

## Mineral equilibria at high PT-parameters

**Chevychelov\* V.Y., Viryus A.A. Conditions for formation of carbonate-aluminosilicate melt at melting of carbonate-pelite rock at conditions of elevated CO<sub>2</sub> partial pressure. UDC 550.42**

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**Abstract.** As a result of experiments on low-pressure melting of limestone from a pyrometamorphic complex containing about 40 wt. % pelitic material at  $T = 1300^{\circ}\text{C}$ ,  $P = 12.3$  MPa and elevated CO<sub>2</sub> partial pressure, a carbonate-aluminosilicate melt of the following composition was synthesized (in wt. %): 46.5 CaO, 19 CO<sub>2</sub>, 14.3 SiO<sub>2</sub>, 10 Al<sub>2</sub>O<sub>3</sub>, 3.0 Na<sub>2</sub>O, 2.5 MgO, 0.7 TiO<sub>2</sub>, 0.4 K<sub>2</sub>O. In the products of the experiment, this phase (quenched carbonate-aluminosilicate glass) is isolated in the form of individual absolutely transparent and homogeneous-looking flat grains up to 200–250 microns in diameter. The relative content of this phase in the experimental products, approximately calculated from the area in the microphotographs, is about 3–7 %. The carbon content in the phase composition was determined using a specially developed technique using electron-probe microanalysis. Using Raman spectroscopy, the presence of CO<sub>3</sub><sup>2-</sup> was diagnosed in the carbonate-aluminosilicate glass under study.

**Keywords:** carbonate-aluminosilicate melt; melting of carbonate-pelite rock; elevated CO<sub>2</sub> partial pressure; experiment

As a result of experiments on low-pressure melting of limestone from a pyrometamorphic complex containing about 40 wt. % pelitic material, at  $T = 1300^{\circ}\text{C}$ ,  $P = 12.3$  MPa and increased partial pressure of CO<sub>2</sub>, a carbonate-alumina silicate melt of

the following chemical composition was synthesized (X-ray spectral electron probe microanalysis method, wt. %): 46.5 CaO, 19 CO<sub>2</sub>, 14.3 SiO<sub>2</sub>, 10 Al<sub>2</sub>O<sub>3</sub>, 3.0 Na<sub>2</sub>O, 2.5 MgO, 0.7 TiO<sub>2</sub>, 0.4 K<sub>2</sub>O. In the products of the experiment, this phase (quenched carbonate-aluminosilicate glass) is isolated in the form of individual absolutely transparent and homogeneous-looking flat grains up to 200–250  $\mu\text{m}$  in diameter (Fig. 1). The relative content of this phase in the experimental products, approximately calculated from the area in the microphotographs, is about 3–7 %.

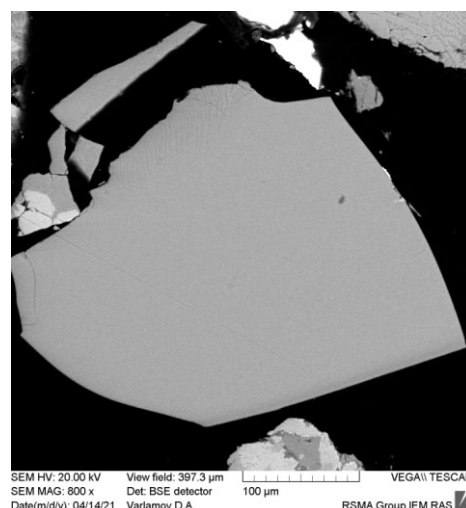


Fig1.(a)

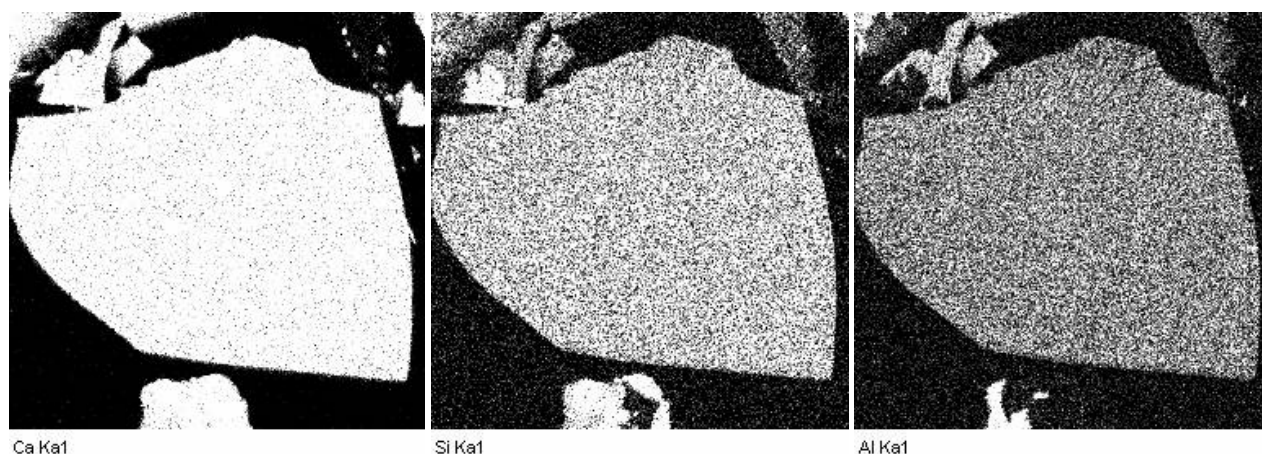
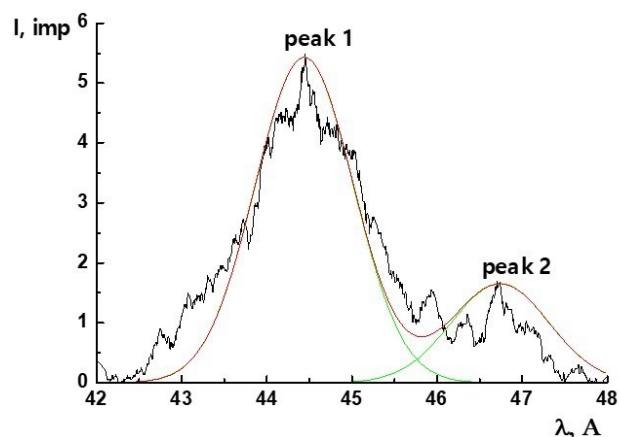


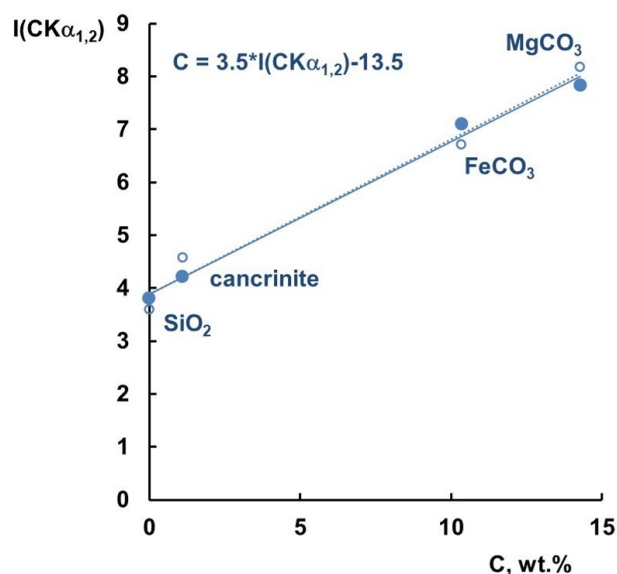
Fig1.(b)

**Fig. 1.** Microphotographs of quenched carbonate-aluminosilicate glass obtained (a) in reflected electrons and (b) in the characteristic X-ray radiation of CaK $\alpha_1$ , SiK $\alpha_1$  and AlK $\alpha_1$ .

The carbon content in carbonate-aluminosilicate glass was determined using a specially developed technique by electron probe microanalysis using a wave spectrometer ( $U = 5$  kV,  $I = 9$  nA, crystal analyzer of LSM60). As a result, X-ray spectra of the  $K\alpha_{1,2}$  line of carbon were obtained in the range of 42–48 Å. Using the Origin program, the X-ray spectra were smoothed, and then the peaks were separated and the areas under each peak were calculated. An example of such a spectrum is shown in Figure 2.



**Fig. 2.** Smoothed X-ray spectrum in the region of the  $K\alpha_{1,2}$  line (peak 1 – 44,57 Å) of carbon, obtained on  $MgCO_3$  (black), and the result of peak separation by a statistical method (Gaussian, red and green).



**Fig. 3.** Calibration curve based on the dependence of  $I(K\alpha_{1,2})$  on carbon content.

The area under peak 1 calculated as a result of peak separation was used as the analytical signal  $I(K\alpha_{1,2})$ .

Based on the calculated values of  $I(K\alpha_{1,2})$

depending on the carbon content in the standards, a calibration curve was constructed (Fig. 3). The standards were measured several times on different days. Calibrations for these standards measured on different days are completely consistent, as can be seen in Fig. 3. (solid line – calibration for November 15 (group 1), dotted line – calibration for November 22 (group 2)), that is, the calibrations are reproduced.

The calibration curve is described by the linear equation:  $y = 0.29x + 3.89$  (1), where  $y = I(K\alpha_{1,2})$  is the area under peak 1 of the  $K\alpha_{1,2}$  X-ray line,  $x$  is the carbon content in wt. %. Accordingly, the carbon content ( $x$ ) can be calculated using the equation derived from (1):  $C$  (in wt. %) =  $3.5 \times I(K\alpha_{1,2}) - 13.5$  (2).

**Table 1.** The results of determining the carbon content in carbonate-aluminosilicate glass, calculated according to the above calibration

| No                                            | $I(K\alpha_{1,2})$ | C, wt. % | $CO_2$ , wt. % |
|-----------------------------------------------|--------------------|----------|----------------|
| <b>Group 1</b>                                |                    |          |                |
| 1                                             | 5.32               | 5.1      | 19.0           |
| 2                                             | 5.45               | 5.6      | 20.7           |
| 3                                             | 5.34               | 5.2      | 19.3           |
| 4                                             | 5.30               | 5.1      | 18.7           |
| 5                                             | 4.75               | 3.1      | 11.6           |
| 6                                             | 5.40               | 5.4      | 20.0           |
| 7                                             | 5.59               | 5.4      | 19.9           |
| <b>Average</b> for group 1 without point 5    | 5.40               | 5.30     | 19.6           |
| D                                             | 0.003              | 0.04     | 0.53           |
| $S_r$                                         | 1.0 %              | 3.7 %    | 3.7 %          |
| <b>Group 2</b>                                |                    |          |                |
| 8                                             | 5.30               | 5.1      | 18.8           |
| 9                                             | 5.23               | 4.8      | 17.9           |
| 10                                            | 5.15               | 4.5      | 16.8           |
| <b>Average</b>                                | 5.20               | 4.8      | 17.8           |
| D                                             | 0.01               | 0.07     | 0.94           |
| $S_r$                                         | 1.4 %              | 5.4 %    | 5.4 %          |
| <b>Statistics for two groups</b>              |                    |          |                |
| <b>Average</b> for two groups without point 5 | 5.32               | 5.10     | 19.0           |
| D                                             | 0.01               | 0.1      | 1.3            |
| $S_r$                                         | 1.7 %              | 6.1 %    | 6.1 %          |

D – dispersion;  $S_r$  – relative standard deviation

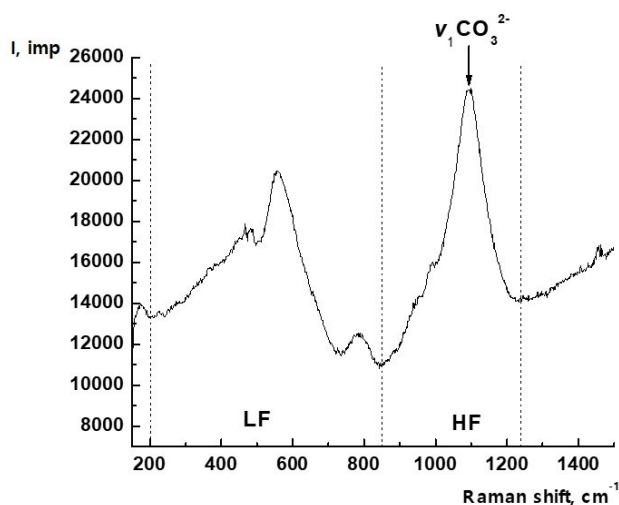
The detection limit of  $C_{\min} = 0.6$  wt. % for carbon using this calibration.

The results of determining the carbon content in carbonate-aluminosilicate glass, calculated using this calibration, are presented in Table 1. In terms of  $CO_2$  content, this content is 19.0 wt. % (average of nine measurements from two groups of analyzes performed on different days). This value is close to the content (20.8 wt. %) determined in the general analysis of carbonate-aluminosilicate glass by

electron probe microanalysis method based on the deficit of the total sum.

The method of Raman spectroscopy in the studied carbonate-aluminosilicate glass diagnosed the presence of  $\text{CO}_3^{2-}$ .

The resulting Raman spectrum contains two regions: low-frequency (LF  $\approx 200\text{--}840\text{ cm}^{-1}$ ) and high-frequency (HF  $\approx 840\text{--}1230\text{ cm}^{-1}$ ), which, depending on the composition and structure of the glass, can shift slightly (Fig. 4). According to a number of studies, it has been established (Morizet et al., 2013) that the low-frequency LF region is a superposition of a large number of different spectral lines that are difficult to separate, decipher and interpret.



