# Mineral equilibria at high PT-parameters

## Chertkova N.V., Spivak A.V., Zakharchenko E.S., Safonov O.G. The structure of oxalic acid dihydrate at high pressures and elevated temperatures: spectroscopic investigation in a diamond anvil cell. *UDC 550.41*

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**Abstract.** Oxalic acid dihydrate ($(COOH)_2{\cdot}2H_2O$) is widely used in the petrological studies as a fluid source for experiments simulating the interaction between rocks and minerals and deep C-O-H fluid. In this work, the phase transitions of oxalic acid dehydrate were investigated at pressures above 10 GPa and temperatures up to 250 °C in a diamond anvil cell using Raman spectroscopy. The results indicate that, at high pressure, the stability regions of the solid phases in this system extend into the higher temperature range.

***Keywords****: experiment; high pressures; C-O-H fluid; oxalic acid dehydrate; phase transitions*

Due to its unique chemical and physical properties, oxalic acid dihydrate has been widely used in experiments aimed at studying geochemical reactions involving rocks and minerals as a source of fluids rich in carbon, oxygen and hydrogen. However, there is a lack of experimental data on the changes in the structure and dissociation order of this compound under conditions corresponding to the depths of the Earth's crust and mantle.

The purpose of this work was to study the structure and stability fields of high-pressure phases of oxalic acid dihydrate at elevated temperatures.

Experiments were carried out using an externally heated, piston-cylinder-type diamond anvil cell at the Mantle Laboratory of the D.S. Korzhinskii Institute of Experimental Mineralogy of the Russian Academy of Sciences. Crystalline oxalic acid dihydrate (99% purity, $(COOH)_2{\cdot}2H_2O$) was used as the starting material for the experiments. During the experiments, the cell was placed in a cooling unit with circulating water and purged with a gas mixture of 98% argon and 2% hydrogen. The entire setup was positioned under an optical microscope equipped with a digital camera and connected to a Raman spectrometer. Upon heating of high-pressure cell, both photographs and Raman spectra were recorded to monitor changes in the sample. Raman spectra were collected in backscattering geometry using a continuous-wave solid-state laser with a wavelength of 532 nm.

The Raman scattering spectrum of the sample placed in a diamond anvil cell at room temperature and atmospheric pressure is shown in Figure 1. Prominent bands are observed near ~480 cm$^{-1}$ and ~850 cm$^{-1}$ in the Phase I spectrum, as well as in the 3420–3460 cm$^{-1}$ range, which correspond to C–C vibrational modes and $H_2O$ stretching modes, respectively (Ebisuzaki and Angel, 1981; Mohaček-Grošev et al., 2009). When the pressure in the cell was increased to 10 GPa, a phase transition to phase IV occurred, accompanied by distinct changes in the Raman spectrum (Figure 2). New intense bands appeared near ~950 cm$^{-1}$ and ~1580 cm$^{-1}$, associated with the vibrations of C–COO and $CO_2$ (Bhatt et al., 2016), while intensity of the $H_2O$ bands in the region of 3420-3460 cm$^{-1}$ decreased significantly. When the sample was heated to 250 °C, no new phase transitions or fluid phase release were observed. The Raman scattering spectrum recorded at this temperature corresponds to Phase IV. After cooling the sample to room temperature and releasing the pressure, a reverse phase transition to solid Phase I was recorded (Figure 2).

Previous studies conducted at atmospheric pressure have shown that heating of oxalic acid dihydrate leads to the loss of crystallographically bound water and the formation of anhydrous oxalic acid. At higher temperatures, oxalic acid undergoes thermal decomposition, releasing $CO_2$ under oxidizing conditions (FMQ buffer) (Holloway et al., 1968; Morgan et al., 1992), and $CH_4$ and $H_2$ under reducing conditions (Mo–$MoO_2$ buffer) (McCubbin et al., 2014).

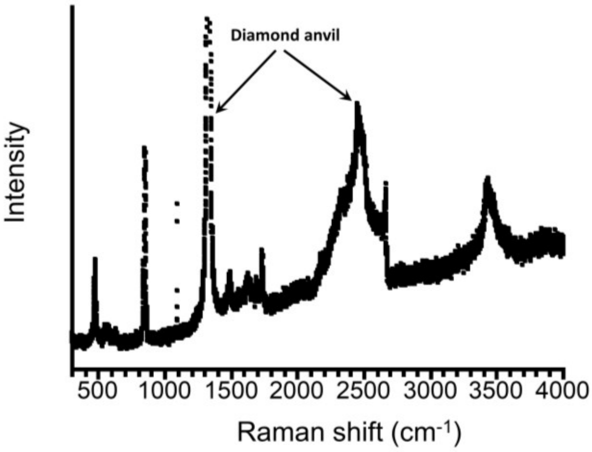

**Fig. 1**. Raman spectrum of oxalic acid dihydrate under atmospheric conditions**.**

In the present study, conducted at pressures exceeding 10 GPa, no fluid phase release was observed within the temperature range up to 250 °C. This indicates that at high pressure, the stability fields of solid phases of oxalic acid dihydrate expand toward higher temperatures. The structural transition to Phase IV is characterized by a reorientation of hydrogen bonds, leading to the strengthening of hydrogen bonding between the $CO_2$ group of the oxalate and $H_2O$, which is crucial for the stability of this phase under extreme conditions (Bhatt et al., 2016).

