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Solid-state redistribution of mineral particles in the upwelling mantle flow as a mechanism of chromite concentration in the ophiolite ultramafic rocks (by the example of Kraka ophiolite, the Southern Urals)

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Abstract. The main regularities of the structure of chromitite-bearing zones of ultramafic rock of the ophiolitic association are considered on the example of Kraka massifs. In all studied chromitite-bearing zones, olivine demonstrates a strong preferably crystallographic orientation, indicating that plastic flow was one of the main factors of petrogenesis and ore formation. A critical review of existing ideas about the origin of ophiolitic chromitites has been carried out. It is shown that for models involving the reaction and magmatic formation of dunites and chromitites, there are a number of difficulties. In particular, the application of the magma mixing model to the mantle ultramafic rocks for the formation of chrome ores is faced with the problem of "free space". Free space is necessary for the deposition of large volumes of ores, which is absent in a very low-porous crystalline upper mantle.

In the "melt-mantle" interaction model, it is difficult to explain the often observed abrupt contacts of dunites and harzburgites, as well as an increase in the content of orthopyroxene in the near-contact parts of harzburgites, which is very often observed in ophiolite massifs. In addition, there is no mechanism for the formation of chromitites as geological bodies in this model. We have shown that the main trend in the composition and structure of the mantle section of ophiolites is stratification, accompanied by the separation of the rheologically most "weak" aggregates of polycrystalline olivine (dunites), which are host rocks for chrome ores. The stratification of the mantle material occurred during the solid-phase redistribution of minerals in the rocks, which are a dispersion system. In this work, a thermodynamic model is substantiated, which demonstrates the possibility of the emergence of solid-state flows in the conditions of the upper mantle and which makes it possible to eliminate some of the difficulties and contradictions characteristic of the magmatic and reaction-magmatic hypotheses.

Keywords: ultramafic rocks, olivine, chromitite, plastic flow, stratification, rheomorphic segregation

Introduction

The origin of ultrabasic rocks of ophiolitic complexes and related chrome deposits has been controversial for many years. In the first half of the 20th century, chromitites were considered as differentiates of ultrabasic magma (dunite or peridotite one) (Loginov et al., 1940; Sokolov, 1948; Kravchenko, 1969; Pavlov et al., 1979; Marakushev, 1988, etc.). The development of the metasomatic hypothesis regarding dunite-harzburgite complexes with chrome ore mineralization as a product of metasomatic transformations of the peridotite (enstatite) substrate (Bakirov, 1963; Moskaleva, 1974; Saveliev, 1977, etc.) was caused mainly by the inability to explain magmatic differentiation of "epigenetic" properties of dunite and chromitite in relation to the surrounding harzburgite. In the works of A.G. Betekhtin, G.G. Kravchenko, A.S. Varlakov, great importance of fluids in the genesis of chromitites was suggested. Nowadays, due to numerous findings of submicron inclusions of "fluid-containing" phases in chromitites, these ideas have more and more supporters (Chashchukhin et al., 2007; Pushkarev et al., 2007; 2015).

In the 1960s and 1970s the ophiolitic assemblages, which include ultramafic rocks, were compared with relics of the paleooceanic crust and upper mantle (Peive, 1969). The ubiquitous distribution of deformational

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structures in ultramafic rocks of ophiolites and the ocean floor has been established, which made it possible to consider the rocks of both assemblages as "mantle tectonites" (Coleman, 1979) and to state their significant similarity to each other. In the future, more and more researchers began to consider chromium mineralization in ophiolites as a result of the depletion of initially homogeneous, undepleted mantle substrate, similar in composition to lherzolite (Savelieva, 1987; Savelieva, Saveliev, 1991; Perevozchikov, 1995).

Detailed studies of the structural features of ultramafic rocks of chromite-bearing zones were carried out on the Uralian massifs (Goncharenko, 1989; Denisova, 1989; 1990, Savelieva, Saveliev, 1991; Shcherbakov, 1990). On the basis of large-scale geological mapping, petrostructural analysis, generalization of data obtained as a result of a large amount of drilling and mining, by the early 1990s, the most publications made a conclusion about the leading role of plastic flow in the genesis of ultramafic rocks and chromitites, but a model linking the plastic flow and the processes of differentiation of matter in the upper mantle was never formulated.

