sulphide phase at 1350 °C and of carbonate phase at 1550 °C, extraction of iron from carbonates and silicates by sulphides, formation of pyrrhotite/pyrrhotite-like liquid, lowering of iron content in carbonates and silicates with crystallization of dolomite, magnesite, diopside and low-ferrous olivine, and formation of phases of elemental carbon (graphite, diamond).

As a result of the present research, processes that potentially can take place in the upper mantle with participation of Fe-, S- and C-bearing crustal phases and lead to producing of sulphid and carbonate melts and extraction of iron from carbonates and silicates and to forming of  $\text{C}^0$  (graphite,  $\pm$  diamond) were studied.

This work was supported by the Russian Science Foundation under Grant No. 14-27-00054.

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**Zdrokov E.V., Bataleva Yu.V., Palyanov Yu.N., Borzdov Yu.M. Experimental study of phase formation in the olivine – ankerite – sulfur and olivine – siderite – sulfur systems under P,T-parameters of the lithospheric mantle**

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## Mineral equilibria at high PT-parameters

**Abstract.** Experimental studies in olivine-Fe-carbonate-sulfur systems aimed at modeling the interaction of the subducted material with mantle silicates were carried out using multi-anvil apparatus of the "split sphere" type (BARS) (6.3 GPa, 1150-1450 °C, 20-60 h). At 1150-1250 °C in the olivine-ankerite-sulfur system, association of newly formed pyrite, aragonite and clinopyroxene, coexisting with low-Fe ankerite, olivine, and predominantly sulfur melt, was established. At higher temperatures, a decrease in the ferruginosity of olivine and carbonate was found, as well as the enrichment of the sulfur melt with the sulphide component. In the interaction of olivine with siderite and sulfur, in the range of 1150-1450 °C, orthopyroxene, pyrrhotite and Mg,Ca,Fe-carbonate ( $\pm$  carbonate melt) were obtained. It has been established that the main processes of olivine-carbonate-sulfur interaction are recrystallization of olivine and carbonate in the sulfur melt, extraction of Fe and Ni into the melt, and crystallization of newly formed pyrite, pyrrhotite, and clinopyroxene.

**Keywords:** *olivine, carbonate, sulfur, mantle sulfides, sulfidation, high-pressure experiment, lithospheric mantle*

Sulfur and carbon, as elements with variable valence, can have a significant effect on the redox evolution of mantle rocks, melts and fluids. It is known that subduction plays a key role in the global cycles of carbon and sulfur. Subduction provides transport of various forms of these elements to the deep zones of the Earth and creates conditions for their interaction with rocks of silicate mantle. In a number of studies (e.g. Evans, 2012), on the estimation of the amount of carbon and sulfur in subduction zones, it was found that the removal of C and S into the atmosphere through volcanic arcs is 3 to 5 times lower than their introduction into the deeper zones of the Earth. Thus, a significant amount of carbonates, sulfides and sulfates is immersed deep into the mantle, where it becomes possible for them to interact with mantle minerals. It is now known that the subduction of the carbonate material of the earth's crust can be carried out to a depth of  $\geq 600$  km (Shirey et al., 2013). Evidences of the possibility of the presence of carbonates in mantle rocks are findings of diamonds with carbonate inclusions (Shirey et al., 2013). Data on the composition of inclusions in minerals of mantle xenoliths and results of experimental studies have shown that in the upper mantle, depending on the pressure, temperature and oxygen fugacity, sulfur can exist as sulfides or sulfide melts (Zajacz et al., 2013), sulfates (Leung, 1990), fluids of the «C – O – H – S» system (Giuliani et al., 2013) or to be present in dissolved form in silicate melts (Zajacz et al., 2013). In recent years the behavior of sulfur in the processes of mantle metasomatism and the connection of these processes with the formation of sulfide minerals in eclogites and peridotites of the upper mantle (Alard et al., 2011) are studied. Some researchers suggest that sulfides can be formed due to the interaction of S-bearing fluids or melts with FeO-bearing mantle silicates, such as olivine. As the main reactions of sulfidation following are assumed:  $\text{Fe}_2\text{SiO}_4 + \text{S}_2 \rightarrow$

$2\text{FeS} + \text{O}_2 + \text{SiO}_2$  (Papike et al., 1995);  $2\text{Fe}_2\text{SiO}_4 + \text{S}_2 \rightarrow 2\text{FeS} + \text{Fe}_2\text{Si}_2\text{O}_6 + \text{O}_2$  (Eggler, Lorand, 1993). Considering that at present experimental studies of sulfur and carbon-bearing phases in subduction processes, as well as their interaction with silicate phases under high pressures and temperatures are very rare, the experimental simulation of silicate - Fe-carbonate - sulfur interaction in mantle P, T-parameters seems to be actual.