Since oxalic acid dihydrate serves as a model compound for studying phase transitions and interactions between fluids, rocks, and minerals under various redox conditions, the experimental results obtained should be taken into account in high-pressure petrological studies aimed at investigating the carbon cycle and behavior of volatiles in deep geological systems.

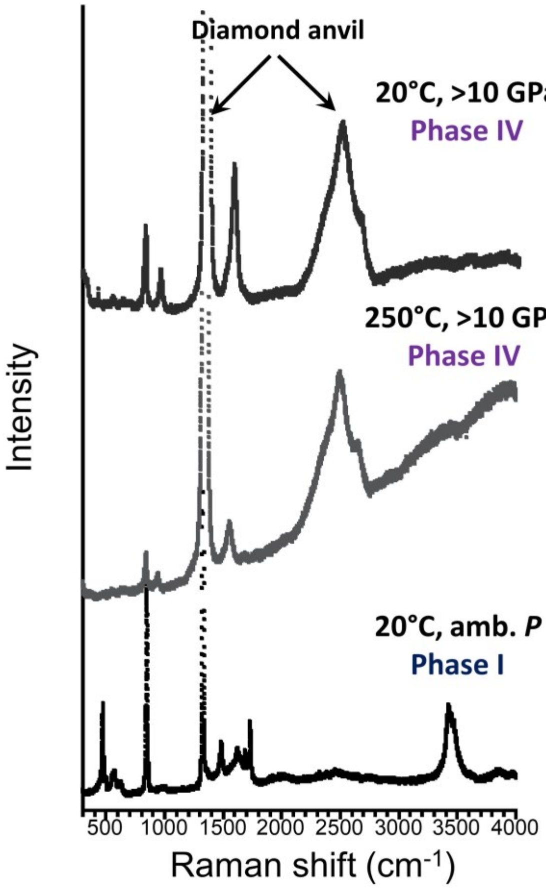

**Fig. 2.** Raman spectra of the sample recorded during experiment in an externally heated diamond anvil cell.

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## Fedkin V.V. Subduction of the Maksyutov eclogite-blueschist Complex: regularities and questions.

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**Abstract.** Using the Maksutov eclogite-blueschist complex (MC) in the Southern Urals as an example, new model concepts of the origin and development of crustal eclogite subduction were tested. The latest geodynamic concept of the "Subduction Initiation Rule" (SI) (Whattam, Stern, 2011) is considered in conjunction with recent studies of the geochemistry of oceanic basalts as applied to solving geodynamic problems (Pearce, 2008). In light of these innovative developments and new analytical data on the composition of rocks and minerals of the MC (Fedkin et al., 2021), the proposed concept was adapted to a specific complex in order to create a universal model for the origin and development of subduction processes in comparison with traditional concepts of the formation of crustal eclogites. Studies have shown that the main criteria and signs of subduction initiation are clearly manifested in the MC and can be used as a universal scheme for the formation of such systems. However, revision and interpretation of the available data within the framework of new patterns reveals a number of controversial issues in the history of MC development, complicating the perception of the established rules as a universal model. It is assumed that these features are random, reflect the specifics of a given region and do not affect the general principles of the origin and development of subduction. However, they require additional attention and clarification, since they affect the fundamental moments of the terrane formation: the issues of time and duration of the complex formation, the subduction polarity of its development, the features of prograde and retrograde metamorphism, the source and origin of the HP/UHP index of minerals - diamond, coesite, etc.

***Keywords**: Maksyutov Complex, eclogite, subduction initiation, HP/UHP metamorphism, mineral equilibria, geodynamics, PT development trend.*

**"The rule of subduction initiation" (SI)** (Whattam, Stern, 2011) considers the processes of subduction initiation in fore-arc basins in relation to the formation of ophiolite complexes, and the formation of a diagnostic magmatic chemostratigraphic sequence in them. The main criteria of the SI: temporal and spatial combination of the eclogite and ophiolite parts of the complex, a clear chemostratigraphic sequence of rocks, the presence of a reconstructed HP/UHP subduction channel are clearly expressed in the MC, which allows us to consider the Maksyutov complex a unique object for testing new developments as a general model for the formation and development of subduction processes. Nevertheless, some features of the structure and development of the complex (geochemical, petrological, geodynamic) make it difficult to perceive the proposed IS Rules as a universal scheme of their development. Even the “unique conditions” of the MC raise a number of controversial issues, most likely related to the characteristics of the orogen than to the general criteria of IS.