Since the early 1990s, the main hypothesis claiming to explain the genesis of mantle dunites and chromitite is the reactive porous melt flow through the mantle peridotites, first formulated in the works by P. Kelemen (Kelemen et al., 1992; 1995) and supported by various researchers (Gonzalez-Jimenez et al., 2014; Miura et al., 2012; Zhou, 1994; Zhou et al., 1996, and others). It should be noted that despite the different terminology, this idea is very close to the above-mentioned metasomatic hypothesis, widely used in the works by a number of Soviet geologists (Moskaleva, 1974; Varlakov, 1978, etc.). However, in the reaction-magmatic model there is no mechanism for the formation of chromitites as geological bodies. Even if we assume that chromite crystallizes in dunite at the dissolution of pyroxenes, the factors that cause it to form separate bodies with differing concentrations, from rarely disseminated to massive ores, remain unclear. In addition, within the framework of the reaction hypothesis, it is difficult to explain the often observed abrupt contacts of dunites and harzburgites, as well as an increase in the content of orthopyroxene in the near-contact parts of harzburgites, which is very often observed in ophiolites.

In a number of publications, we have substantiated the rheomorphic model for the formation of ore concentrations of Cr-spinels in mantle ultramafic rocks (Saveliev, 2013; Saveliev et al., 2008; etc.) and started the development of a physical model of rheomorphic differentiation (Saveliev, Fedoseev, 2011, 2014) as a logical continuation of studies that established the tectonic nature of mantle section of ophiolites. This paper presents the results of thermodynamic modeling of

solid-phase segregation of chromite in ascending plastic flows of ultramafic rocks.

Factual material

Kraka massifs located within the Zilair mega-zone of the western slope of the Southern Urals (Fig. 1) were chosen as the object of study. Ultramafic rocks occupy an area of about 900 km² and form four large bodies of oval or isometric shape. The structure of the massifs is dominated by variously serpentinized spinel peridotites with a subordinate value of spinel-plagioclase varieties and rare dunite bodies.

The main feature of peridotites is the almost ubiquitous distribution of primary banding, which is expressed in frequent alternation of bands with different quantitative ratios of rock-forming minerals – olivine, orthopyroxene, clinopyroxene and Cr-spinel. The thickness of bands varies from tenths of a centimeter to the first tens of meters. Almost always banding is accompanied by foliation and lineation (Fig. 2a, b).

Macroscopically, mineral slaty cleavage is expressed in the regular arrangement of tabular pyroxene crystals; when studying rocks under a microscope, a similar orientation is observed even more for olivine. Lineation – the elongation of individual crystals in one direction – is also characteristic of olivine grains. At the same time, Cr-spinels and pyroxenes most often show
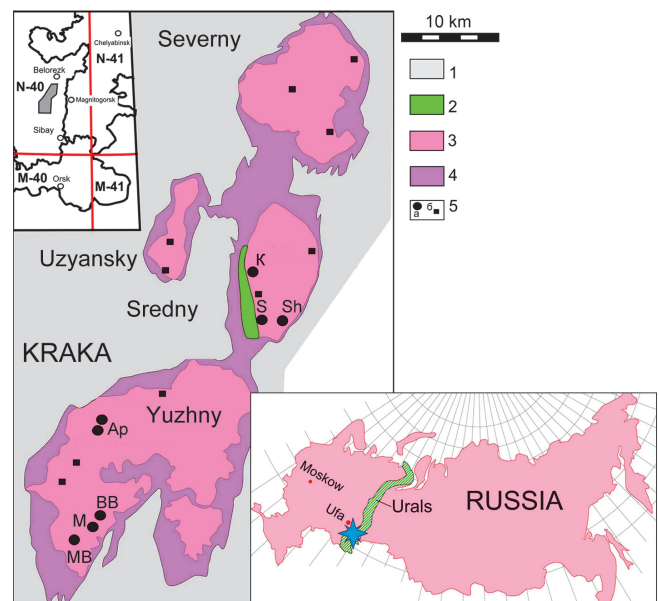