Experimental studies were carried out in  $\text{Mg}_{1.85}\text{Fe}_{0.14}\text{Ni}_{0.01}\text{SiO}_4\text{-CaFe}_{0.49}\text{Mg}_{0.49}\text{Mn}_{0.02}(\text{CO}_3)_2\text{-S}$  и  $\text{Mg}_{1.85}\text{Fe}_{0.14}\text{Ni}_{0.01}\text{SiO}_4\text{-Fe}_{0.94}\text{Mg}_{0.02}\text{Mn}_{0.04}\text{CO}_3\text{-S}$  systems, at a pressure of 6.3 GPa and a temperature range of 1150-1450 °C (the temperature step of the experiments was 100 °C). The duration of the experiments carried out at 1150 and 1250 °C was of 60 h, and for relatively high temperature experiments the duration was reduced to 20 h. The experiments were carried out on a multi-anvil apparatus of the "split-sphere" type (BARS). The chemical and phase compositions of the samples were determined using a microprobe analysis (Center for collective use of scientific equipment for multi-element and isotope studies of the SB RAS). Analyses of silicates, oxides and sulfides was carried out by spraying with carbon (25 nm), accelerating voltage 20 kV, probe current 20 nA, sampling angle 40 °, counting time 10 s on each analytical line and probe diameter from electron beam 2-3  $\mu\text{m}$ . The investigation of the phase relationships in the experimental products and determination of the composition of the phases obtained was performed using an electronic scanning microscope "TESCAN MIRA 3 LMU".

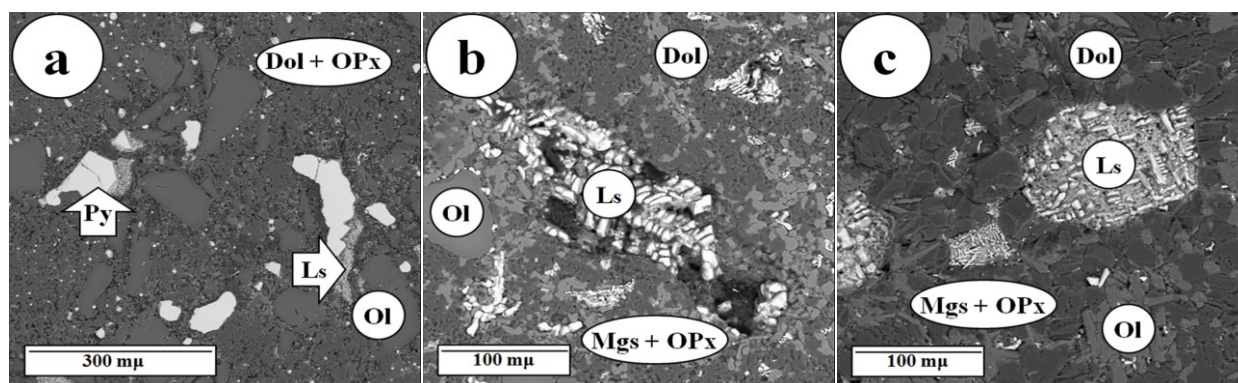
Experimental studies of the interaction in the olivine-ankerite-sulfur system showed that in the temperature range of 1150 – 1350 °C association of olivine, dolomite, ( $\pm$  magnesite at 1350 °C), pyrite and orthopyroxene, coexisting with predominantly sulfur melt/fluid (Fig. 1a,b) is formed. It was found that the recrystallization of olivine and ankerite, as well as the partial extraction of Fe and Ni from olivine and the almost complete extraction of Fe from ankerite into the melt, were realized; as a result, the crystallization of pyrite, dolomite and orthopyroxene occurred. Advantageously sulfur melt, which forms in this case, was enriched in the sulfide component. At 1150 °C there are two generations of olivine crystals in the system - the initial and recrystallized. Recrystallized olivine is characterized by reduced iron content (Table 1). However, it should be noted that the extraction of iron from carbonates is more intense than from silicates. The main reaction (shown schematically) performed in the olivine-ankerite-sulfur system in the temperature range 1150 – 1350 °C, is  $(\text{Mg,Fe,Ni})_2\text{SiO}_4 + \text{Ca}(\text{Fe,Mg,Mn})(\text{CO}_3)_2 + \text{S} \rightarrow (\text{Mg,Fe,Ni})_2\text{SiO}_4 + (\text{Mg,Fe})_2\text{Si}_2\text{O}_6 + (\text{Mg,Ca})\text{CO}_3 \pm \text{MgCO}_3 + (\text{Fe,Ni})\text{S}_2 + [\text{S} + \text{FeS}]_L$ . As a result of the interaction in the olivine-