**Geochemical studies of high-pressure MC rocks,** carried out on a wide range of chemical elements (including HFSE and LILE) (Fedkin et al., 2021), and their interpretation in accordance with the “IS Rules” and geodynamic affiliation (Pearce, 2008) make it possible to clarify some controversial structures of the terrane and identify new aspects of its structure and development. The available geochemical data on the composition of HP/UHP MC rocks are quite traditional. They complement the main features of the IS, characterize the subduction conditions and create certain prerequisites for its occurrence. A characteristic feature of the MC rocks is a wide variation in their composition both in major elements (in particular, in SiO2: from 41.8 to 61.12 wt.%) and in rare and trace elements (from ocean island basalts (OIT, OIA) to island arc tholeiites (IAT) and N-MORB and E-MORB basalts). Basalts form a continuous evolutionary series from tholeiitic to calc-alkaline composition. Such a variation in the compositions of the eclogite rocks of the complex and the geodynamic diversity of their origin require at least a three-component source of the original material: enriched OIB mantle, depleted N-MORB and E-MORB type mantle and some contribution of the subduction component (crustal contamination). In this regard, the question arises about the time of the beginning of its accumulation (the beginning of subduction) and the duration of the existence of the Maksyutov complex, possibly from the early Paleozoic to the Devonian (Dobretsov et al., 1996).

**The most important feature of the composition of high-pressure rocks of the MC is their enrichment in niobium** with the formation of so-called Nb-enriched basalts (NEB), which is an indicator of the subduction of oceanic ridges. On this basis, the idea of reconsidering the polarity of the MC subduction from east to west arises (Ryazantsev, Tolmacheva, 2016). The main event in the geodynamic evolution of the MC in this case is the subduction of the Paleo-Asian oceanic crust under the continent, and not the subduction of the margin of the East European Craton under the Magnitogorsk island arc (Puchkov, 2010).

In parallel, **the question of the participation of crustal contamination in the IS arises.** Geochemical data on the HP/UHP composition of MK rocks for rare and trace elements (Fedkin et al., 2021) in accordance with model calculations (Pearce, 2008) determine the contribution of the subduction component in MK rocks from 1 to 4%. It is not yet clear whether this component was in the composition of MK rocks at the beginning of the subduction process or it appeared during the development of the complex. But the calculations clearly indicate its participation in subduction. Perhaps its presence is associated with supra-subduction changes in the oceanic lithosphere during the formation of the Early Devonian P-MORB ridge in the Southern Urals in Ordovician time (Ryazantsev et al., 2008). This is also indicated by the spatial proximity of boninite ophiolites in the west of the Magnitogorsk zone.

One of the most difficult issues of the formation of the Maksyutov complex remains **the issue of the evolution of metamorphism during the subduction and exhumation of the terrane.** There are two points of view regarding the main stage of eclogite metamorphism of the MK - Early Paleozoic - 533±4.6 million years (Dobretsov et al., 1996), and Late Paleozoic - 375-390 million years. Some researchers see this as a two-stage development of the complex. (Shatsky et al., 1997, Valizer et al., 2015). However, recently a kind of consensus has been reached on this issue - 390 million years.

The maximum parameters of metamorphism obtained by the methods of phase correspondence and mineralogical thermobarometry reach T=800-910 $^{o}$C and P~3.5-4.0 GPa (Valizer et al., 2015; Fedkin et al., 2021). However, the main feature of MK metamorphism is not the extremely high parameters, but its cyclical reciprocal pulsating nature, when the phenomena of the prograde and retrograde stages are repeated many times, and the PT trends constructed from the compositions of the Grt-Cpx-Pl-Qtz paragenesis form conjugate pairs that characterize the modes of individual cycles of terrane development (Fedkin, 2020). At least four such cycles have been recorded according to microprobe studies of the composition of coexisting phases in the Grt+Cpx+Pl+Qtz paragenesis (Table 1).