Fig. 1. Overview map of Kraka massifs. 1 – enclosing Paleozoic sedimentary rocks of the Zilair mega-zone, 2 – mafic and ultramafic rocks of the transitional mantle-crust complex (gabbro, verlite, clinopyroxenite), 3 – predominantly spinel peridotites with subordinate dunites, 4 – melange serpentinites, 5 – chrome deposits and ore occurrences, and the most significant of them are: K – Klyuchevsky, S – Sakseysky, Sh – Shatransky, Ap – objects of Apshaksky Area, BB – Bolshoy Bashart, M – named after Menzhinskiy, MB – Maly Bashart.
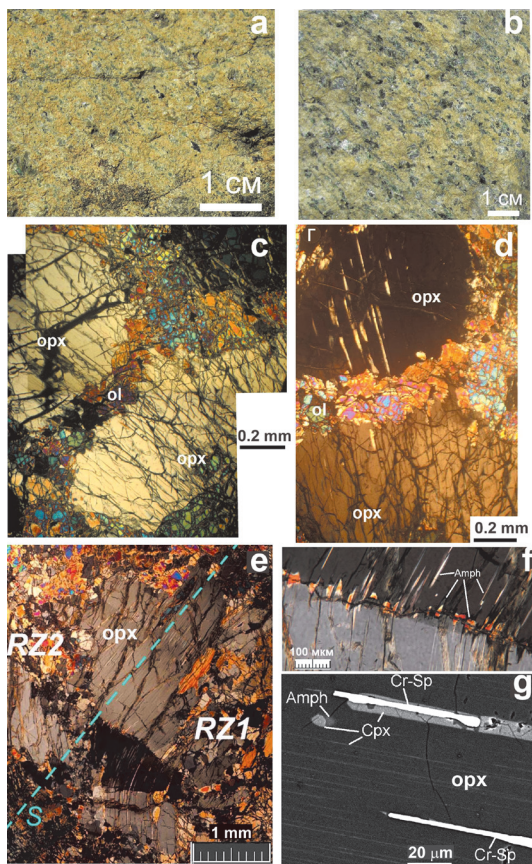
Fig. 2. Typical textures of ultramafic rocks with well-pronounced foliation and banding: a, b – picture of peridotites in outcrop, the structure is emphasized by the streamy distribution of pyroxenes and Cr-spinels; c, d – structural relationship between olivine (ol) and orthopyroxene (opx), e, f – a bended orthopyroxene crystal, plastic deformation of which causes the formation of chromium-rich pargasite (amph) in the plane (100) and on the bend line along the periphery of large recrystallization zones (RZ1 and RZ2) are formed with small equiaxial neoblasts of pyroxenes, olivine and spinel; S is the trace of the plane of the mineral flattening of peridotite, W is the formation of lamellae of diopside (cpx), Cr-spinel (Cr-Sp) and chromium-rich pargasite (amph) in a deformed orthopyroxene crystal.

aggregative lineation, which is expressed in grouping the grains of these minerals into chains oriented in a certain direction.

The internal structure of Kraka massifs was previously studied by E.A. Denisova and G.N. Savelieva (Denisova, 1989; 1990; Savelieva, 1987, etc.). The geometric analysis of plane and linear structures carried out by these authors, using the results of petrostructural studies, allowed us to establish the ubiquity of deformation structures indicating the formation of massifs as a result of predominantly layer-by-layer plastic flow accompanied by folding (Denisova, 1990). The mantle origin of dunite-peridotitic banding, foliation and lineation was proved by the fact that the structure elements are formed by primary minerals without the participation of aqueous silicates.

The microstructural features of ultramafic rocks indicate a different pattern of plastic deformation of the main rock-forming minerals, olivine and orthopyroxene (Fig. 2c, d). Olivine crystals experience a significant flattening and elongation. Fragmentation occurs with the formation of a developed substructure with a predominance of low-angle boundaries. These features indicate the plastic nature of the mineral during deformation. For orthopyroxene, on the contrary, "quasi-brittle" behavior is more characteristic, which is expressed in grain breaking, the formation of numerous neoblasts with high-angle boundaries, the formation of a lamellar structure due to the presence of stacking faults and phase transitions. These observations suggest that the separation of dunites (monomineralic olivine layers) during the plastic flow of mantle peridotites could be due to the higher mobility of olivine aggregates.