ankerite-sulfur system at 1450 °C, an association of olivine, dolomite, magnesite and orthopyroxene is formed, coexisting with a sulfur-sulfide melt (Fig. 1c). It was found that, under these conditions, olivine and ankerite were recrystallized, which was accompanied by the extraction of Fe and Ni from olivine and ankerite into a melt of sulfur, which resulted in the enrichment of the sulfur melt with the

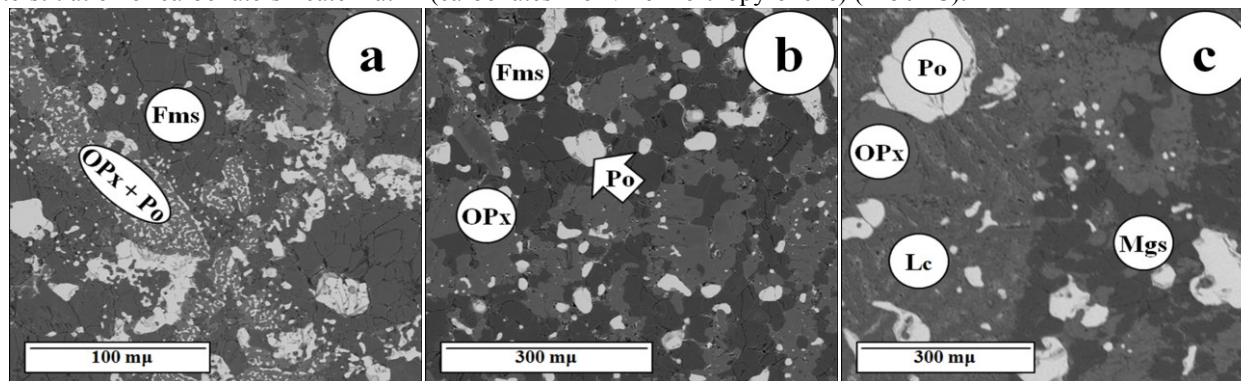
sulfide component and the crystallization of the iron-free phases, dolomite, magnesite and orthopyroxene. The principal interaction reaction in the olivine-ankerite-sulfur system at a temperature of 1450 °C is  $(Mg,Fe,Ni)_2SiO_4 + Ca(Fe,Mg,Mn)(CO_3)_2 + S \rightarrow (Mg,Fe,Ni)_2SiO_4 + (Mg,Fe)_2Si_2O_6 + (Mg,Ca)CO_3 + MgCO_3 + [FeS_2 + S]_L$ .

**Table 1.** Compositions of silicate and carbonate phases of the olivine – ankerite – sulfur system. Dol – dolomite, Mgs – magnesite, Ol – olivine, OPx – orthopyroxene, N<sub>A</sub> – number of analysis points, (x) – standard deviation.