**Fig. 4.** Raman spectrum obtained on carbonate-aluminosilicate glass. The spectrum shows low-frequency (LF  $\approx 200\text{--}840\text{ cm}^{-1}$ ) and high-frequency regions (HF  $\approx 840\text{--}1230\text{ cm}^{-1}$ ) and the  $\nu_1 \text{CO}_3^{2-}$  line, the peak position of which corresponds to  $\approx 1090\text{ cm}^{-1}$ .

In the high-frequency HF region there are lines related to stretching vibrations of various aluminosilicate structural units (Merzbacher and White, 1991; Mysen and Richet, 2005, etc.). In the high-frequency region of the spectrum there is also a line of symmetrical stretching vibrations ( $\nu_1 \text{CO}_3^{2-}$ ) of the  $\text{CO}_3^{2-}$  anion, which can be in the range of 1060 and  $1090\text{ cm}^{-1}$  in aluminosilicate glasses. Its position corresponds to the known range of Raman lines  $\nu_1$  for crystalline carbonates (for example, Rividi et al., 2010; Boulard et al., 2012, etc.). For different glass compositions, the position of the  $\nu_1 \text{CO}_3^{2-}$  line may vary slightly. In the carbonate-aluminosilicate glass sample we studied, the peak position of the  $\nu_1 \text{CO}_3^{2-}$  line corresponds to  $\approx 1090\text{ cm}^{-1}$ .

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## Fedkin V.V. Chemical heterogeneity of garnet and diversity of its manifestations in eclogite-blueschist complexes.

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**Annotation.** The unique properties of garnet to remember, change and maintain its composition under the influence of metamorphic conditions were discovered during the study of crustal eclogites of the Maksyutov complex (Southern Urals). It turned out that garnet is capable of recording the smallest nuances of changes in PT parameters of metamorphism, even with a radical change in its trend. They are reflected in its composition, both within specific samples and in individual zonal grains. Additional studies of the composition and zoning of garnet, carried out in high-pressure rocks of the complex, showed a wide variety of its chemical heterogeneity, caused by frequent changes in PT crystallization conditions against the background of transience and, possibly, thermodynamic disequilibrium of metamorphic processes. In the multi-stage history of the Maksyutov complex, metamorphism is of a recurrent pulsating nature, consisting of four separate stages (cycles) of its evolutionary development. Taken together, they form a single trend of retrograde evolution of metamorphism and have certain common features characteristic of the entire complex. However, questions remain about the causes and mechanism of the pulsating reciprocating thermobaric regime of complex formation. It is not yet clear how the mechanism of cyclic metamorphism with periodic subsidence and ascent of the UHP plate is created.

**Keywords:** high-pressure metamorphism, thermobaric processes, Maksyutov complex, tectonic melange, coherent processes, PT trends in the evolution of metamorphism.

The Maksyutov complex is a very famous and well-studied complex. The presence in its

composition of high-pressure mineral associations with the participation of diamond and coesite determines the top parameters of its metamorphism at  $T = 650\text{--}800\text{ }^{\circ}\text{C}$  and  $P = 3.0\text{--}3.2\text{ GPa}$ . Our studies (Fedkin, 2020; Fedkin, 2021) and the latest works of Ural geologists (Valizer et al., 2015) confirm these parameters: prograde stage  $800\rightarrow 900\text{ }^{\circ}\text{C}$ , retrograde  $910\rightarrow 730\text{ }^{\circ}\text{C}$ .

However, the main feature of the metamorphism of the Maksyutov complex is its return-pulsation nature, when the phenomena of prograde and retrograde metamorphism are repeated many times, and PT trends, constructed from the compositions of the Grt-Cpx paragenesis, form conjugate pairs, that characterize the regimes of individual stages (cycles) of the development of the terrane. Based on a detailed study of the composition and zoning of garnet in the Grt+Cpx+Pl+Qtz paragenesis, the parameters of mineral formation of each of them were determined, the totality of which made it possible to reconstruct the entire thermobaric history of the formation of the complex. Below are several examples of the diversity of garnet zoning in the UHP rocks of the complex.

1. At the initial stages of thermobaric transformations, relict garnet inclusions with prograde zoning are preserved in the high-pressure (UHP) rocks of the complex brought to the surface in the form of boudins and tectonic blocks (Fig. 1). Crystallization of garnet begins in the center of the grain at  $T = 568\text{--}751\text{ }^{\circ}\text{C}$ . Then there is a retrograde replacement of the central part with secondary minerals and the formation of a high-temperature rim at  $T = 689\text{--}789\text{ }^{\circ}\text{C}$ . Relics of Pl and Cpx in the center of the original garnet grain allow us to estimate the pressure at  $1.3\text{--}1.7\text{ GPa}$ . As a result, the PT parameters of the original prograde metamorphism with a maximum temperature range of  $570\text{--}790\text{ }^{\circ}\text{C}$  are preserved.

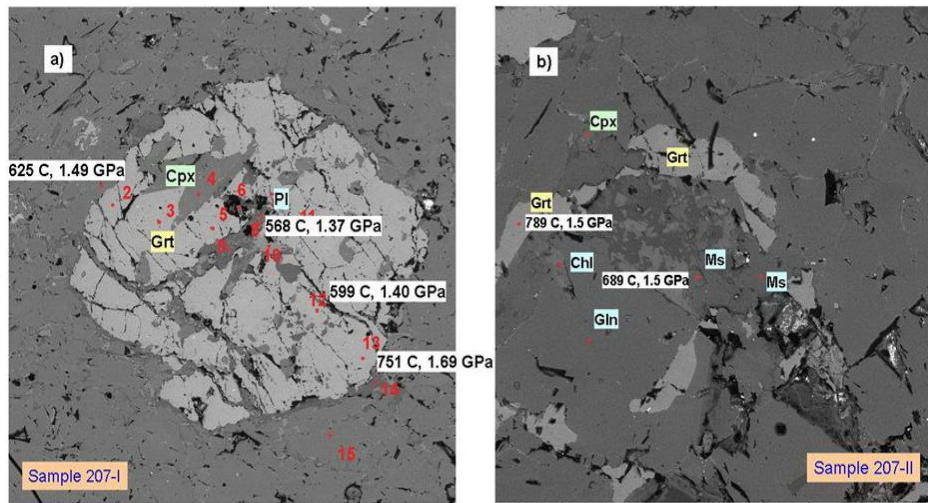
2. Intense retrograde processes of the next stage lead to periodic changes in the direction of the PT trend of metamorphism. Garnet acquires complex, multidirectional, and sometimes inversion zoning. In the central part of the grain, the composition of garnet fixes the parameters of the regressive stage of the 2nd cycle:  $695\text{ }^{\circ}\text{C}/1.6\text{GPa} \blacktriangleright^1 615\text{ }^{\circ}\text{C}/1.4\text{GPa}$  (Fig. 2). And in the newly formed overgrown rim, Grt in equilibrium with Cpx and Pl shows a progressive trend of the 3rd stage:  $630\text{ }^{\circ}\text{C}/1.44\text{GPa} \blacktriangleright 660\text{ }^{\circ}\text{C}/1.46\text{GPa}$ , demonstrating the pulsating nature of metamorphism and the change in the PT

trend of metamorphism from regressive to progressive, recorded in one grain.

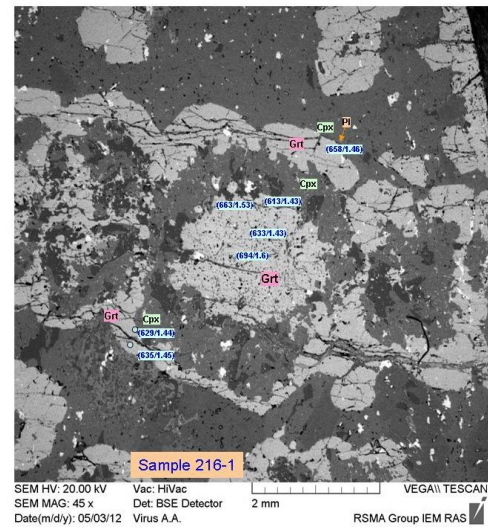
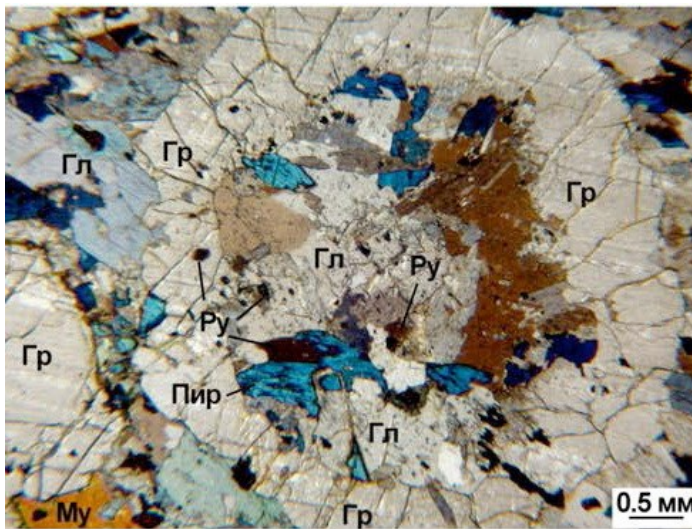
3. In specimen 185 from the eclogite boudina of the Antangan area, in different garnet grains, an opposite inversion transition of its zoning and a change in the morphology of grains was recorded as the process of retrograde metamorphism developed within one sample. The original euhedral porphyroblastic grains contain practically no inclusions and have weak fracturing parallel to the schistosity of the rock. In equilibrium with Cpx, the composition of garnet shows a prograde PT trend in the range of  $473\text{--}657\text{ }^{\circ}\text{C}$ . As metamorphic changes in the rock develop, progressive zoning is still preserved in the garnet grain, but small inclusions of acidic plagioclase Pl  $0.95\text{--}0.90$  appear. Fractures in garnet no longer coincide with the schistosity of the rock, and in the most altered grains they are surrounded by accumulations of quartz, sphene and glaucophane, creating a flowing shadow structure of rotation and dragging with retrograde zoning  $617\text{--}518\text{ }^{\circ}\text{C}$ .

4. The ability of garnet to form grains with a different composition and zonation is most clearly manifested in eclogite layers in the host gneiss-schist matrix (Fig. 4). In specimen 200 (Karayanovo area), the progressive zoning of garnet in the center of the eclogite layer turns into a regressive one, decreasing and reaching thermodynamic equilibrium at the boundary with the host matrix:  $680\blacktriangleright 622\text{ }^{\circ}\text{C}$  - in altered grains,  $770\blacktriangleright 547\text{--}516\text{ }^{\circ}\text{C}$  - in more recent grains.

<sup>1</sup>  $\blacktriangleright$  Here and below, the triangle (brighter arrow) shows changes in the PT parameters.

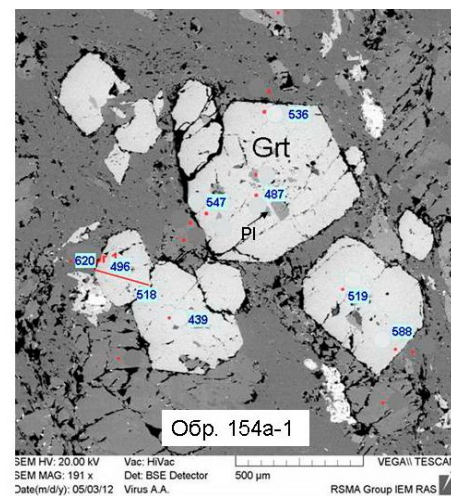
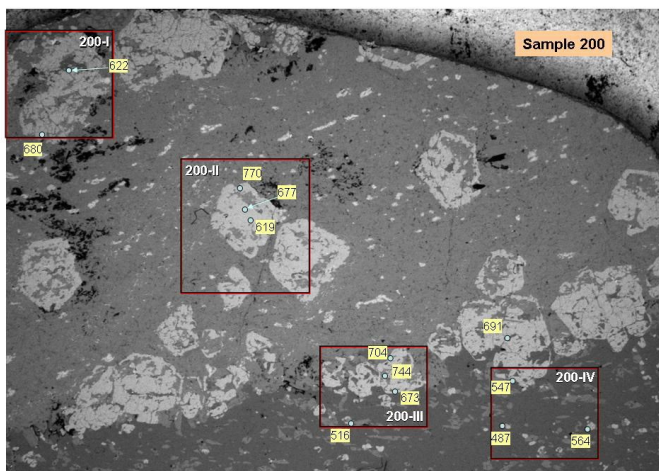


**Fig. 1.** Two-stage prograde crystallization of garnet in the eclogite of the Maksyutov complex at the stage of tectonic melange of boudin: (a) altered progressive (568-751°C) garnet grain from boudin of the Karayanovo area with a relict inclusion of plagioclase; (b) replacement of garnet with secondary minerals Ms+Gln+Chl in the center of the grain and the formation of a high-temperature rim upon reaching maximum metamorphic parameters (689-789 °C, P~1.5 GPa).



**Fig. 2.** Contrasting inversion zoning of garnet in eclogites of the Maksyutov complex at stage II►III of the interstage transition (sample 216-1, Karayanovo area): regressive - in the center of the grain 695 °C/1.6 GPa → 615 °C/1.4 GPa and weakly progressive in the rim 630 °C/1.44 GPa → 660 °C/1.46 GPa.

**Fig. 3.** Temperature distribution in a zonal inversion garnet crystal (Sample 216-1): regressive - in the center of the grain 695 °C/1.6 GPa → 615 °C/1.4 GPa and slightly progressive in the marginal part 630 °C/1.44 GPa → 660 °C/1.46 GPa.