Within the massifs, numerous small deposits and ore occurrences of chrome are known, which are confined to flat (tabular) dunite bodies among the harzburgites, or to extensive areas of marginal dunites at the boundary between the mantle and crustal section of ophiolites. All the variety of ore concentrations of chromite in the Kraka fits well with the known structural and morphological classifications of chrome ore deposits in ophiolites (Cassard et al., 1981; Hock et al., 1986). In addition, according to the degree of mineralization concentration, a continuous series of gradual increase in the Cr-spinel ore content and mineralization scale can be built – from thin intermittent segregations of Cr-spinel grains in thin dunite interlayers through concordant deposits of disseminated ores to typically podiform bodies of massive structure.

Let us consider the geological structure of the three deposits (Saksey, Maly and Bolshoy Bashart) (Fig. 1), which differ in the scale and concentration of mineralization. Saksey-Klyuchevskaya area is located in the southwestern part of the Middle Kraka massif and includes several chromite-bearing dunite zones parallel to the mantle-crust boundary (paleo-Moho). Transitions between ore-hosting dunites and peridotites are gradual. Transient varieties of rocks with a small number of pyroxene grains are noted. Within the area, two ore occurrences of poorly disseminated ores (Saksey, Klyuchevsky) and the Shatransky deposit (Shumikhin, 1979; Saveliev, Snachev, 2012) are known.

In **the Saksey area**, mineralization is represented by several (from two to five) intermittent parallel bodies of disseminated chromitites of tabular form inside a thick dunite layer at the boundary of the mantle and crustal section (Fig. 3). The sizes of the ore veins vary: length – from the first tens of meters to 100 m, width – from a few meters to the first tens of meters, thickness – from several centimeters to 2 m. The bodies of chromitites have a submeridional strike (from NNW330º to NNE 10º) and
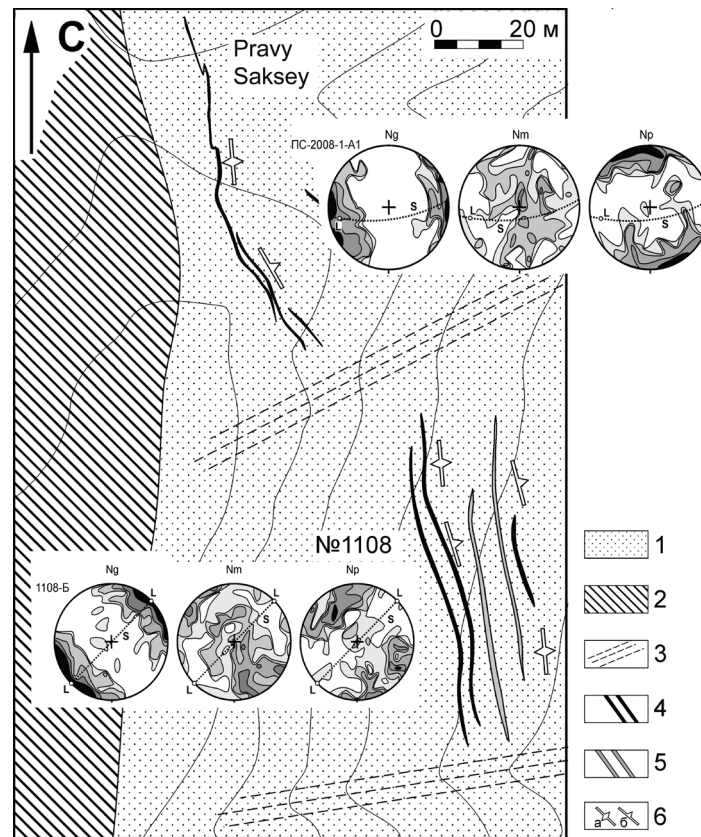
Fig. 3. The geological structure of the deposit area Pravy Saksey. According to P.G. Farafontiyev (1937) and the data of the works (Saveliev, 2013; Saveliev et al., 2008). Legend: 1 – dunites, 2 – clinopyroxenites and verlites, 3 – crushing zones, mainly composed of chrysotile serpentinites, 4-5 – chromitites, 4 – 20-40 % Cr_2O_3, 5 – 5-20 % Cr_2O_3, 6 – the occurrence of primary banding. On the sidebar – petrostructural patterns of olivine from dunites, the projection on the upper hemisphere of the Wulf grid, contours are drawn: 1108 and PS-2008-1-A1 – 1-2-3-5-8% (100 grains each); PS-2008A – 1.5-3-5-7% (60 grains); S is the banding and mineral flatness of olivine, L is the mineral linearity.