**Table 1.** Generalized RT trends of prograde-retrograde stages (cycles) of development of the Maksyutov eclogite-blueschist complex (Fedkin, 2020).

| № | Prograde Trends | Retrograde Trends | Age, Ma* |
|---|---|---|---|
| 1. | T=800→900 °C, P=3,5 GPa | T=910→730 °C, P=3,5 GPa | 515-533 [1] 385 [2] |
| 2. | T=500→790 °C, P=2,5→3,0 GPa | T=740→610 °C, P=2,5→1,4 GPa | 360 [1, 2] 360-380 [3] |
| 3. | T=460→680 °C, P=1,1→1,5 GPa | T=690→430 °C, P=1,3→1,0 GPa | 335 [2] |
| 4. | T=310→515 °C, P=0,9→1,2 GPa | T=545→310 °C, P=1,0→0,6 GPa | 310-315 [2] |

*) Age determinations are given according to the data: 1. Valizer et al., 2013, 2. Beane, Leech, 2007, 3. Dobretsov et al., 1996.

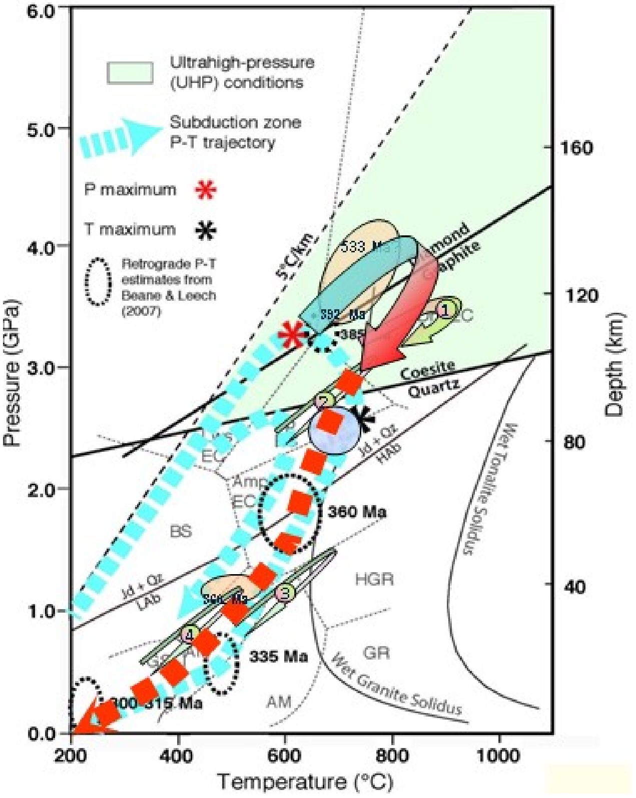

**Fig.1.** Physicochemical conditions for the formation of the Maksyutov complex.

PT tracks of 4 stages together form a general trend of prograde-retrograde evolution of the complex, characterizing the main events of its development (Fig. 1). The intervals of PT parameters of prograde and retrograde trends at each stage practically coincide, recording a change in the direction of metamorphic evolution. The time interval of inversion, as a rule, does not exceed 20 million years, which indicates the rapidity of the pulsation process. It is characteristic that the conjugate trends of metamorphism stages are repeated in almost each of the five studied areas of the complex, sometimes simultaneously recording several cycles in one outcrop and even in one sample. At the same time, the geochemical spectrum of eclogites for rare and dispersed elements in all areas shows a constant ratio of depleted and enriched compositions (in a proportion of ~1:2), regardless of the degree of metamorphism, which indicates a single process of complex formation in time and space. Prograde thermal zoning of garnet in the Grt-Cpx paragenesis is statistically observed 4 times more often than retrograde zoning, which reflects the main tendency of prograde subsidence of the slab against the background of less significant moments of step-by-step emersion. Traces of these temperature transformations are recorded in the composition of zonal garnet in the Grt+Cpx+Pl+Qtz paragenesis. Prograde stages of the 4th, 3rd and 2nd cycles (Table 1, Fig. 1) form a generalizing PT trend of subduction prograde subsidence, which ends with the parameters of the 1st cycle, at which inclusions of ultramafic (Ol-En) and eclogite (Jd-Gros) UHP rocks are formed in the lower unit of the MC. Their ancient age (~533 Ma) and maximum formation parameters at T>700 °C and P>3.5-4.0 GPa (Valizer et al., 2013, 2015) stand apart and sharply differ from the general line of previous events. Since there are no adakites in MC, the products of initial slab melting, the origin of ultramafic inclusions is most likely associated with **mantle-crust interaction at the subduction peak and tectonic eject as part of a mantle plume.**

**Mantle-crust interaction** is well interpreted by the ratio of rare and trace elements in the composition of MC rocks. Calculations using Pearce diagrams (Pearce, 2008) show that the interaction of

a mantle plume with a depleted mantle for MC rocks begins at P from 3.5 GPa (Shchipansky et al., 2012). In the range of P from 3.5 to 2.0 GPa in the OIB source there is an increase in the degree of partial melting from 5% to 20%, where N-MORB and E_MORB melts are formed. Thus, the maximum subduction parameters at P~3.5 GPa limit the stability region of the HP rocks of the complex, reducing the probability of the appearance of diamond in them - the main ghost of the UHP conditions of the MC. Findings of diamond in the MC rocks, which are usually associated with ultramafic inclusions and high parameters of their formation, therefore cannot be a sign of the UHP level of MC subduction, since its origin is not the result of the prograde evolution of metamorphism.