**Fig. 4.** Temperature variations in the eclogite layer at the boundary with the host matrix Grt-Cpx-Gln-Mu-Qtz under the influence of coherent processing of the rock.

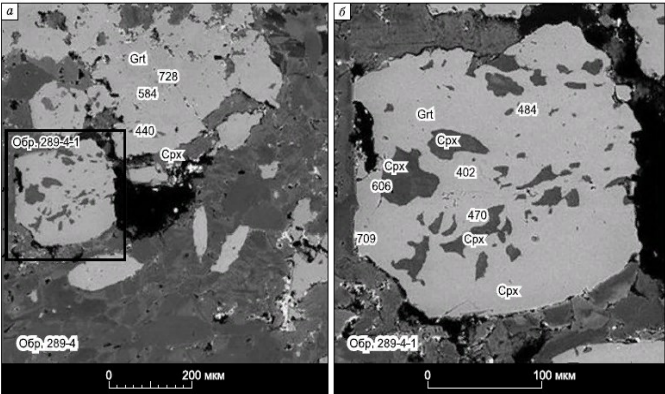
**Fig. 5.** Progressive zoning of garnet in sample 154a, (Shubino village) from the matrix of the 4th stage of metamorphism.

5. Newly formed euhedral crystals of garnet, pyroxene, and plagioclase of a different composition and independent size, appear in the bulk of the matrix environment, at stages III-IV of the development of the complex. They contain almost no inclusions and record relatively low prograde trends in the interval  $T \sim 490-565^\circ\text{C}$ . Newly formed garnet crystals, however, retain the ability to change their composition depending on crystallization conditions (Fig. 5), repeating the progressive zoning of garnet of the third stage:  $T = 450-620^\circ\text{C}$ .

6. At stages III-IV of the complex development, independent small newly formed idiomorphic crystals of garnet, pyroxene, plagioclase of different composition appear in the matrix. They contain virtually no inclusions and have relatively low

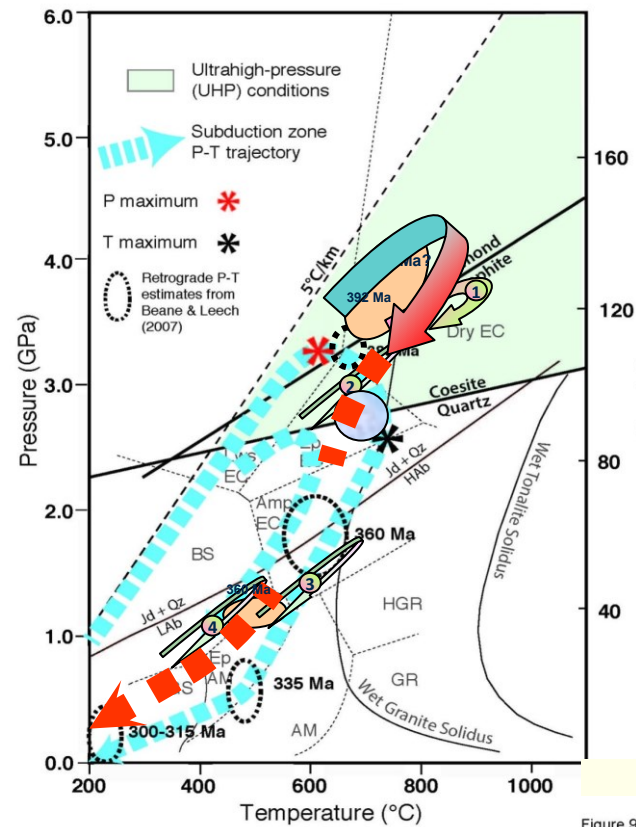
progressive trends in the range of  $T \sim 490-565^\circ\text{C}$ . However, newly formed garnet crystals retain the ability to change their composition depending on crystallization conditions (Fig. 5), repeating the progressive zoning of garnet of the third stage:  $T = 450-620^\circ\text{C}$ .

7. The counter thermodynamic equilibrium has been achieved in a large garnet grain, (Fig. 6). The grain is split by a crack, along which the fluid flow in 2 of its parts forms the opposite retrograde zoning with a ranges of  $225-290^\circ\text{C}$  and  $T = 728-440^\circ\text{C}$  and  $P = \sim 2.0\text{ GPa}$  in the altered grain (Fig. 6a) and at  $T = 709-484^\circ\text{C}$  and  $P = \sim 3.0-3.5\text{ GPa}$  in its more recent part (Fig. 6b).



**Fig. 6.** Counter retrograde zoning of the grant at the junction of two grains along a crack in the zone of fluid flow, causing a sharp decrease in its crystallization temperature - by  $\sim 225-290^\circ\text{C}$ .

Retrograde trend in altered grain at  $T = 728-440^\circ\text{C}$  and  $P = \sim 2.0\text{ GPa}$ ;  
Retrograde trend in fresher grain at  $T=709-484^\circ\text{C}$  and  $P = \sim 3.0-3.5\text{ GPa}$ ;



**Fig. 7.** Physicochemical condition of the Maksyutov complex formation.

**Table 1.** Prograde-retrograde trends of the exhumation of the Maksyutov blueschist complex (Fedkin, 2020)

| Cycles | Prograde trends<br>Retrograde trends                                                                                                                 | Age, Ma        |
|--------|------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| 1      | $T=800\rightarrow 900^\circ\text{C}$ , $P=3,5\text{ ГПа}$<br>$T=910\rightarrow 730^\circ\text{C}$ , $P=3,5\text{ ГПа}$                               | 545-533 [1, 3] |
| 2      | $T=500\rightarrow 790^\circ\text{C}$ , $P=2,5\rightarrow 3,0\text{ ГПа}$<br>$T=740\rightarrow 610^\circ\text{C}$ , $P=2,5\rightarrow 1,4\text{ ГПа}$ | 360 [1]        |
| 3      | $T=460\rightarrow 680^\circ\text{C}$ , $P=1,1\rightarrow 1,5\text{ ГПа}$<br>$T=690\rightarrow 430^\circ\text{C}$ , $P=1,3\rightarrow 1,0\text{ ГПа}$ | 335 [4, 5]     |
| 4      | $T=310\rightarrow 515^\circ\text{C}$ , $P=0,9\rightarrow 1,2\text{ ГПа}$<br>$T=545\rightarrow 310^\circ\text{C}$ , $P=1,0\rightarrow 0,6\text{ ГПа}$ | 345-315 [4]    |

Age according to: [1] Vakizer et al., 2015; [2] Leech, Willingshofer, 2004; [3] Dobretsov et al.,1996; [4] Beane, Connolly, 2000; [5] Beane, Leech, 2007.

#### Features of metamorphic evolution^

- close PT values of trend parameters;
- frequency of cycles;
- pulsating character;
- small inversion interval ( $\sim 20\text{ Ma}$ );
- general retrograde direction;
- reproducibility of cycle parameters on different parts of the complex.

Four prograde-retrograde cycles (stages) of metamorphism development were recorded as a result of studies of the composition and zoning of garnets and coexisting phases in Grt-Cpx-Pl-Qtz associations in high-pressure rocks of the Maksyutov complex (Fig. 7, Table 1). Each cycle has a certain timing and is fixed by the new formation of rock-forming phases and/or a change in their composition. Taken together, they form a single trend in the retrograde evolution of metamorphism with characteristic features for the entire complex: close values of the PT parameters of the prograde-retrograde branches of the cycle, short time intervals (~18-20 Ma) between them, periodic changes in the direction of the trend within the cycle, the pulsating nature of metamorphism in within each cycle, and the entire complex, reproducibility of cycle parameters in different parts of the complex.

PT data from successive cycles of metamorphism, obtained on the basis of the composition and zoning of garnet in the key paragenesis Grt+Cpx+Pl+Qtz, make it possible to estimate the parameters and reconstruct the thermobaric history of the development of the complex as a whole.

## Conclusions

1. In the crustal eclogites of the Maksyutov complex the unique properties of garnet were studied - within one grain/sample, it can change and maintain its composition, recording the most subtle and dramatic changes in the conditions of the metamorphic regime.

2. The combination of the high inertness of garnet to changes in its composition and high activity to the crystallization of new grains and growths makes it possible to remember the slightest changes in the PT conditions of mineral formation and reproduce the entire course of the history of the metamorphic evolution of the complex.

3. The cyclical nature of the metamorphism of the Maksyutov complex with characteristic conjugate prograde-retrograde trends in the development of each cycle has been established.

4. Four episodes of reciprocating metamorphism form a single trend in the retrograde evolution of the complex and characterize the main events at the stage of its exhumation. Each cycle has a certain timing and is fixed by the new formation of rock-forming phases and/or a change in their composition.

5. Questions remain about the causes and mechanism of the pulsating (cyclical) reciprocating regime of the formation of the complex: the speed of the exhumation process, the low power and high buoyancy of the rising plate, the constant, frequent and rapid change of the metamorphism regime within

one cycle and the complex as a whole.

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## Fedkin V.V.<sup>1</sup>, Shchipansky A.A.<sup>2</sup> Coherent processes of formation and exhumation of the maksyutov eclogite-blueschist complex (Southern Ural).

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**Annotation.** The main processes and events in the development of the subduction structure of the Maksyutov eclogite-blueschist complex (Southern Urals) are considered. The characteristics of the initial stages of the terrane formation are given: the age and geochemistry of the protolith, the tectonic position and bulk composition of the rocks involved in the subduction process, physicochemical conditions and features of the thermobaric transformations of the UHP rocks. Particular attention is

paid to the most informative coherent processes of the exhumation period. A 4-stage return-pulsation nature of metamorphism is established at the retrograde stage of the complex development. Possible reasons and conditions for the occurrence of its cyclicity in UHP conditions are discussed: the transience and no equilibrium of mineral transformations, fluid saturation and high buoyancy of submerged plates, participation in the processes of subduction initiation.

**Keywords:** *high-pressure metamorphism, thermobaric processes, Maksyutov complex, initiation of subduction, coherent processes, and PT trends in the evolution of metamorphism.*

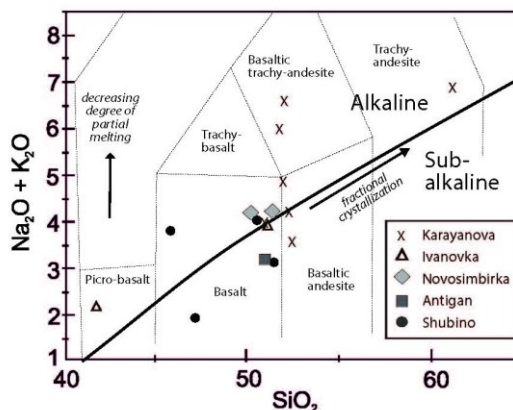
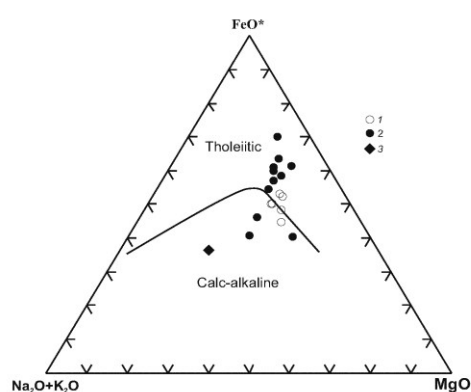
The long history of studying the Maksyutov eclogite-blueschist complex and the large amount of factual material accumulated during this time create ample opportunities for testing new geodynamic ideas in relation to established traditional ideas about the structure and history of the terrane. Such ideas include a new geodynamic concept, the “Subduction Initiation Rule (SIR)” (Whattam and Stern, 2011), which considers the processes of subduction initiation (SI) in fore-arc basins in relation to the formation of ophiolite complexes and allows, based on geochemical indicators, to establish patterns in the distribution of petrochemical rock types in time and space, and to estimate the parameters of these processes. The key issue for solving this problem is the search for geochemical criteria and geodynamic causes of subduction initiation. The solution to this problem is facilitated by the innovative development of geochemical criteria for the belonging of oceanic basalts to fragments of the earth's crust - participants in the subduction process (Pearce, 2008). In addition, our studies (Fedkin, 2020; Fedkin et al., 2021) and the works of Ural geologists (Valizer et al. 2013, 2015) showed unusual features of the metamorphism of the Maksyutov Complex at the exhumation stage - its cyclic reciprocating nature, which may be an indirect sign of SI.

The Maksyutov Complex is a unique object for

studying the SI phenomenon, since along with the diagnostic magmatic chemostratigraphic sequence of the process and ophiolite, the terrane is a reconstructed HP-UHP subduction channel. This is of primary importance for understanding the geodynamics of the SI, since the timing of HP-UHP metamorphism of the Maksyutov complex coincides with the emergence of the Magnitogorsk intraoceanic island arc in the Early Devonian (Brown, Spadea, Puchkov, et al., 2006; Puchkov, 2010).