almost vertical dipping; banded densely and moderately disseminated ores of fine-grained structure are the most common. Chromitites also have an occluded silicate texture, which usually develops against a banding background. It is expressed in Cr-spinel aggregates flowing around olivine clusters of ellipsoidal shape up to 2.5 cm in length. The long axes of the olivine aggregates are usually oriented in accordance with the chains of chromitite; they are characterized by a flattened shape with a ratio of length to width from 2 to 5.

Dunites and chromitites have veins of clinopyroxenites that intersect the ore banding at an acute angle (from 10 to 30º). These veins can be single or form a network. Chromite strips are often bended into gentle folds, in some places there are swellings or nodules forming different angles with respect to the direction of banding. Dunite streaks are marked, crossing the ore stripes also at different angles. Similar veinlets on other ophiolites were previously described as "intra-ore dunites" (Thayer, 1964; Kravchenko, 1969, etc.).

The microstructure of the wall dunites was formed as a result of the plastic flow of the mantle substance. In the dunites enclosing the disseminated mineralization of the Saksey area, mineral fabrics are recorded everywhere,

formed with the leading role of intragranular olivine gliding on the {0kl}[100] system (Fig. 3); the subordinate role belonged to both syntectonic and post-tectonic recrystallization (Saveliev, 2013). The above-noted features of the internal structure of the Saksey section suggest the formation of mineralization under the conditions of non-uniform plastic flow of the ore-bearing dunite-chromitite assemblages.

The largest of the Kraka massifs – the South – is most saturated with small chromite occurrences localized in the narrow bodies of dunites among spinel peridotites. The length of the chromite-bearing bodies of dunites varies from the first tens of meters to a kilometer (Menzhinsky deposit), and the thickness varies from a few meters to 50 meters.