**As for diamond, cases of its findings in MC rocks are quite rare** and are not always confirmed instrumentally. Only 2-3 nanosized grains in two eclogite samples in the form of inclusions in garnet were studied by Raman spectroscopy (Bostick et al., 2003). Our repeated attempts to expand such a search at the same university, using similar equipment, were unsuccessful. **References to isolated diamond finds in concentrates** cannot be reliable evidence of its origin as a result of prograde metamorphism. **Cuboids graphite formations** (Leech, Ernst, 1998) usually form at low temperatures and are not associated with diamond graphitization (Korsakov et al., 2019). As a result, the origin of diamond in MK rocks - metamorphic, arising during subduction, or captured by a mantle plume in ultramafic inclusions - remains questionable. **Coesite is very rare in eclogites** and the supposed pseudomorphs of quartz based on it (Chesnokov, Popov, 1965) are also not convincing. **Thus, the ultra-high-pressure (UHP) conditions of the formation of the Maksyutov complex have not been reliably proven and require clarification** (Dobretsov et al., 1996; Korsakov et al., 2019).

**The causes of the emergence and development of cyclic recurrent-pulsation metamorphism** are not yet entirely clear. The presence of mineral zoning and PT trends of different directions, temperature levels and scales (from an individual sample to a local area and the complex as a whole) in the rocks of the complex indicates the incompleteness of the metamorphic processes due to frequent changes and short-term conditions of local (mosaic) equilibrium. Perhaps the cause of this phenomenon was periodic collisions of plates of different polarity and status (submerged or emerging) with short-term and frequent changes in the direction of their movement, which made it possible to propose the idea of a global change in the polarity of the subduction of the complex from east to west (Ryazantsev, Tolmacheva, 2016). Geochemical and petrological features of the MC: the joint presence of depleted and enriched eclogite compositions, Nb-enriched and Nb-under saturated rocks, samples with prograde and retrograde zoning of minerals at each stage of the complex's development, support this possibility. But in general, the idea of a fundamental change in the direction of subduction of the entire terrane requires clarification and analysis of more general causes of this process. These could be the rate of subduction and slab ascent, the low thickness of the rising plate, its fluid saturation, or the high buoyancy of rocks (Beane, Sorensen, 2007).

## Summary and Conclusions

1. The main criteria and features of subduction initiation – the temporal and spatial combination of eclogite and ophiolite formation, a clear chemostratigraphic sequence, and the presence of a reconstructed UP/UHP subduction channel – are quite clearly manifested in the MC rocks, suggesting that the IS Rules can be used as a universal model for crustal eclogite formation.

2. The geochemical, petrological, and geodynamic features of the complex complicate the interpretation of the IS Rules, leaving a number of controversial issues related to the development and structure of the orogen.

3. The formation of HP/UHP MC rocks requires at least a three-component source of initial material: enriched OIB mantle, depleted N-MORB and E-MORB mantle, and some contribution from the subduction component (crustal contamination). New geochemical data on the HP/UHP composition of MK rocks for rare and trace elements allowed us to estimate the contribution of the subduction component in MK rocks from 1 to 4%.

4. The wide range of compositions of MK eclogites from different mantle sources requires a long (possibly since the Early Paleozoic) accumulation of the initial protolith material, and the question of the onset time of subduction and the duration of the Maksyutov complex remains open.

5. The high niobium content in MK rocks is an indicator of the subduction of the oceanic crust, which gives rise to the idea of revising the polarity of the subduction of the complex from east to west. The main event in the geodynamic evolution of MK is the subduction of the Paleoasian oceanic crust under the continent, and not the subduction of the margin of the East European Craton under the Magnitogorsk island arc. The issue requires clarification, since the nature of the evolution of metamorphism indicates the possible periodicity and short duration of such events.

6. The ratio of rare and trace elements in high-pressure rocks of the Maksyutov complex allows us to determine the parameters of mantle-crust interaction and magma generation in the mantle plume and depleted mantle, determining the maximum parameters of MK formation in the pressure range from 3.5 to 1.5 GPa.