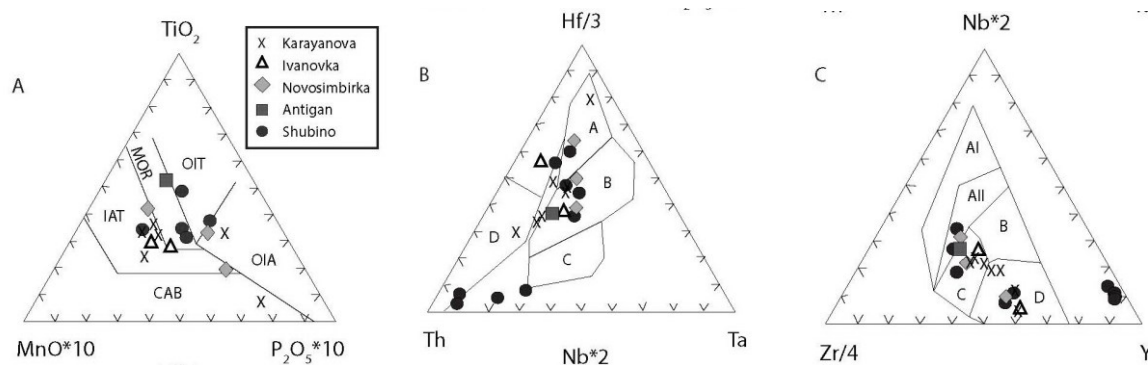
In this paper, based on precision XRF and ICP MS analyses of the bulk composition of representative samples of garnet-bearing mafic rocks of the MC, an attempt was made to review and identify the temporal, tectonic and geochemical features (indicators) of the SI process and to assess their role in the geodynamic development of the complex. The general geochemical characteristics of the protolith of high-pressure rocks of the complex were obtained from data on their composition in terms of the main rock-forming, rare and trace elements, as well as on the results of studying the composition of rare earth elements (REE).

**In terms of the main rock-forming components,** the chemical composition of the high-pressure rocks of the complex (eclogites and Grt-Cpx-Gln rocks) corresponds to the composition of basalts/gabbros with a gross SiO<sub>2</sub> content of ~ 47-52 wt% (Fedkin, et al., 2021). In AFM coordinates, the composition points of the eclogites form a single compositional trend of various petrogenetic series - tholeiitic and calc-alkaline, including both depleted and enriched compositions (Fig. 1), which indicates the origin of their protolith from different mantle sources: N-MORB and OIB, respectively. Differentiation trends of the protolith (Fig. 2) bear the features of metamorphic HP-UHP rocks and do not allow identifying a single magmatic source for them.



**Fig. 1.** Compositions of the Maksyutov complex eclogites on the AFM diagram. 1-2 – basaltic compositions: 1 – depleted, 2 – enriched; 3 – andesitic composition.

**Fig. 2.** Diagram of the ratio of alkalis and silica in the Maksyutov complex eclogites.



**Fig. 3.** Discrimination diagrams of rare and trace elements.

The data on rare and trace elements confirm the conclusions made. On the discrimination diagrams (Fig. 3) the bulk compositions of the rocks overlap the fields of ocean island basalts (OIT, OIA), the fields of N-MORB and E-MORB basalts and island-arc tholeiites (IAT), demonstrating a wide range of possible plate tectonic settings of their origin. The absence of the Eu minimum on the REE spider diagrams also indicates the metamorphic (not primary magmatic) nature of the garnet.

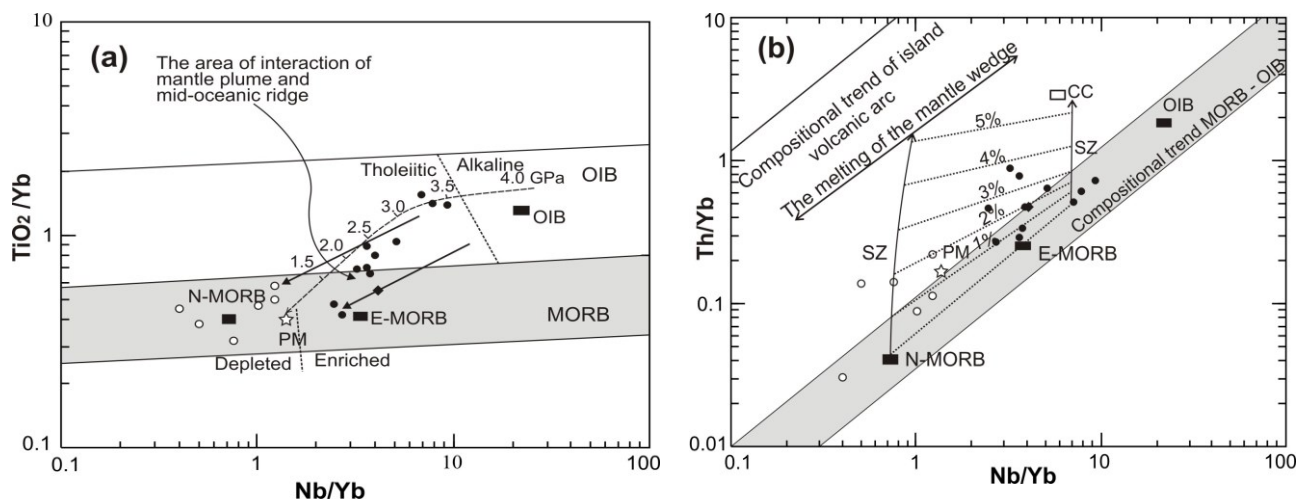
The geochemistry of rare earth elements shows that the protolith crystallized from an oceanic basaltic melt with inherited features of a subduction component and mantle-plume interaction. The enrichment of rocks in light REE also suggests a combination of subduction features with metasomatic changes in oceanic metabasalts. The absence of positive Eu and Sr anomalies, typical of intracrustal gabbro intrusions that have undergone eclogite facies metamorphism, proves that the origin of most Grt-bearing rocks was due to the transformation of basalts.

The role of mantle plumes in the initiation of MC subduction. The compositions of the Maksyutov complex eclogites reveal both depleted ( $\text{La/YbN} \sim 0.5\text{--}1.5$ ) and enriched ( $\text{La/YbN} \sim 2\text{--}4.7$ ) varieties (Shchipansky, Fedkin, Ernst, Leech, 2012). Their compositions are well interpreted by the model of interaction between an OIB-type mantle-plume source and a MORB-type depleted mantle source (Pearce, 2008). The  $\text{TiO}_2/\text{Yb-Nb/Yb}$  ratios (Fig. 4a) allow us to estimate the depths and parameters of magma generation of the complex eclogite protolith, as well as to separate depleted and enriched varieties. During interaction between a mantle-plume source of the OIB type and a depleted mantle source of MORB at depths of  $\sim 3.5\text{--}2.0$  GPa, the degree of partial melting of the OIB source increases from  $\sim 5\%$  to  $\sim 20\%$ , and at a depth of  $< 2$  GPa, N-MORB and E-MORB compositions are formed. Such interaction and distribution of enriched and depleted

compositions is characteristic of P (plume) - MORB ophiolites and is described in modern plate convergence settings (Pearce, 2008). The participation of tectonic mantle-crust inclusions in the formation of the Maksyutov complex is confirmed by the presence in its composition of ancient ( $\sim 533$  Ma) UHP ultramafic (Ol-En) and eclogite (Jd-Gross) rocks, structurally and genetically related to each other and formed at  $T > 700^\circ\text{C}$  and  $P > 3.5\text{--}4.0$  GPa (Valizer et al., 2015).

Role of crustal contamination in initiation of MC subduction. The compositions of the Maksyutov Complex eclogites demonstrate variable Nb anomalies, which indicate the absence (at  $\text{Nb/ThN} > 1$ ) or presence (at  $\text{Nb/ThN} < 1$ ) of crustal or subduction contamination. The  $\text{Th/Yb} - \text{Nb/Yb}$  diagram (Fig. 4b) is a sensitive indicator of crustal contamination or the contribution of the subduction component to the petrogenesis of mafic volcanics.

It reveals the presence of another component in the source of magma generation of the protolith of the Maksyutov Complex eclogites. Some of the depleted and enriched compositions inherit the contribution of the subduction component, which, according to model calculations, is from 1 to 4%. It is possible that such a picture may be related to the fact that the formation of the Early Devonian P-MORB ridge in the Southern Urals occurred on the oceanic lithosphere that underwent suprasubduction changes in the Ordovician time (Ryazantsev et al., 2010). Thus, the geochemistry of the eclogites of the Maksyutov complex shows that the geodynamics of the formation of their protolith cannot be reduced to any simple model. This process includes three different sources: the depleted mantle of N-MORB, the enriched mantle of OIB, and the contribution of the subduction component. Apparently, the most probable geodynamic settings where such mixing processes were realized could be fore- or back-arc areas of plate convergence.



**Fig. 4.** Compositions of eclogites of the Maksyutov complex in diagrams: a)  $\text{TiO}_2/\text{Yb}$ - $\text{Nb}/\text{Yb}$  - interaction of N-MORB and E-MORB protoliths with the mantle plume OIB (shown by arrows) and b)  $\text{Th}/\text{Yb}$ - $\text{Nb}/\text{Yb}$  - model estimates of the degree contribution of the subduction component; CC - continental crust (Pearce, 2008).

## Conclusion

1. The geochemical composition of eclogites (1), the spatial and temporal combination of eclogite and ophiolite complex formation (2), and the presence of a reconstructed HP/UHP channel (3) indicate that the initiation of Early Devonian subduction occurred on oceanic lithosphere that had undergone earlier suprasubduction changes involving crustal contamination and mantle-plume interaction.

2. The presence of boninite ophiolites in the region emphasizes the involvement of the mantle-plume mechanism in the subduction process, which developed in the suprasubduction environment of the island-arc complex.

3. The data obtained most likely indicate the subduction of the Paleo-Asian oceanic crust under the continent as the main final event in the geodynamic evolution of the complex, rather than the subduction of the margin of the East European Craton.

4. The specific reciprocating nature of the retrograde metamorphism of the complex (Fedkin, 2020; Fedkin, et al., 2021) may be an additional sign of subduction initiation.

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**Gorbachev N.S., Kostyuk A.V., Gorbachev P.N., Nekrasov A.N., Sultanov D.M. Experimental study of the influence of C-O-H-S fluid on phase relationships in basalt-(FeS+Fe) system: immiscibility of FeS+Fe-C melt, interphase distribution of siderophile elements. UDC 123.456**

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**Abstract.** The influence of fluid of C-O-H-S composition on phase relations in the basalt-(FeS+Fe) system at 1250°C, 0.5 GPa has been studied experimentally. The experiments were carried out on the gas bomb at IEM RAS in Pt ampoules lined with graphite. Mokulay basalt glass of Siberian Trappe basalt (75%), a mixture of synthetic pyrrhotite and metallic iron in a 2 : 1 ratio (21.5%), with the addition of metallic Re, Os, Co, Ni (0.5%) and S-containing oil (3%) as a source of C-O-H-S fluid were used as starting compositions. Upon melting the initial mixture, the silicate melt coexisted with the sulfide melt, which separated into Fe-sulfide (Ms) and Fe-metallic (Mc) liquids. Mc melt was enriched with strongly siderophilic elements Re, Os, with  $D_{Mc/Ms} > 1000$ , and moderately siderophilic elements Co, Ni with  $D_{Mc/Ms} < 500$ . Mc saturation of Re and Os melt with separation of excess phase of variable Fe-Re-Os composition in the Mc matrix was observed. The results of the studies showed that oil is a reliable source of C-O-H-S fluid with reducing properties, exerting an effective and complex influence on the phase composition of the ore fraction.

**Keywords:** stratification, metal, sulfide, experiment, ore, Norilsk

The melting and phase relations in the basalt-(FeS+Fe) system are of interest because unlike the Fe-S (Fei et al., 1997; Liu et al., 2001) and Fe-C binary systems (Lord et al, 2009), in which there are eutectic relations between Fe-metallic and Fe-sulfide (or Fe-carbide) phases with complete miscibility between their melts. The separation of the sulfide melt into Fe-metallic (Mc) and Fe-sulfide (Ms) melts immiscible with silicate melt (L) is observed in the Fe-S-C system.

A sensitive indicator of these processes is the distribution of Re, Os, Pt, Ni, Co between Mc and Ms melts. Geochemically, these elements are characterized by dual properties: siderophilic and chalcophilic. In Mc-L equilibria, these elements are effectively concentrated in the Mc melt with  $D_{Mc/L}$  partition coefficients reaching 3 or more orders of magnitude (Siebert et al., 2011; Mann et. al., 2012; Brenann et al. 2016;). In Ms-L equilibria, the same elements also possess chalcophilic properties with  $D_{Ms/L}$  reaching 3-5 orders of magnitude (Naldrett, 1989; Kiseeva, Wood, 2013; Mungall, Brenan, 2014). It is of geochemical interest to elucidate which properties, siderophilic or chalcophilic are predominant for each of these elements. Immiscible Mc-Ms liquids in the Fe-S-C system makes it possible to study in one experiment the distribution of Co, Ni, Re, Os, Pt between Mc and Ms melts. This will allow the chalcophilic and siderophilic properties of each of these elements to be estimated from the value of the partition coefficients  $D^i_{Mc/Ms} = C^i(Mc)/C^i(Ms)$  between Mc and Ms melts.

The paper presents the results of experimental study of phase relations and element distribution in the basalt-sulfide-C-O-H-S fluid system at 0.5 GPa, 1250°C, and discusses the influence of hydrocarbon fluid.

Experiments in the basalt-sulfide-C-O-H-S fluid system with a duration of 24 h were carried out in the IEM RAS at the high gas pressure unit with internal heating at 0.5 GPa, 1250°C, at oxygen fugacity corresponding to the C-CO-CO<sub>2</sub> buffer, using the sandwich quenching technique.

The starting materials were: finely ground glass of basalt of the Mokulaevskaya Formation of the Norilsk region (samples provided by V.A. Radko); the ore fraction consisted of a mixture of metallic iron (chemically pure reagent) and synthetic pyrrhotite of composition (wt.%): Fe = 57.06, S = 34.60 (Fe<sub>0.94</sub>S<sub>1.0</sub>) in the ratio 1 : 2. The amount of ore fraction in relation to basalt was 1 : 3. Os, Re, Ni, Co, 0.3 wt% each were added to the ore fraction to study the trace element behavior. As a source of hydrocarbon fluid, 1.5 wt.% S-bearing petroleum hydrocarbons (oil), with a sulfur content of 3.9 wt.% was added to the system (Lakhova et.al., 2022).