In **the Malo-Bashartovsky area**, mineralization was traced at a distance of 500 m with a dunite width from 10 to 50 m (Fig. 4). It is represented by a series of parallel discontinuous veins of disseminated chromitites, which form an ore zone, occurring according to the contacts of enclosing dunites body and pyroxene foliation in the surrounding peridotites. In the northwestern part, the strike of the planar structural elements is latitudinal; in this part there are numerous flattened inclusions of harzburgites in
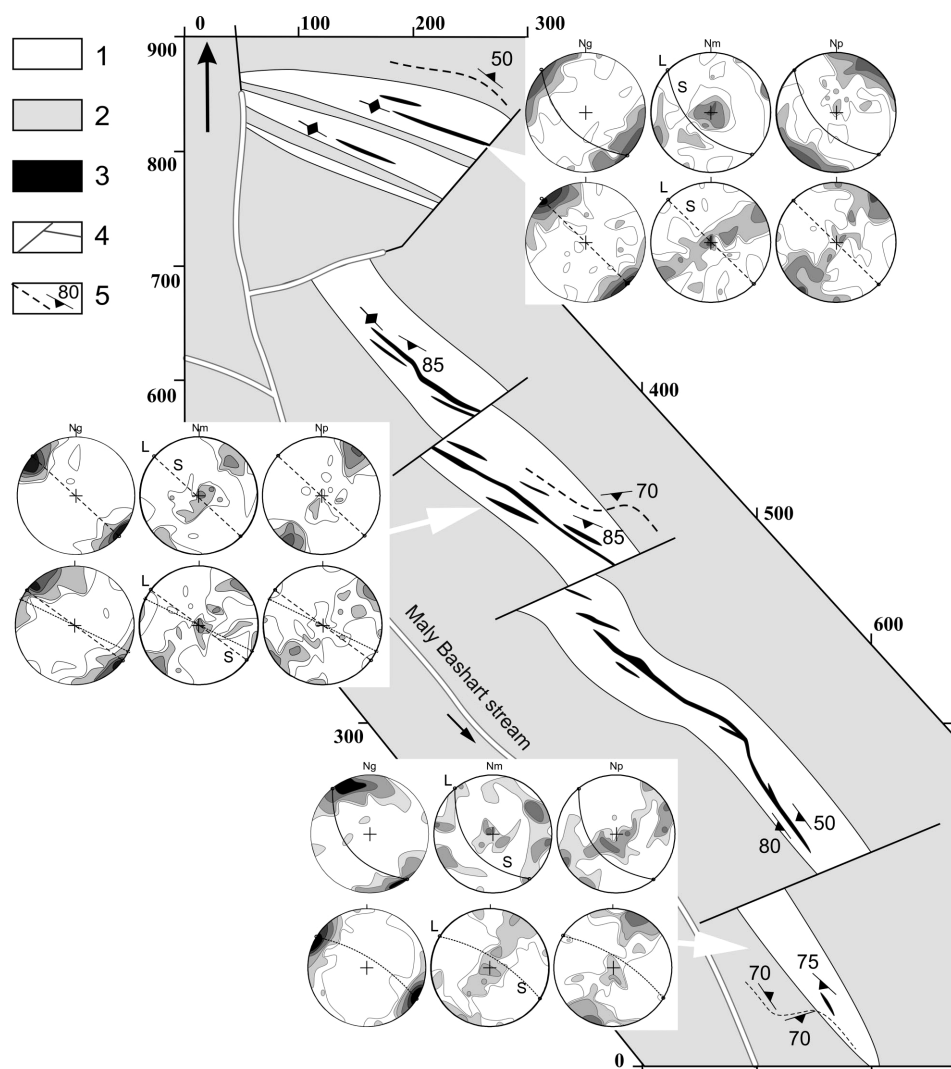
Fig. 4. Geological structure of the Maly-Bashart chromite-bearing zone. Legend: 1 – dunites, 2 – spinel peridotites, 3 – chromitites, 4 – faults, 5 – occurrence of primary banding. On the sidebar – petrostructural patterns of olivine from dunites, the projection on the upper hemisphere of the Wulf grid, from 100 to 110 grains were investigated in all samples, the contours were drawn through 1-2-4-8 %; S is the banding and mineral flatness of olivine, L is the mineral linearity.

dunites; to the south, the strike changes to the northwest. Bodies of chromitites with a thickness of 0.1 to 0.4 m are developed in the deposit, their structures are dominated by densely impregnated varieties with a Cr_2O_3 content of 30-40 %. In some cases, there are zones with poor impregnation with a thickness of up to 1.5 m. Earlier, the richest parts of the ore bodies (sections IV and V) were worked out, where the thickness of densely disseminated and massive chromitites reached 1 m. (section III), in the center they have an NW strike of 290-300º and a steep dipping to the south-west (sections IV and V).

The structure of veins is dominated by a banded medium-disseminated texture with a gradual transition to densely impregnated and massive chromitites, as well as to more poorly-divided differences. The structure of ores is inequigranular with a predominance of grains 1-3 mm in diameter. Structural studies of dunites and peridotites of this area showed that olivine in all the studied samples has well-developed preferred orientations of the axes of the optical indicatrix. This indicates the typical tectonite

origin of both country peridotite and chromite-bearing dunites. Plastic deformation of olivine was carried out in the high-temperature creep mode by intragrain sliding. The main slip systems for olivine in rocks are {0kl} [100] in dunites and (010)[100] in peridotites (Fig. 4). In some cases, transitional fabrics were recorded between these slip systems.