7. High parameters of formation of ultrabasite-eclogite inclusions (T> 750 oC and P> 4.0-4.4 GPa) and the cyclic reciprocal pulsating nature of MK metamorphism determine the nature of the UHP

index minerals (diamond and coesite) in the rocks of the Maksyutov complex as captured by the mantle plume during mantle-crust interaction, and their metamorphic nature has not been reliably proven. On this basis, the ultra-high-pressure (UHP) conditions of formation of the Maksyutov complex should be considered as not reliably proven.

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## **Kostyuk A.V., Gorbachev N.S., Novikov M.P., Nekrasov A.N. Experimental study of basalt-anhydrite system at 0.1 mPa, 1250°C: phase composition and distribution of elements.** *UDC 123.456*

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**Abstract.** The melting of the basalt-marl-anhydrite rock system at 0.1 MPa, 1250℃ for 2, 3.5 and 5 hours was experimentally studied. The phase composition was described, and the contents of impurity elements were determined by mass spectrometry (ICP-MS) with inductively coupled plasma both in the original samples of basalt and marl-anhydrite rock, and in the experimental samples. The results of studies have shown that in marl-anhydrite rock the increased values of concentrations normalised to primitive mantle are observed in a number of REEs (La, Ce, Pr, Nd, Sm), in the majority of rare elements, including refractory W, Nb, Ta, Mo, as well as Cs, Tl, Rb, Ba, Th, U, Be. In all experimental and initial samples, the minimum concentrations of Cr, Ni, Co, and in the marl-anhydrite rock Cu, Zn, and Sc were recorded. In the experimental melts a decrease in the concentrations of Ni, Cu, Co, Pt is observed depending on the duration of the experiment. This effect may be related to the increase in the rate of mobilisation of elements from basaltic melt to sulphide melt with increasing melting time.

***Keywords**: contamination, basalt, sulphide, anhydride, experiment, element distribution*

Experimental studies are of priority importance in studying the mechanism of sulfide melt formation in basaltic magma, which is the main factor in the formation of sulfide deposits (Kavanagh et al. 2015; Yao and Mungall, 2021; Gorbachev et al., 2023). Particular attention in the study of deposits in the Norilsk region was focused on investigations of contamination of basaltic melts by components of sulfur-bearing rocks of the sedimentary layers (Grinenko, 1984; Gorbachev and Grinenko, 1973; Gorbachev et al., 2021). Assumptions about the possibility of assimilation of ‘heavy’ sulfur from crustal source by magmas of ore-bearing intrusions are confirmed by the data on the presence of recycled crustal material in the magmatic formations of the area, the share of which is estimated at 30-40% (Sobolev et al., 2004). However, the physical and chemical mechanisms of assimilation of sulphur, carbon and other components of sedimentary rocks by magmas, as well as their role in the processes of liquation, differentiation and ore-bearing of trap magma are still insufficiently studied.

This paper presents the results of experimental study of contamination of basaltic melt, which is close in composition to the ancestral melt of ore-bearing Norilsk intrusions, with sedimentary rocks of the platform cover on the example of basalt-mergel-anhydrite rock system at 0.1 MPa and 1250°C.

Experiments at atmospheric pressure were carried out in improved high-temperature furnaces of the KAO-40 type using alund crucibles. Buffer mixture $BaCO_3$+BaO+C in a separate crucible was added to the system to control oxygen fugacity.

The initial substances were samples of rocks from the Norilsk region: basalt of the Mokulaev Formation with composition (wt.%): $SiO_2$ – 47.65, $TiO_2$ – 1.26, $Al_2O_3$ – 15.31, FeO – 12.92, MgO – 7.30, CaO – 10.72, $Na_2O$ – 2.09, $K_2O$ – 0.38, $SO_3$ – 0.02 and marl-anhydrite sedimentary rock of composition: $SiO_2$ – 45.56, $TiO_2$ – 0.58, $Al_2O_3$ – 10.80, FeO – 5.60, MgO – 10.52, CaO – 19.10, $Na_2O$ – 0.25, $K_2O$ – 3.0, $SO_3$ – 4.4 (samples were provided by V.A. Radko, «Norilskgeologiya»).

The products of experiments were studied on a digital scanning microscope Tescan Vega II XMU with an energy dispersive X-ray spectrometer (EDS) with a semiconductor Si (Li) detector INCA Energy 450 and a wave dispersive spectrometer (WDS) INCA Wave 700 in Energy Plus mode (analyst A.N. Nekrasov). The limits of detection with 95% probability are equal to 2σ. The results of analyses were processed using the programmes INCA ver. 4.06 and Atlas in IEM RAS.

The contents of elemental impurities in the initial and experimental samples were determined by inductively coupled plasma mass spectrometry (ICP-MS) (X Series 2, Thermo Elemental, USA) in the Analytical Certification Test Centre of Institute for Problems of Microelectronics Technology and High-Purity Materials of the Russian Academy of Sciences (Chernogolovka, ASIC IPTM RAS, analyst Karandashev V.K.). Determination of the elemental composition of rock samples was carried out according to the method NSAM 499-AES/MS (version 2022, FR.1.31.2017.26932).