Products of experiments were studied on a digital scanning microscope Tescan Vega II XMU with energy dispersive X-ray spectrometer (EDS) with semiconductor Si(Li) detector INCA Energy 450 and wave dispersive spectrometer (WDS) INCA Wave 700 in Energy Plus mode (analyst A.N. Nekrasov).

The basalt part is represented by quenched homogeneous glass of silicate melt. In contrast to the starting glass composition of Mokulaev basalt after the experiment, the magnesia  $Mg^* = (MgO/MgO+FeO)$  of the silicate melt

decreases from 0.29 to 0.24, and the amount of alkali ( $\text{Na}_2\text{O}+\text{K}_2\text{O}$ ) decreases from 3.2 to 1.8 wt.%. The concentration of  $\text{SO}_3$  in the melt increases to 0.6 wt.%. In the marginal parts of the silicate part there are multiple sulfide droplets of 5-10 microns in size with signs of liquid metal-sulfide (Ms-Ms) immiscibility of the "drop-in-drop" type. The chemical composition of the droplets in wt. %: (Ms) S - 29, Fe - 63, Co - 4, Ni - 4; (Ms) Fe - 79, Co - 11, Ni - 7. Re, Os, Pt are below the detection limit.

The ore part of the quenched sample consisted of a large (up to 2 mm) sulfide drop with Ms matrix

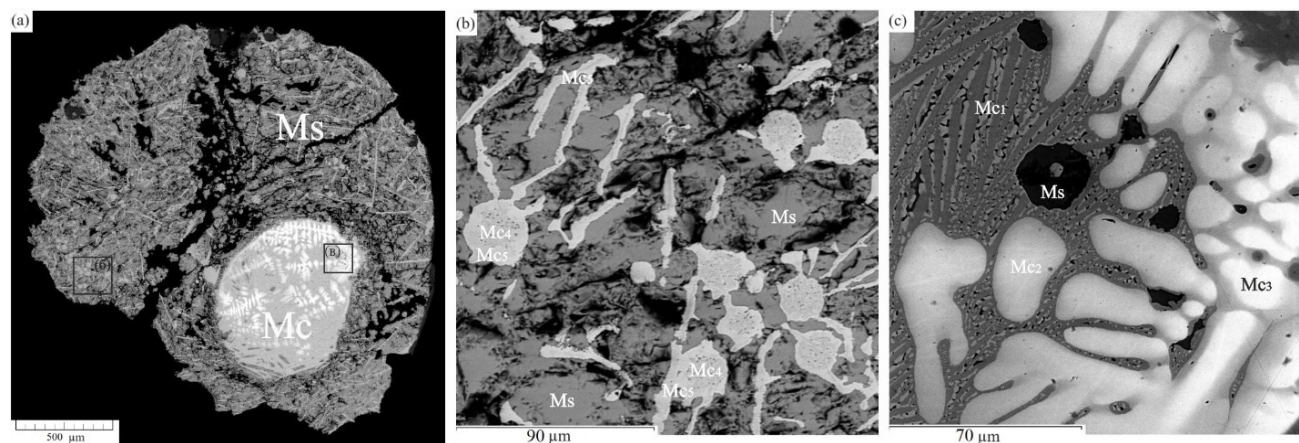
containing an oval-shaped inclusion of the main metallic phase Mc (Fig. 1a). The sulfide Ms matrix of heterogeneous composition contained quenching inclusions of Fe-metallic phase in the form of small veins and drop-shaped inclusions up to 30-40  $\mu\text{m}$  in diameter ( $\text{Mc}_4$  and  $\text{Mc}_5$ ) with high content of Ni (5-17 wt.%) and Co (9-11 wt.%) (Table 1, Fig. 1b). According to the processing of microphotographs in the Atlas program, which calculates the percentage of coexisting phases in the photo, the large sulfide-metallic drop in Fig. 1a consists of 45% of metallic phase and 55% of sulfide phase.

**Table 1.** Representative chemical compositions of coexisting phases in the ore part of the sample

| Element | Ms drop |               |               | Mc drop       |               |               | Bulk composition |       |
|---------|---------|---------------|---------------|---------------|---------------|---------------|------------------|-------|
|         | Matrix  | Inclusions    |               | Matrix        | Inclusions    |               | Matrix           |       |
|         | Ms      | $\text{Mc}_4$ | $\text{Mc}_5$ | $\text{Mc}_1$ | $\text{Mc}_2$ | $\text{Mc}_3$ | Ms               | Mc    |
| S       | 35.67   | 0.37          | 1.00          | —             | —             | —             | 24.94            | 2.30  |
| Fe      | 60.50   | 85.13         | 70.46         | 79.64         | 72.93         | 63.75         | 55.85            | 80.44 |
| Co      | 1.61    | 8.77          | 11.24         | 6.64          | 6.84          | 5.62          | 2.72             | 6.48  |
| Ni      | 1.03    | 5.34          | 16.56         | 3.26          | 3.78          | 2.96          | 3.82             | 3.46  |
| Re      | 0.21    | —             | —             | 3.80          | 7.62          | 11.45         | —                | 4.99  |
| Os      | 0.33    | —             | —             | 0.39          | 3.80          | 9.80          | —                | 1.42  |
| Pt      | 0.49    | —             | —             | 0.41          | 0.24          | 0.22          | —                | 0.24  |
| Total   | 99.83   | 99.61         | 99.26         | 94.14         | 95.21         | 93.80         | 87.38            | 99.33 |

The main Fe-metallic phase Ms in the Ms matrix consisted of matrix  $\text{Mc}_1$  with inclusions of rounded-shaped zonal inclusions of Fe-Re-Os-metallic phases  $\text{Mc}_2$  and  $\text{Mc}_3$  with variable concentrations of Re and Os (Fig. 1c, Table 2). In addition to Fe-Re-Os inclusions, the  $\text{Mc}_1$  matrix contains the products of

sulfide melt entrapment Ms. In the composition of the matrix of the main metal droplet, the  $\text{Ms}_1$  phase accounts for 43%;  $\text{Ms}_2$  - 45%,  $\text{Mc}_3$  - 12% of the total surface area of the droplet.



**Fig. 1.** BSE micrographs of the ore part of the sample. Immiscible Fe-sulfide (Ms) and Fe-metallic (Ms) melts: a) general view of sulfide-metallic drop; b) enlarged section of sulfide matrix Ms with metallic inclusions  $\text{Mc}_4$  and  $\text{Mc}_5$ , c) enlarged section of Fe-metallic drop with matrix  $\text{Ms}_1$  and inclusions  $\text{Ms}_2$  and  $\text{Ms}_3$ .

*Distribution of Ni, Co, Re, Os and Pt between Fe-metal and Fe-sulfide phases.* Table 2 summarizes the concentrations of S, Fe, Co, Ni, Re, Os, Pt (wt.%) in the Mc and Ms phases, and the partition

coefficients  $D_{\text{Mc/Ms}}$  of each element between the Ms and Ms melts.

The concentrations of Re, Os, and Pt in the Fe-sulfide phase are up to 0.5 wt.% in the Ms matrix and

are completely absent in the metal quenched phases Mc<sub>4</sub> and Mc<sub>5</sub>. The main concentration of these elements is in the metallic Mc droplet (Table 1, Fig. 1). The matrix of Fe-metallic drop Mc<sub>1</sub> is characterized by the minimum concentration of Re (up to 4 wt.%) and Os (up to 0.4 wt.%), the maximum concentration of Pt (up to 0.4 wt.%), the values of Ni and Co in all three phases Mc<sub>1-3</sub> vary insignificantly 3-4 and 6-7 wt.%, respectively. Maximum concentrations of Re (up to 12 wt.%) and Os (up to 10 wt.%) are observed in Mc<sub>3</sub>.

The partition coefficients ( $D^i$  Ms/Ms) and distribution coefficients ( $Kd^{ij}$  Ms/Ms) between Fe-metal and Fe-sulfide melts presented in Table 2 were calculated based on the composition of the sulfide matrix Ms and the bulk composition of the Mc droplet (obtained by extended probe beam analysis over the area of the Fe-metal droplet, including all three metallic phases Mc<sub>1</sub>, Mc<sub>2</sub>, and Mc<sub>3</sub>).

**Table 2.** Concentrations of S, Fe, Co, Ni, Re, Os, Pt (wt.%) in Mc and Ms phases, the partition coefficients between Ms and Ms melts, ratios and distribution coefficients of individual elements

| Element | Mc          | Ms          | D Mc/Ms  |
|---------|-------------|-------------|----------|
| S       | 2.3         | 35.67       | 0.06     |
| Fe      | 80.44       | 60.50       | 1.33     |
| Co      | 6.48        | 1.61        | 4.02     |
| Ni      | 3.46        | 1.03        | 3.36     |
| Re      | 4.99        | 0.21        | 23.76    |
| Os      | 1.42        | 0.33        | 4.3      |
| Pt      | 0.24        | 0.49        | 0.49     |
| Ratio   | in Mc phase | in Ms phase | Kd Mc/Ms |
| Re/Os   | 3.51        | 0.63        | 5.57     |
| Pt/Os   | 0.17        | 1.48        | 0.11     |
| Re/Pt   | 20.79       | 0.43        | 48.35    |
| Ni/Co   | 0.53        | 0.64        | 0.83     |

The D (Mc/Ms) of Co, Ni, Re and Os > 1 (3.36 - 4.02 - 4.3 - 23.76, respectively) increased in the sequence: Ni < Co < Os < Re. The maximum affinity for Fe-metallic phase is possessed by Re. Platinum with D (Mc/Ms) < 1 is preferentially distributed into the sulfide phase.

Phase relations of the basalt-sulfide-C-O-H-S fluid system at 0.5 GPa, 1250°C indicate partial melting with formation of heterogeneous sulfide-metallic phase with Fe-sulfide matrix and Fe-metallic phase inclusions in the ore part. Structural relations between them, the form of separation of Fe-metallic phase inclusions suggest the liquation nature of Mc and Ms phases.

The formation of stratified sulfide-metallic droplets in the basaltic melt indicates the effective

interaction of sulfur and carbon C-O-H-S fluid with silicate and Fe-sulfide melts. The ore part shows immiscible Fe-sulfide and Fe-metallic liquids. Saturation of Fe-metallic melt with ore trace elements was observed, with formation of Fe-metallic phases enriched with Re, Os, Ni, Co. Underestimated sums of analyses (94-96 wt.%) of these phases testify to carbon dissolution in metallic melts from 3 to 5 wt.%. Significant concentrations of sulfur in the metallic melt (up to 2 wt.%) and the partition coefficients of sulfur D (Ms/Ms) indicate its solubility in Fe-metallic melts.

Thus, S-containing petroleum hydrocarbons can serve as a source of C-O-H-S fluid with reducing properties, which has an effective and complex influence on the phase composition of the ore fraction in sulfide-silicate systems.

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**Kostyuk A.V.<sup>1</sup>, Gorbachev N.S.<sup>1</sup>, Nekrasov A.N.<sup>1</sup>, Brovchenko V.D.<sup>2</sup>, Novikov M.P.<sup>1</sup>**  
**Interaction of basalt melt with S-containing oil- and gas-saturated rocks (based on experimental data). UDC 123.456**

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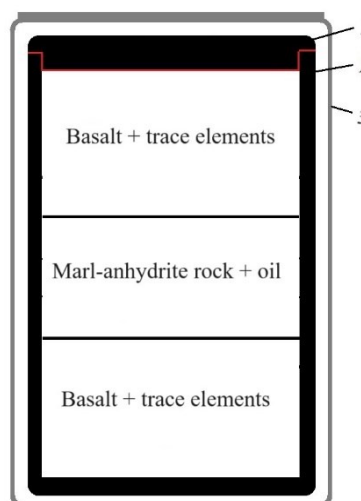
**Abstract.** The paper presents the results of experimental study of basaltic melt interaction with oil-gas-saturated sedimentary rocks of the platform cover of the Norilsk region. Experiments were carried out in the basalt–marl–anhydrite–oil system at 0.2–0.5 GPa, 1250°C on a gas bomb. The results of comparison of two systems, which differed in concentration of trace elements, pressure and presence of graphite container – an additional carbon source, are presented. Sulfide-silicate liquation of silicate melt is observed in all experiments. Sulfide immiscibility of sulfide melt on sulfide and metal liquids is observed only at 0.5 GPa in the presence of additional carbon source and trace elements. The studies indicate an important role of C-O-H-S fluid in the processes of differentiation of silicate and sulfide melts, as well as the formation of metallic and sulfide ore formation during the interaction of basaltic magmas with oil-and-gas-saturated host rocks. Experimental studies of contamination of basaltic melts with rocks of the platform cover can be used to develop a number of search criteria and prediction of sulfide magmatic deposits.