T, °C	t, h	Phase	N <sub>A</sub>	Composition, weight %						
				SiO <sub>2</sub>	FeO	NiO	MgO	CaO	CO <sub>2</sub>	Σ
1150	60	Dol	9	–	–	–	19 <sub>(1)</sub>	32 <sub>(1)</sub>	48.9 <sub>(6)</sub>	99.90
		Ol	9	41.0 <sub>(2)</sub>	9 <sub>(1)</sub>	0.5 <sub>(1)</sub>	49.4 <sub>(8)</sub>	–	–	100.03
		Ol	7	42.9 <sub>(2)</sub>	0.35 <sub>(2)</sub>	–	56.7 <sub>(2)</sub>	0.09 <sub>(8)</sub>	–	100.04
1250	60	Dol	8	–	0.00 <sub>(0)</sub>	–	23.0 <sub>(4)</sub>	28 <sub>(1)</sub>	49.0 <sub>(8)</sub>	100.00
		Ol	9	41.0 <sub>(1)</sub>	9.1 <sub>(7)</sub>	0.46 <sub>(7)</sub>	49.3 <sub>(6)</sub>	–	–	99.86
		OPx	7	54.9 <sub>(7)</sub>	0.2 <sub>(1)</sub>	–	20 <sub>(1)</sub>	24.6 <sub>(8)</sub>	–	99.70
1350	20	Mgs	7	–	0.3 <sub>(2)</sub>	–	38 <sub>(1)</sub>	9 <sub>(1)</sub>	52.6 <sub>(5)</sub>	99.90
		Dol	8	–	0.23 <sub>(4)</sub>	–	25.9 <sub>(8)</sub>	24.9 <sub>(4)</sub>	49.0 <sub>(6)</sub>	100.03
		Ol	9	41.3 <sub>(2)</sub>	8.4 <sub>(8)</sub>	0.42 <sub>(4)</sub>	49.8 <sub>(7)</sub>	–	–	99.92
		OPx	9	55.3 <sub>(9)</sub>	0.2 <sub>(1)</sub>	–	21.9 <sub>(7)</sub>	22.7 <sub>(9)</sub>	–	100.10
1450	20	Mgs	7	–	0.1 <sub>(1)</sub>	–	40.1 <sub>(3)</sub>	5.0 <sub>(2)</sub>	54.8 <sub>(3)</sub>	100.00
		Dol	8	–	0.00 <sub>(0)</sub>	–	20 <sub>(2)</sub>	30 <sub>(2)</sub>	49.7 <sub>(6)</sub>	99.70
		Ol	9	41.7 <sub>(2)</sub>	6.8 <sub>(6)</sub>	0.3 <sub>(2)</sub>	51.2 <sub>(6)</sub>	–	–	100.00
		Ol	8	42.9 <sub>(7)</sub>	3 <sub>(1)</sub>	0.2 <sub>(2)</sub>	54 <sub>(1)</sub>	–	–	100.10
		OPx	9	59.7 <sub>(4)</sub>	0.3 <sub>(2)</sub>	–	37.6 <sub>(5)</sub>	2.4 <sub>(2)</sub>	–	100.00



**Fig. 1.** SEM micrographs: (a) crystals of olivine (Ol) and pyrite (Py), and predominantly sulfur melt in a fine-crystalline aggregate of dolomite (Dol) and orthopyroxene (OPx) (1250 °C). (b) Microdendritic quench aggregate sulfur + pyrite in polycrystalline aggregate of dolomite, orthopyroxene and olivine (1350 °C). (c) Structure of sulfur-sulphide melt (Ls) in interstition of carbonate-silicate matrix (carbonates + olivine + orthopyroxene) (1450 °C).



**Fig. 2.** SEM micrographs: Polycrystalline aggregate of ferromagnesite (Fms), orthopyroxene (OPx) and pyrrhotite (Po) at 1250 °C (a) and at 1350 °C (b). (c) Structure of carbonate melt (Lc) and crystals of orthopyroxene (OPx) and pyrrhotite (Po) (1450 °C).

## Mineral equilibria at high PT-parameters

Experimental studies of the interaction in the olivine-siderite-sulfur system showed that in the temperature range 1150 – 1350 °C the same phase association was formed. Starting from a temperature of 1150 °C, the initial olivine and siderite are completely consumed. The process of their recrystallization is accompanied by the extraction of Fe and Ni from olivine and siderite into a melt of sulfur, which in turn is enriched with a sulfide component, resulting in the formation of an association of three newly formed minerals - orthopyroxene, ferromagnesite and pyrrhotite. As the temperature of the experiments increases, there is a general decrease in the iron content of

ferromagnesite and orthopyroxene (Tab. 2). At the temperature of 1450 °C, a carbonate melt of variable composition is formed in association with orthopyroxene, ferromagnesite and pyrrhotite (Fig. 2c). An increase in the temperature of the experiments leads to an increase in the size of the grains of the newly formed phases (Fig. 2). As the main reaction of interaction of olivine with siderite and sulfur, the following (shown schematically) can be proposed:  $(Mg,Fe,Ni)_2SiO_4 + Fe,Mg,Mn(CO_3) + S \rightarrow (Mg,Fe)_2Si_2O_6 + (Mg,Ca,Fe)CO_3 + Fe_{x-1}S \pm [(Mg,Ca)CO_3 + S]_L$ .