Bolshoy Bashart deposit is composed of parallel veins of chromitites with a thickness of 0.5 m to 2.5 m inside the body of serpentinized dunite with a thickness of about 20 m (Fig. 5). The dunite is surrounded by massive peridotite with a high concentration of enstatite (25-30 %). The occurrence of the ore chromite-dunite zone is almost horizontal with the prevailing northern dipping at an angle of 10-15º. At the field, massive and densely disseminated chromitites are often prevalent, often showing signs of tectonic flow, which is fixed by "pull-apart" textures, folding and boudinage (dunite in chromite and chromite in dunite), as well as snowball-like structures in chromite grain aggregates.
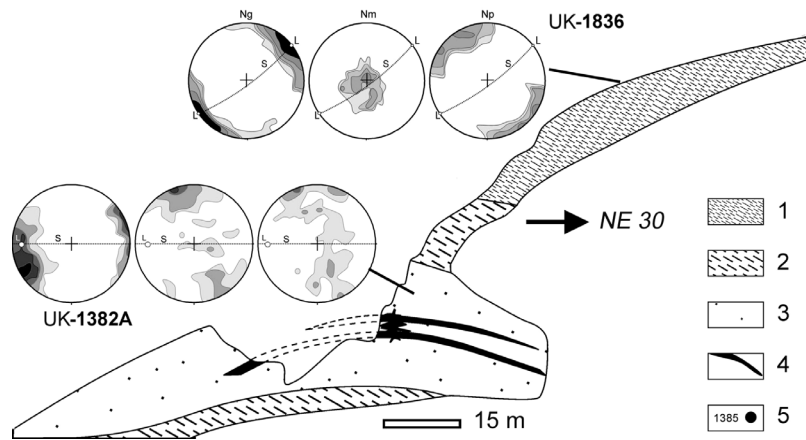
Fig. 5. A cross-section of the Bolshoy Bashart deposit. According to the works (Pavlov, Grigorieva-Chuprynina, 1973; Saveliev, 2013) with additions. Legend: 1 – spinel-plagioclase peridotites, 2 – harzburgites, serpentinized by 80-100 %, 3 – serpentinized dunites, 4 – chromitites. On the sidebar – petrostructural patterns of olivine from dunites and peridotites, a projection on the upper hemisphere of the Wulfe grid, contours are drawn: UK-1386 – 0.8-1.6-2.4-4-6.5 % (80 grains), UK-1382 – 2-4-6-8-12 % (150 grains); S is the banding and mineral flatness of olivine, L is the mineral linearity.

In the peridotites of Bolshoy Bashart deposit, the olivine fabric is interpreted as formed under the conditions of translational slip on the (010)[100] system, and in the wall dunites, the plastic flow was performed during the translational slip along the {0kl} [100] system (Fig. 5). This means that the entire chromite-bearing sequence was formed under conditions of high-temperature plastic flow by means of dislocation creep, and the flow mobility was higher in dunites (Saveliev, 2013).

Mineralogical and geochemical characteristics of chromite-bearing ultramafites

The chemical composition of minerals from ultramafic rocks and chromites of the Kraka is considered in sufficient detail in the works (Saveliev, 2012; Saveliev et al., 2008, etc.), and therefore only a brief summary of the main mineralogical and geochemical features is given below.

The composition of olivine in Kraka peridotites varies from Fa = 10 – 12 in lherzolites and harzburgites to Fa = 6 – 10 in ore-bearing dunites. Ultramafic rocks exhibit a wide range of Cr/Al ratios in the composition of spinels. The Cr# = Cr/(Cr + Al) changes in the range of 0.1-0.5 in lherzolites to 0.6-0.8 in dunites (Fig. 6), Mg# = Mg/(Mg + Fe) reaches maximum values in peridotites (0.6-0.9) and decreases to dunites and chromitites, varying in the range of 0.4-0.7. The TiO_2 content in accessory Cr-spinels is very low (up to 0.1 wt.%). Chromites from dunite bodies exhibit a higher content of titanium (up to 0.3 wt.% TiO_2).