**Keywords:** contamination, basalt, sulfide, fluid, experiment

One of the actual problems related to ore formation of magmatic sulfide deposits is the interaction of C-O-H-S fluid of oil-and-gas-saturated rocks of the sedimentary cover with basaltic melt. The possibility of assimilation of "heavy" sulfur from a crustal source by magmas of ore-bearing intrusions has been considered by various scientists for a long time (Vinogradov and Grinenko, 1964; Gorbachev and Grinenko, 1973; Grinenko and Grinenko, 1974; Naldrett, 2003; Sobolev and Hofmann, 2004, etc.). However, these hypotheses met experimental (mechanism of sulfate-sulfide sulfur transformation)

and petrological (calcium problem) objections (Likhachev, 2002; Ryabov et al., 2018). The thick sedimentary cover of the Norilsk region is enriched not only with sulfur (anhydrite, pyrite), but also with carbon, the source of which is black shale, oil-and-gas-bearing and coal-bearing sediments enriched with hydrocarbon fluid. Experimental studies of basaltic melt interaction with different types of host rocks with the participation of C-O-H-S fluid will make it possible to clarify not only the physical and chemical conditions of differentiation of silicate and sulfide melts, but will also make it possible to evaluate the potential possibilities of magma interaction with oil-and-gas-saturated rocks of the sedimentary cover as a source of heavy sulfur in sulfide deposits.

The features of phase relations in the basalt–marl–anhydrite rock–C–O–H–S fluid system at 0.2–0.5 GPa, 1250°C are discussed below. The influence of petroleum hydrocarbons on the formation and liquid immiscibility of sulfide melts during the interaction of basaltic melts with sedimentary rocks is discussed.



**Fig. 1.** Scheme of sample assembly for the experiment at 0.5 GPa. 1 - graphite container, 2 - graphite container lid, 3 - platinum ampoule.

Experiments in the basalt–marl–anhydrite–rock–fluid system with a duration of 24 hours were carried out in the IEM RAS at a high gas pressure facility with internal heating at 0.2 and 0.5 GPa, 1250°C, at oxygen fugacity corresponding to the C–CO–CO<sub>2</sub> buffer, using the sandwich quenching technique. The experiment at 0.2 GPa was carried out in an AuPd ampoule, the experiment at 0.5 GPa – in a Pt ampoule using a graphite container (Fig. 1).

As starting compositions, we used finely ground glass powders of basalt of the Mokulaevskaya Formation (Mk baz) of the Norilsk District and marl–anhydrite rock (Sample17) from the sedimentary cover of the Norilsk District (samples provided by

V.A. Radko). The average chemical compositions of the initial samples are presented in Table 1. The marl-anhydrite rock contains inclusions of pyrite ( $\text{Fe}_{1.0}\text{S}_{1.8}$ ) of composition (wt.%): Fe – 45.0, S – 47.5.

The ratio of rock to basalt in the system was 1 : 4. Between 0.2 and 0.5 wt% of trace elements (Cu, Ni, Co, Os, Re, Pt, Rh, Pd, Ir) were added to the basalt to observe their behavior in the system. No trace elements were added to the experiment at 0.2 GPa. S-containing petroleum hydrocarbons (oil) from the Volga-Ural oil and gas basin were used as a source of

hydrocarbon fluid. This oil sample belongs to type A<sup>1</sup> (according to the classification of Petrov Al.A.), lies at a depth of more than 250 m in anhydrite and carbonate rocks of the Artinskian Stage of the Permian period (Petrov, 1984), contains 3.9 wt% of sulfur, 18 mg/kg of nickel (Lakhova et.al., 2022). In the experiment at 0.5 GPa, a drop of oil (about 10 wt % in the system) was mixed with rock powder and placed in the center of the sample. In the 0.2 GPa experiment, a cube-shaped piece of rock was placed in oil for 24 hours and then added in the center of the sample.

**Table 1.** Representative chemical compositions of starting materials (wt.%).

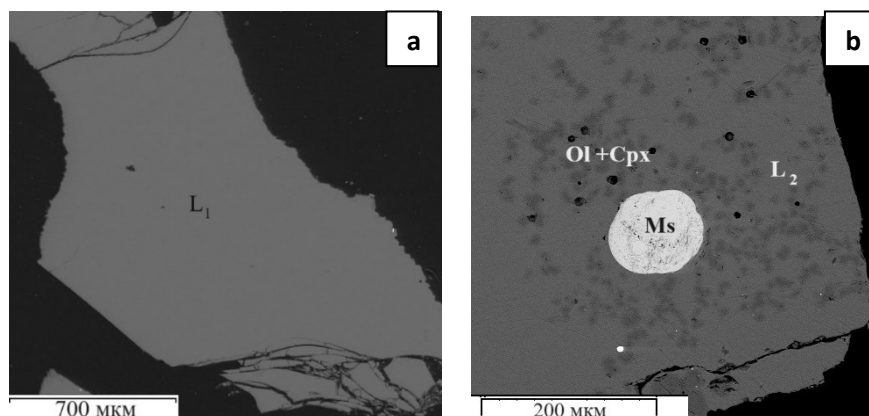
| Phase/oxide | SiO <sub>2</sub> | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | FeO   | MgO   | CaO   | Na <sub>2</sub> O | K <sub>2</sub> O | SO <sub>3</sub> | Total |
|-------------|------------------|------------------|--------------------------------|-------|-------|-------|-------------------|------------------|-----------------|-------|
| Mk baz      | 50.02            | 1.85             | 14.51                          | 14.03 | 5.85  | 10.40 | 2.50              | 0.72             | -               | 99.88 |
| Sample 17   | 45.56            | 0.52             | 13.89                          | 3.61  | 10.52 | 17.73 | 0.32              | 4.65             | 2.59            | 99.39 |

In the experiment at 0.2 GPa, the starting compositions were loaded layer by layer into an Au-Pd ampoule. In the experiment at 0.5 GPa, the starting composition were placed layer by layer into a graphite ampoule, the assembled graphite container was tightly closed with a lid, and then lowered into a platinum ampoule with a diameter of 8 mm and hermetically welded. After the experiments, the ampoules were weighed, opened by sawing lengthwise, pressed into polystyrene and polished for further study.

Products of experiments were studied on a digital scanning microscope Tescan Vega II XMU with energy dispersive X-ray spectrometer (EDS) with semiconductor Si (Li) detector INCA Energy 450 and wave dispersive spectrometer (WDS) INCA Wave 700 in Energy Plus mode (analyst A.N. Nekrasov). The wave dispersion spectrometer was used to analyze minimum concentrations of Os, Re, Ni, Co, Cu, Cu, Pt, Rh, Ir, and Pd. The studies were performed at an accelerating voltage of 20 kV, the current of absorbed electrons on the Faraday cylinder

was 82 nA, the time of spectrum acquisition on the EDS was equal to 200 seconds, the number of analyses of each sample phase was at least 10. WDS data set time: standardization 40 sec; spectrum set time for S, Fe, Ni, Co, Cu - 40 sec; for Os, Re, Pt, Pd, Rh, Ir -100 sec. Under these conditions, the detection limits with a probability of 99.73% are equal to 3 sigma. The results of the analyses were processed using the programs INCA ver. 4.06 in IEM RAS.

After the experiment in basalt-marl-anhydrite-rock-C-O-H-S fluid system at 0.2 GPa, 1250°C, the sample consisted of separate blocks of well-quenched homogeneous glassy basalt melt ( $L_1$ ) (Fig. 2a) and the same blocks consisting of Ol-Cpx association cemented by intergranular silicate melt ( $L_2$ ) with inclusions of sulfide globules (Fig. 2b). The chemical compositions of coexisting silicate phases are given in Table 2. The silicate melts of the boundary and central parts differ slightly in the concentration of alkali and iron, and their compositions are on the boundary between basalts and andesibasalts.



**Fig. 2.** BSE micrographs of a quenched sample in the basalt-marl-anhydrite-rock-oil system at 0.2 GPa: a) a section of homogeneous basaltic melt  $L_1$ ; b) sulfide droplets (Ms) surrounded by Ol-Cpx association cemented by intergranular silicate melt ( $L_2$ ).

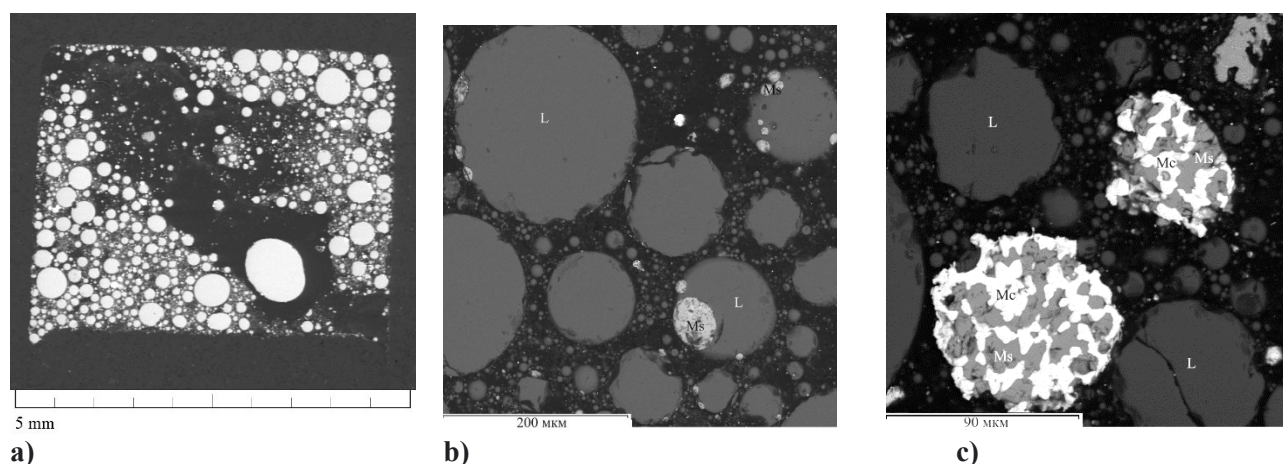
The sulfide phase is represented by multiple small drop-like secretions of 5–10 microns and rare large globules up to 100 microns in size. The sulfides are homogeneous and have pyrrhotite composition (FeS) (in wt.%): Fe – 63.57, S – 37.33.

After the experiment at 0.5 GPa, the sample partially crumbled when opened in the central part, but enough matter remained for further study. The

inner part of the graphite container is composed of basaltic melt droplets (L) (Fig. 3a.) coexisting with smaller isolated, or adjacent to silicate droplets, sulfide extractions (Ms) (Fig. 3 b, c). Silicate droplets are homogeneous and have clear contours. The composition of the melt differs slightly from the starting composition of the Mokulayev basalt; the chemical composition is given in Table 2.

**Table 2.** Representative chemical compositions of coexisting silicate phases after experiments in the basalt-marl-anhydrite-rock-C-O-H-S fluid system

| Phase          | SiO <sub>2</sub> | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | FeO   | MgO   | CaO   | Na <sub>2</sub> O | K <sub>2</sub> O | SO <sub>3</sub> | Total  |
|----------------|------------------|------------------|--------------------------------|-------|-------|-------|-------------------|------------------|-----------------|--------|
| P = 0.2 GPa    |                  |                  |                                |       |       |       |                   |                  |                 |        |
| L <sub>1</sub> | 52.07            | 1.6              | 16.10                          | 7.50  | 7.64  | 12.42 | 2.20              | 0.55             | -               | 100.08 |
| Ol             | 41.37            | -                | -                              | 10.81 | 46.40 | 0.44  | -                 | -                | -               | 99.02  |
| Cpx            | 51.36            | 0.71             | 3.21                           | 2.97  | 17.76 | 21.56 | 0.24              | 0.19             | -               | 98.00  |
| L <sub>2</sub> | 52.19            | 1.29             | 16.17                          | 4.53  | 7.82  | 11.32 | 1.71              | 2.09             | 0.23            | 97.36  |
| P = 0.5 GPa    |                  |                  |                                |       |       |       |                   |                  |                 |        |
| L              | 50.85            | 1.38             | 15.72                          | 10.22 | 6.94  | 11.40 | 2.04              | 1.38             | -               | 99.93  |



**Fig. 3.** BSE micrographs of a quenched sample in the basalt-marl-anhydrite rock-oil system at 0.5 GPa: a) general view of the sample, longitudinal section, b) homogeneous silicate and sulfide droplets, c) stratified sulfide droplets. μm

The sulfide melt is represented by both homogeneous and heterogeneous drops with the size from 10 to 100 microns (Fig. 3c). Small homogeneous sulfide droplets on the surface of silicate droplets have pyrrhotite composition (in wt.%): Fe - 57.53, S - 34.02, Ni - 2.46, Cu - 0.83, Co - 0.59, Pt - 1.32. Individual larger sulfide droplets have two- or three-phase composition with pyrrhotite matrix (Ms) of FeS composition and Fe-metal inclusions (Mc) representing by Fe-Ir, Fe-Pd or Fe-Ni alloys.

In the basalt-marl-anhydrite-rock-C-O-H-S fluid system, different degrees of melting and phase relations of the experimental samples were observed.

At 0.5 GPa, marl-anhydrite rock in interaction with basalt melt and C-O-H-S fluid completely melted, forming a homogeneous silicate melt coexisting with a heterogeneous sulfide-metallic

phase. The sulfide liquid was saturated with trace elements (Ni, Co, Cu, Pd, Ir) resulting in the separation of Fe-metallic phases from sulfide phases. Structural relations between sulfide and metallic phases, as well as the form of separation suggest the liquation nature of these formations. Concentrations of Re, Os, Rh in both silicate and sulfide and metallic melts are below the microprobe detection limit (< 0.01 wt.%), which indicates a low degree of solubility and fluid transport of these elements at given T-P parameters.

Ol-Cpx association cemented by intergranular silicate glass coexisting with homogeneous sulfide melt was formed at 0.2 GPa as a result of partial melting. The absence of metallic phases in sulfides may be related not only to the absence of trace elements in the system, but also to the lower activity of the hydrocarbon fluid associated with the absence

of an additional carbon source - the graphite container. Petroleum hydrocarbons were sufficient for formation of sulfide melt, but at the same time not enough for its stratification into sulfide and metal fluids.