**Table 2.** Compositions of silicate and carbonate phases of the olivine – siderite – sulfur system. Fms - ferromagnesite, Mgs - magnesite, OPx - orthopyroxene,, N<sub>A</sub> – number of analysis points, (x) – standard deviation.

T, °C	t, h	Phase	N <sub>A</sub>	Composition, weight %						
				SiO <sub>2</sub>	FeO	MnO	MgO	CaO	CO <sub>2</sub>	Σ
1150	60	Fms	8	–	18 <sub>(1)</sub>	2.1 <sub>(2)</sub>	32 <sub>(1)</sub>	0.2 <sub>(1)</sub>	47.2 <sub>(6)</sub>	99.5
		Fms	8	–	14.5 <sub>(3)</sub>	2.0 <sub>(4)</sub>	35.1 <sub>(4)</sub>	–	48 <sub>(1)</sub>	99.6
		OPx	8	55.3 <sub>(6)</sub>	16 <sub>(2)</sub>	1.7 <sub>(3)</sub>	27 <sub>(2)</sub>	–	–	100
1250	60	Fms	9	–	14 <sub>(1)</sub>	2.2 <sub>(5)</sub>	36.0 <sub>(8)</sub>	0.01 <sub>(1)</sub>	47.7 <sub>(9)</sub>	99.91
		Fms	7	–	17.4 <sub>(5)</sub>	2.7 <sub>(2)</sub>	32.7 <sub>(5)</sub>	0.3 <sub>(2)</sub>	47.0 <sub>(4)</sub>	100.1
		Fms	9	–	21 <sub>(2)</sub>	3.3 <sub>(6)</sub>	30 <sub>(2)</sub>	0.20 <sub>(3)</sub>	45.5 <sub>(2)</sub>	100
		OPx	8	54.9 <sub>(2)</sub>	16.5 <sub>(7)</sub>	1.9 <sub>(3)</sub>	26.5 <sub>(7)</sub>	0.1 <sub>(1)</sub>	–	99.9
1350	20	Fms	7	–	15.9 <sub>(6)</sub>	2.22 <sub>(8)</sub>	33.9 <sub>(4)</sub>	1.8 <sub>(2)</sub>	46 <sub>(2)</sub>	99.82
		OPx	8	55.1 <sub>(4)</sub>	15.8 <sub>(8)</sub>	1.67 <sub>(2)</sub>	26.9 <sub>(7)</sub>	0.5 <sub>(2)</sub>	–	99.97
1450	20	Mgs	7	0.00 <sub>(0)</sub>	4.25 <sub>(3)</sub>	0.77 <sub>(8)</sub>	39.9 <sub>(7)</sub>	3.3 <sub>(7)</sub>	51.7 <sub>(5)</sub>	99.92
		OPx	9	56.60 <sub>(8)</sub>	11.0 <sub>(5)</sub>	0.98 <sub>(6)</sub>	31.4 <sub>(6)</sub>	0.00 <sub>(0)</sub>	–	99.98
		OPx	7	58.2 <sub>(1)</sub>	4.4 <sub>(4)</sub>	0.49 <sub>(8)</sub>	35.8 <sub>(7)</sub>	1.2 <sub>(1)</sub>	–	100.09

Thus, the studied interactions of olivine-ankerite-sulfur and olivine-siderite-sulfur can be considered as a basis for modeling of metasomatic processes accompanied by the formation of mantle sulfides via the subduction of crustal material into a silicate mantle. It has been established that the interaction of the reduced carbonates and sulfur with mantle silicates at high P,T parameters leads to the generation of potential metasomatic agents - sulfur-enriched reduced melts/fluids and carbonate melts. It has been experimentally demonstrated that S-bearing reduced melts/fluids can provide total transformation of the FeO-bearing silicate-carbonate matrix (olivine, ankerite and siderite), which is accompanied by the extraction of iron and nickel from the solid phases and is accompanied by the formation of mantle sulfides.

This work was supported by the Russian Science Foundation under Grant No. 14–27–00054.

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