After the experiments, the surfacing of xenoliths enriched with volatiles in the first two or three hours of the experiment with the formation of a reaction fringe was observed in the longitudinal section. Their degassing led to the formation of a large number of bubbles in the upper part of the sample (Fig. 1). After 3.5 h, partial dissolution of xenolith was observed, and after 5 h, complete melting was observed with the formation of homogeneous basaltic melt in the form of glass. After 2 h of melting high alkaline melts of trachy-basalt composition with $Na_2O$+$K_2O$ content up to 5.5 wt.% were formed. After 5 h of melting xenolith components were completely mixed with basaltic melt components and homogeneous basaltic glass contained from 2.5 to 3.5 wt.% $Na_2O$+$K_2O$. The parameter of basaltic melt homogenisation during dissolution of marl-anhydrite rock was the horizontal trend of rock-forming oxide concentrations in the glass along the selected profile from the xenolith-basalt contact, and during complete dissolution of xenolith - in the vertical section of the crucible (green arrows in Figure 1). The average chemical compositions of the basaltic melts are given in Table 3, and the analyses were taken with an extended probe beam at 5 mm spacing.

Melting of xenolith was accompanied by dissolution of initial sulfide phases ($FeS_2$) with formation of sulfide globules of pyrrhotite composition (FeS) in silicate matrix. As a result of active degassing in the first 3 hours of the experiment, sulfide droplets were concentrated both in the matrix and deposited on the walls of gas bubbles in the silicate melt, and after 5 hours, sulfides were concentrated in the matrix of the basaltic melt. Homogeneous sulfide droplets with sizes from 10 to 100 μm had indistinct contours (insets in Fig. 1). No metallic phases were detected, the concentrations of Ni and Cu in the sulfide melts increased with increasing duration of the experiment and were 1.0-3.7 and 0.6-5.8 wt.%, respectively.

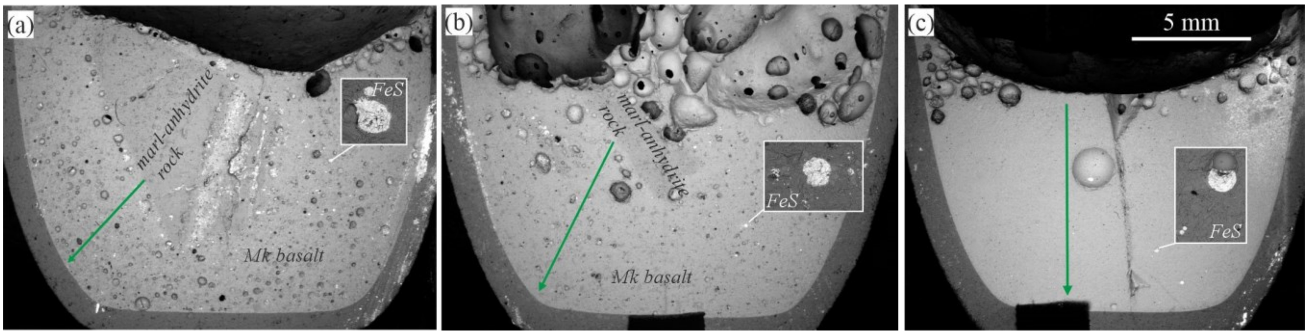

**Fig. 1.** BSE micrographs of longitudinal sections of experimental samples at 1250°C, 0.1 MPa in basalt-marl-anhydrite rock system after: (a) 2 h of melting; (b) 3.5 h of melting; (c) 5 h of melting.