The studies confirm the important role of C-O-H-S fluid in the processes of differentiation of silicate and sulfide melts, as well as the formation of metallic and sulfide ore formation during the interaction of basaltic magmas with oil-and-gas-saturated host rocks. Experimental studies of contamination of basaltic melts with rocks of the platform cover can be used to develop a number of search criteria and prediction of sulfide magmatic deposits.

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**Kuzyura A.V.<sup>1</sup>, Spivak A.V.<sup>1</sup>, Zakharchenko E.S.<sup>1</sup>, Kriulina G.Y.<sup>2</sup>, Skryabina A.V.<sup>2</sup>, Korepanov V.I.<sup>3</sup> Residual stress of trapped mineral inclusions in diamond from the**

### **Zapolyarnaya pipe by Raman spectroscopy data. UDC 552.11**

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**Abstract.** Mineral inclusions in diamond 7-5 from the Zapolyarnaya kimberlite pipe were studied using Raman spectroscopy in the planes of inclusions in the diamond and the diamond area itself. It has been shown that the trapped inclusions (olivines) are under residual stresses. The calculated residual pressure of the primary inclusions reaches up to 1.86 GPa. The host diamond itself is also experiencing residual stresses. At the same time, the distribution of residual stresses in both the trapped inclusions and the host diamond is heterogeneous. The obtained data can be used to further evaluation the PT-conditions of capture of olivine inclusions by diamonds.

**Keywords:** upper mantle; residual pressure; trapped minerals; host diamond; Raman spectroscopy; two-dimensional mapping

Diamond is a physically and chemically stable mineral formed in the mantle. In the process of growth it captures deep minerals from the common growth parental medium. After the carrying out of diamonds from the mantle depths to the Earth's surface, the difference in thermal expansion and compressibility between the diamond and the mineral inclusions captured by it from the mantle causes residual pressure around and inside these inclusions. In general cases, the volume of inclusion in diamond should become less than that occupied by the mineral filling it, after reducing the pressure and temperature to parameters currently corresponding to environmental conditions (Kagi et al., 2009). Due to the hardness and stability of the host diamond, the mineral inclusions captured by it from the mantle depths are able to preserve and "freeze" their primary chemical and isotopic properties, as well as residual pressure. The determination of residual stresses of captured minerals and the area around them is valuable information for a possible assessment of the PT conditions for the capture of inclusions and their joint crystallization with the host diamond (Kagi et al., 2009, Zedgenizov et al., 2004, S. L. Soboleva et al., 2000). It can represent both tensile and compression deformations. The residual stress can be detected with following structural-sensitive methods: Raman spectroscopy (Sobolev et al., 2000; Shobryakov, Nechaev, 2015; Korsakov et al., 2010), X-ray-diffracton (Glinnemann et al., 2003; Sobolev et al. 2000, Keizer et al., 2008), and IR spectroscopy (Navon, 1991).

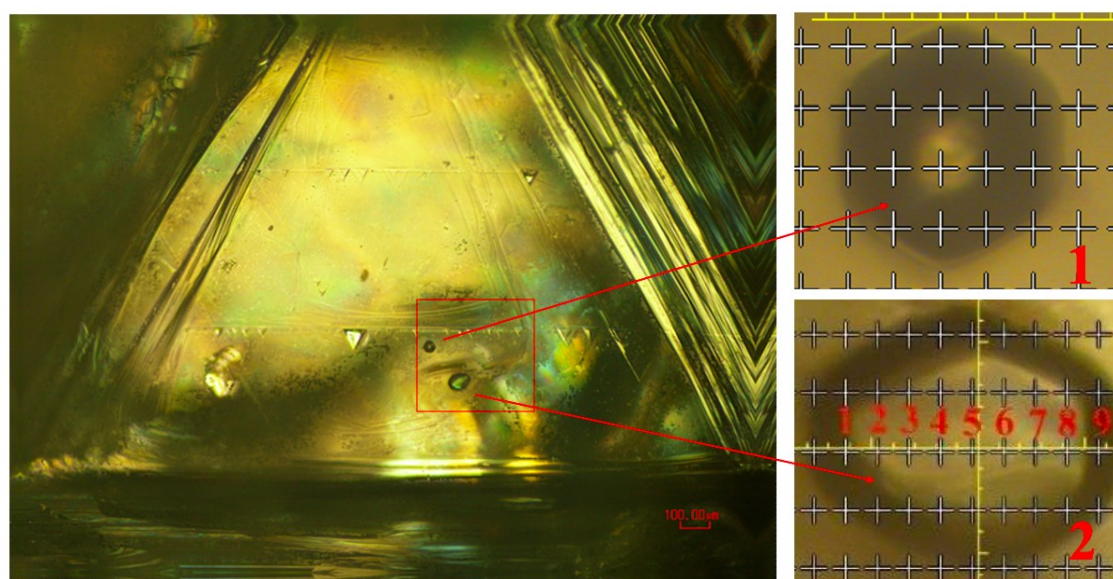
The purpose of the work was to determine the residual stress of captured minerals in diamond from

the Zapolarnaya pipe using Raman spectroscopy.

The host diamond itself can be considered practically incompressible and retains the initial volume of the inclusion, which was at the time of its formation, unlike the inclusion substance, which is highly compressible and tends to expand after pressure relief. Therefore, the Raman bands are often shifted when measuring the Raman spectrum of inclusion in a diamond under normal conditions. This indicates the presence of a frozen residual pressure in the inclusion, from which the PT conditions of diamond growth can be calculated.

A diamond crystal from the Zapolyarnaya kimberlite pipe (Yakutsk diamond-bearing province) containing monomineral primary olivine inclusions was selected for the study. Sample 7-5 is a single

crystal from a Zapolarnaya pipe, concern to the 1st octahedron according to the Orlov classification (Orlov, 1984), colorless and transparent. It has a significant degree of etching in the form of negative triangular pits. Surface corrosion is negligible. The degree of shape distortion is insignificant in the form of flattening along  $L_3$  and elongation along  $L_2$ . There are several small olivine inclusions in the intermediate zone. There are several multi-dimensional cracks, some of them are graphitized. The surface is planar, medium-layered. There are no signs of mechanical wear. There are 2 systems of traces of plastic deformation. It is important that no cracks were found around the studied inclusions in the diamonds, which may indicate the preservation of stress inside the diamond. (Fig.1).

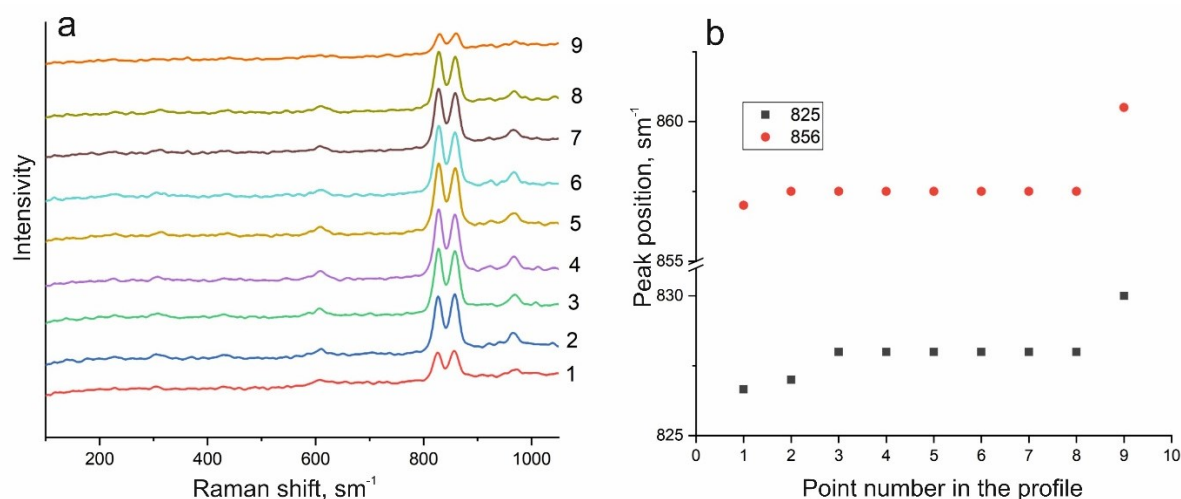


**Fig. 1.** Photo of a diamond crystal with monomineral olivine inclusions olivine -1 and -2. The photo was taken with a Nikon eclipse LV100N GSM polarization petrographic microscope, magnification 5 $\times$ . The numbers 1-9 indicate the Raman profile of olivine-2

Raman spectra in the planes of mineral inclusions and the diamond region around them were obtained using a microcombination scattering system (Bruker Senterra) equipped with a computer-controlled slide table at ISMMS RAS. Camera parameters: magnification by a wavelength of 532 nm, laser power at the discharge point -10 MW, interval 20 $\times$  (NA 0.75), shooting time 4 $\times$ 0.6 s. 256 Raman spectra were obtained around each inclusion. Figure 2 shows the Raman spectra of olivine-2 inclusion, taken along profile 1-9 (see Figure 1). The data analysis was performed in Python using *SciPy* and *NumPy* and an open source baseline algorithm. Figure 3 shows results of 256 Raman spectra processing as maps of the positions of the main diamond peak ( $\text{cm}^{-1}$ ) in the

plane of inclusion of olivine-1 and olivine -2 and the values of FWHM ( $\text{cm}^{-1}$ ) in the plane of inclusion of olivine-1 and olivine-2.

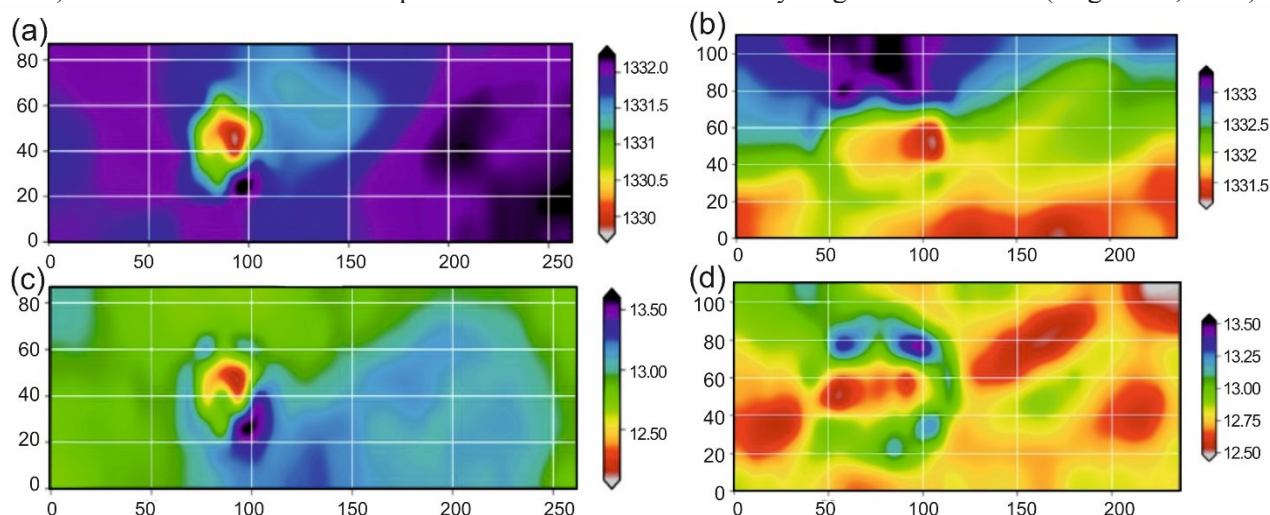
According to Raman spectroscopy data, the monocrystalline inclusion of olivine-2 experiences residual stresses, since there is a shift of the most intense modes of olivine Ag(Si-O)-str by (+2.96) – (+6.3) and Ag(Si-o)-str by (+0.6) – (+5.1)  $\text{cm}^{-1}$ . For the model composition (forsterite) the calculated residual pressure values correspond to  $\square$ 0.98 GPa for the central part, and they range within  $\square$ 0.86 -  $\square$ 1.86 GPa for the rim one (Liu Lin-Gong, Mernagh, 1993). A higher value of the residual stress is observed at the inclusion-diamond boundary.



**Fig. 2.** Raman spectra (a) and the position of the main peaks of olivine ( $\text{cm}^{-1}$ ) (b) along the profile (inclusion of olivine - 2) (see Fig.1).

Analogue pressure values in stressed olivine inclusions in diamond from Udachnaya pipe were obtained by Izraeli with co-authors (Izraeli et al, 1999). Their calculated residual pressure in several

olivine inclusions was 0.13 – 0.65 GPa. The residual pressure is 0.69 GPa around the inclusion of olivine in a diamond from Internationalnaya pipe was defined by Kagi and co-authors (Kagi et al., 2009).



**Fig. 3.** Mapping of the main diamond peak positions ( $\text{cm}^{-1}$ ) in the plane of inclusion of olivine-1 (a) and olivine-2 (b) and the values of FWHM ( $\text{cm}^{-1}$ ) within the plane of inclusion of olivine-1 (c) and olivine-2 (d).

According to Raman spectroscopy data, the monocrystalline inclusion of olivine-2 experiences residual stresses, since the shift of the most intense olivine modes  $\text{Ag}(\text{Si-O})\text{a-str}$  to  $(+2.96) - (+6.3)$  and  $\text{Ag}(\text{Si-O})\text{s-str}$  to  $(+0.6) - (+5.1)$  ( $\text{cm}^{-1}$ ) is observed. For the model composition (forsterite), the calculated residual pressure values correspond to  $\square 0.98$  GPa for the central part, and for the marginal part they range from  $\square 0.86$  -  $\square 1.86$  GPa (Liu Lin-Gun, Mernagh, 1993). A higher value of the residual stress is observed at the inclusion-diamond boundary.

Such pressure values in stressed olivine inclusions in diamond from the Udachnaya pipe were

obtained by E. Izraeli with co-authors (Izraeli et al, 1999). Their calculated residual pressure in several olivine inclusions was 0.13 – 0.65 GPa. The residual pressure is 0.69 GPa around the inclusion of olivine in a diamond from pipe Internationalnaya was defined by Kagi and co-authors (Kagi et al., 2009).

Using an equation of the dependence of the residual stress pressure value on the frequency shift of the main diamond peak (Di Liscia et al., 2013), the residual stress values of the diamond were calculated. In the olivine-1 inclusion region, this value ranges from -0.60 to 0.07 GPa, and in the olivine-2 inclusion region from -0.1 to 0.41 GPa. In this case, the

maximum values of FWHM (cm<sup>-1</sup>) are fixed along the boundary of inclusions.

As a result of preliminary studies, it was shown that the prisoner inclusions (olivines) are under residual stresses. The calculated residual pressure of primary inclusions at the boundary with the host diamond reaches 1.86 GPa. The host diamond itself also experiences residual stresses up to ~0.6 GPa. At the same time, the heterogeneity of the distribution of residual stresses is noted both in the trapped inclusions and in the host diamond, which does not contradict the presence of traces of plastic deformation.

Researchers remark (Kagi et al., 2009, Bardukhinov et al., 2016) that many minerals, in particular olivine, found as inclusions in diamonds, demonstrate thermoelasticity, which shows a small residual pressure after the diamond has been transported to the Earth's surface. In this regard, it is assumed that the calculation of PT- conditions of capture by one trapped olivine in diamond crystal is ineffective due to the influence of various variable factors.

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- Kuzyura A.V.<sup>1, 2</sup>, Kriulina G.Y.<sup>2</sup>, Spivak A.V.<sup>1</sup>, Zakharchenko E.S.<sup>1</sup>, Skryabina A.V.<sup>2</sup>, Golunova M.A.<sup>1</sup>, Sharapova N.Y.<sup>1</sup> Inclusions in diamonds of the Zapolyarnaya pipe (Yakutia) by Raman spectroscopy data. UDC 567.6, 568.1, 551.79**
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- Abstract** A diamond crystal from the Zapolyarnaya pipe in the Yakutian diamond-bearing kimberlite province has been studied using Raman spectroscopy. More than 20 different types of inclusions have been identified within it. Among the identified mineral phases, garnet is dominant, with other minerals including rutile, carbonates such as calcite and magnesite, pyroxenes such as omphacite and diopside, and sometimes in association with calcite. Based on the composition of the garnets, a mineral composition has been calculated. In the garnet inclusions studied, pyrope makes up the majority (0.40-0.47), followed by almandine (0.33-0.41) and grossular (0.19-0.21) components. These inclusions are believed to be related to peridotite paragenesis. Quantitative evaluation of the contents of the major components and the calculation of magnesia number of clinopyroxenes demonstrate a difference in origin, phases of both peridotite paragenesis and those characteristic of eclogite were revealed.
- Keywords:** *Raman spectroscopy, diamonds, inclusions, Zapolyarnaya pipe, garnets, clinopyroxenes, carbonates, peridotites, eclogites*
- Mineralogical studies of primary inclusions indicate that the parent medium is multicomponent, heterogeneous and variable in chemical and phase compositions (Shrauder, Navon, 1994; Garanin et al, 1991; Garanin, 2017; Stachel, 2001; Zedgenizov et

al, 2007, 2015; Logvinova et al., 2019 and others). To date, a large amount of mineralogical data on inclusions in diamonds from various deposits has been accumulated, obtained during complex analytical studies of both "open" and "closed" inclusions. Raman spectroscopy is widely used to study "closed" inclusions – one of the non-destructive methods available for the study of materials. Due to Raman spectroscopy data, it is possible to obtain high-quality information about the phase composition, as well as the structural characteristics of the material under study. In addition, various techniques have recently been developed that allow the chemical composition to be estimated using Raman spectroscopy data (Huang et al, 2000; Lyalina, 2000; Wang et al, 2001; Bersani et al, 2009; Ishibashi et al, 2012; Smith, 2015; Kalugina et al, 2023).

The aim of this work is to study inclusions in diamonds from the Zapolyarnaya pipe of the Yakutian diamond-bearing kimberlite province using Raman spectroscopy.

The object of the study was a diamond crystal with association of inclusions from the Zapolyarnaya kimberlite pipe (Yakutian diamondiferous kimberlite province). The crystal is colorless and transparent, of a combinational shape with the faces of an octahedron and a dodecahedron of the I variety according to the classification of Yu. L. Orlov (Orlov, 1973) with a slight protomagmatic cleavage of one vertex. The size of inclusions varies in the range of 10-250 microns.

Diamond and inclusions were described using binocular ADF STD16 and polarizing Nikon Eclipse LV100Npol microscopes.

The Raman spectra were measured in the backscattering geometry on an installation consisting of an Acton SpectraPro-2500i spectrograph with a cooled to -70 °C CCD Pixis2K detector and an Olympus microscope. A continuous solid-state single-mode laser with a wavelength of 532 nm and diode pumping was used to excite the Raman. The laser beam was focused on the sample using an Olympus 50 lens into a spot of ~5 mm in a diameter. The laser radiation line in the scattered beam was suppressed using an optical super-notch filter with an optical density of OD=6 and a bandwidth of ~160 cm<sup>-1</sup>. The signal accumulation time was 540sec (3×180sec). Fityk 1.3.1. and OriginPro 2021 software were used for data processing. The identification of the phases of inclusions by Raman spectra was carried out using the CrystalSleuth software and the RRUFF Project database (Lafuente et al, 2015).

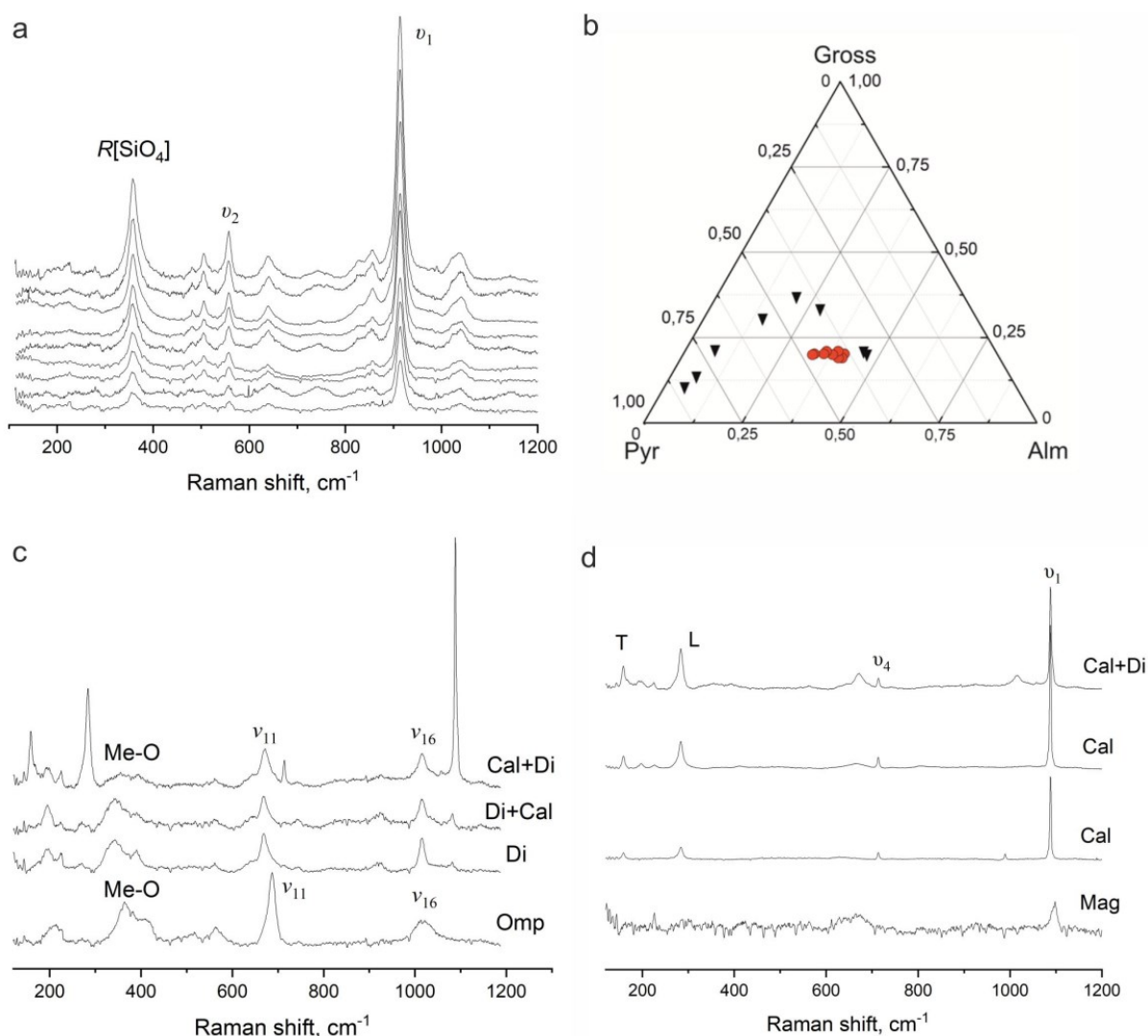
More than 20 different inclusions were found in

the crystal, varying in colour, shape and size. High-quality RAMAN spectra were obtained from eight inclusions. Some of the inclusions are polyphase accretions. Among the identified mineral phases, most are garnets, the inclusion of garnet together with rutile, several inclusions of carbonates, pyroxenes and their accretions were also found.

Garnet inclusions are related to the pyrope-almandine series, according to Raman spectroscopy data (Fig. 1a). The analysis of the obtained Raman spectra in this work showed that the position of the main peaks is in the range for  $\nu_1$  – 913.6-914.4, and for  $R[\text{SiO}_4]$  – 357.2-357.2 cm<sup>-1</sup>. The calculation of the minerals according to the method described by Lyalina [Lyalina, 2000] revealed the predominance of pyrope (0.40-0.47) mineral over almandine one (0.33-0.41), with the content of grossular one - 0.19-0.21.

Clinopyroxenes from inclusions in diamond are represented by omphacite and diopside, including in association with calcite, according to Raman spectroscopy (Fig. c). The most intensive and characteristic modes are Me-O translation in the range of  $\square$  300-500 and Si – O<sub>br</sub> ( $\nu_{11}$ )  $\square$  670, Si – O<sub>br</sub> ( $\nu_{16}$ )  $\square$  1000 cm<sup>-1</sup> valence vibrations. The magnesia number (mg#) of inclusions was estimated from the position of bands corresponding to translational Me-O and valence Si – O<sub>br</sub> vibrations (Wang et al, 2001). The calculated values of mg# were 0.44-0.45 and 0.37 for different clinopyroxene inclusions, which are characteristic of peridotite and eclogite paragenesis. Quantitative assessment of the contents of the main components (CaO, MgO, Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>) for mantle clinopyroxenes using the Raman spectroscopy method (Kalugina et al, 2021) also showed a difference in the composition of these inclusions. Values typical for peridotite paragenesis are: CaO – 17.48-19.94, MgO – 16.78-19.62, Na<sub>2</sub>O – 1.46-2.93, Al<sub>2</sub>O<sub>3</sub> – 0.42-3.87 by wt. %; and values of eclogite paragenesis are: CaO – 8.03-9.68, MgO – 5.78-6.42, Na<sub>2</sub>O – 7.36-8.67, Al<sub>2</sub>O<sub>3</sub> – 15.94 – 16.15 wt.%.

Carbonates were identified in three inclusions: single phase inclusion, in association with wollastonite and clinopyroxene. According to Raman spectroscopy, carbonates in inclusions are represented by calcite and magnesite (Fig. 1 d). It should be noted that some inclusions are surrounded by a system of cracks, while cracks have not been detected on the crystal surface. At the same time, the inclusion of calcite and diopside intergrowth has no visible cracks and other signs of plastic deformation, which indicates the primary preservation of this inclusion.



**Fig 1.** Raman spectra of inclusions in diamond from the Zapolyarnaya pipe: (a) garnets, (c) clinopyroxenes and (d) carbonates; (b) triple diagram of the garnets compositions of pyrope-grossular-almandine series from inclusions of the Zapolyarnaya pipe. Symbols: red circles – this work, black triangles – (Bardukhinov et al., 2018); Pyr – pyrope, Gross – grossular, Alm – almandine.

Thus, the most of the studied inclusions are related to peridotite paragenesis, which is consistent with the previously obtained data on the study of the defective impurity composition of the diamond collection from the Zapolyarnaya pipe (Vyatkin et al., 2021). However, clinopyroxene (Omp) inclusions identified in the studied diamond may be related to eclogite paragenesis. This can be a consequence of a complex multi-stage history of diamond crystal growth, including the evolution of parental diamond-forming medium. The possibility of ultrabasic-basic evolution of magmatism and petrogenesis of peridotite and eclogite rocks of the Earth's upper mantle was previously substantiated theoretically and experimentally (Litvin et al., 2019). The obtained results on carbonate phases in inclusions confirm their important role in diamond crystallization and are another mineralogical evidence of the mantle-carbonatite concept of diamond genesis and syngenetic phases (Litvin et al., 2016).

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