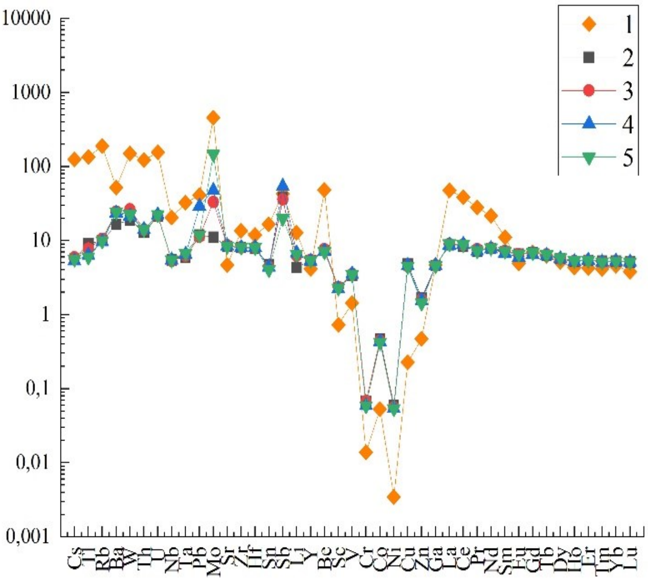

**Fig. 2**. Spider diagram of rare and rare-earth elements distribution before and after experiments in the basalt-marl-anhydrite rock system at 0.1 MPa, 1250°C. Element concentrations in rocks are normalised to the primitive mantle (Sun and McDonough, 1989).
1 - in the marl-anhydrite rock, 2 - in the Mokulayev basalt, 3 - 2 hours after melting, 4 - 3.5 hours after melting, 5 - 5 hours after melting

The element-impurity contents by inductively coupled plasma mass spectrometry (ICP-MS) were determined in the initial samples of basalt and marl-anhydrite rock, and after their melting after 2, 3.5 and 5 h at 0.1 MPa, 1250°C. As can be seen from the data shown in the spider diagram (Fig. 2), in the marl-anhydrite rock the increased concentration values normalised to the primitive mantle are observed in the range of light rare-earth elements (La, Ce, Pr, Nd, Sm), in the majority of rare elements, including refractory W, Nb, Ta, Mo, as well as Cs, Tl, Rb, Ba, Th, U, Be. In all samples the minimum concentrations of Cr, Ni, Co, and in the marl-anhydrite rock Cu, Zn, and Sc were recorded. In the experimental melts, a decrease in the concentrations of Ni, Cu, Co, Pt is observed depending on the duration of the experiment. This effect may be related to an increase in the rate of mobilisation of elements from basaltic melt to sulphide melt with increasing melting time.

Depending on redox conditions, the measure of which is the oxygen fugacity in basaltic melts, sulfur can be in the oxidised form of sulfate ion $SO_4^{2-}$ and in the reduced form of sulfide ion $S^{2-}$. The transition from reduced to oxidised forms occurs rapidly at $fO_2$ close to NNO (Ni-NiO)+1 oxygen buffer (Jugo, 2009; Jugo et al., 2005). At interaction of marl-anhydrite rock with basalt at the first stage anhydrite dissolution occurs according to the scheme:

$CaSO_4$ (xenolith) → Ca2+ (melt) + $SO_4^{2-}$ (melt) (1),
followed by reduction of oxidised sulphate sulphur ($SO_4^{2-}$) to sulphide sulphur ($S^{2-}$) in the melt:

$SO_4^{2-}$ (melt) = $S^{2-}$ (melt) + $O^{2-}$ (melt) (2)

Further, $S^{2-}$ interacts with $Fe^{2+}$ of the melt to form FeS cluster in the melt:

$S^{2-}$ (melt) + $Fe^{2+}$ (melt) (3)

When the melt is saturated with sulphur, liquation will be observed to form an iron-sulphide melt:

FeS (melt) = FeS (sulphide melt) (4)

For sulphate saturation at a given $fO_2$ high - up to 2 wt.% sulphur concentrations are required ($SO_4^{2-}$ ion in basalt melt interacts with $Ca^{2+}$ ion and $CaSO_4$ melt is formed during saturation). Sulfide saturation of basaltic melt at the same $fO_2$ requires low - about 0.2 wt.% sulfur concentrations (Masotta and Kepler, 2015; Iacono-Marziano et al., 2017). Given the different saturation concentrations of sulfate and sulfide sulfur in the basaltic melt, it can be expected that during the transition from oxidative to reductive conditions, when $SO_4^{2-}$ is converted to $S^{2-}$, excess dissolved sulfate sulfur will precipitate as FeS melt droplets, which is what we observed in the basalt-marl-anhydrite rock system.

Thus, as a result of the studies, it was established that the interaction of basalt melt with marl-anhydrite rock results in melting of anhydrite, saturation of basalt melt with its components, reduction of sulfate sulfur to sulfide sulfur, resulting in sulfide-silicate liquation already after 2 hours of melting. With increasing duration of the experiment, the concentration of ore elements (Ni, Cu) in basaltic melt decreased, and in sulfide melt - increased. The reduction of anhydrite sulphate sulphur to sulphide sulphur, the formation of sulphide melt, as well as the extraction of Ni, Cu and other ore elements by it occurs simultaneously, in a very short time, and taking into account the geological time scale - almost instantaneously. Based on the analysis of publications and experimental data obtained by us, contamination of basaltic melt with sulphur-bearing rocks of the platform cover of the Norilsk region can lead to liquation, differentiation and ore-bearing trap magma - the source of ore-bearing intrusions of the Norilsk type.

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