On the Saksey area, the composition of chrome spineids in dunites and chromitites is fairly mature. The value of Cr # is 0.7-0.85, and the ratio Mg/(Mg + Fe) is slightly lower (0.5-0.6) than in the spinels of the internal parts of the mantle section. The Cr# in spinels from the enclosing peridotites is lower (Cr# = 0.3-0.5).
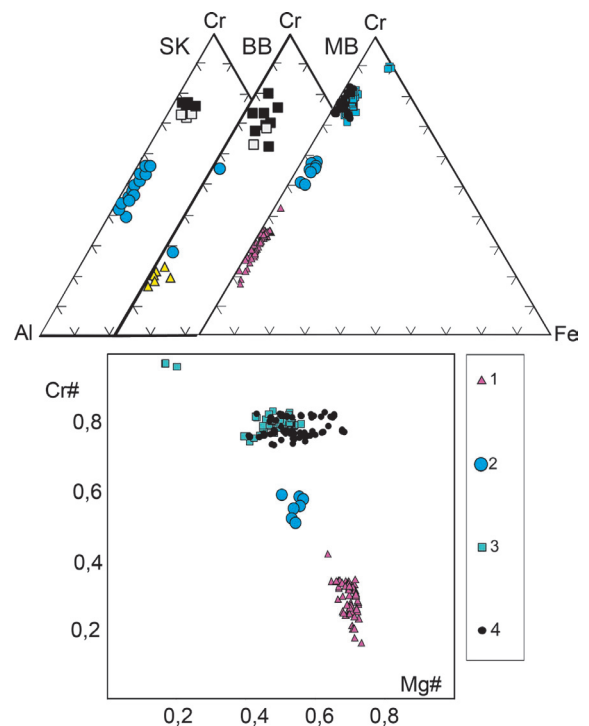

Fig. 6. The chemical composition of accessory and ore-forming spinels of Kraka massifs. Legend: 1 – Lherzolites, 2 – Harzburgites and Dunite-Harzburgites, 3 – Dunites, 4 – Chromitites; SK– Saksey, BB – Bolshoy Bashart, MB – Maly Bashart.

The composition of the Cr-spinels on Maly and Bolshoy Bashart varies in a considerable range (Fig. 6). In the surrounding peridotites, accessory spinels are high-Al (Cr# = 0.2 – 0.3) and the ratio Cr/(Cr + Al) increases to 0.6 only in one sample of harzburgite near the dunite body. In dunites and chromitite, there is a sharp increase in chromium and Cr# is 0.7-0.85. Mg# in the section of ore zones varies slightly.

Thus, on the scale of the ore zones, there is always a gap in the Cr# = Cr/(Cr + Al) ratio between peridotites on the one hand and chromitites and near-ore dunites

on the other. The magnitude of this gap in the diagram varies depending on the type of the deposit, increasing from tabular bodies composed of disseminated ores to typically podiform massive chromitites.

The textural and structural features of the disseminated chromitites in the Kraka dunites suggest that they are of tectonic origin with the leading role of high-temperature plastic flow (Fig. 7). The symmetric nature of the zonation of mineralization (peridotite-dunite-chromitite), the intermittent nature of banding, the frequent presence of small folds should be pointed out among the main features. The noted signs are in good agreement with the assumption about formation of this section in the conditions of the hydrodynamic field influence.

The constant association of chromitites with dunites is explained by the fact that, firstly, a significant part of Cr-spinels is formed in dunites by the impurity segregation mechanism (Saveliev et al., 2016), and secondly, the higher rate of plastic flow in dunite layers could contribute to more efficient separation of particles of the matrix (olivine) and the dispersed phase (chromite). An increase in the Cr# in spinels, from peridotites to ore bodies, may be due to the diffusion mobility of aluminum during deformation (Saveliev, Blinov, 2015) and its removal as a part of low-melting phases (amphibole) during partial melting.

The formation of new crystals of Cr-spinels caused by plastic deformation of rock-forming silicates

Plastic deformation of rock-forming silicates is accompanied not only by structural, but also mineralogical and geochemical changes. The most significant source of new chromium-spinel grains in mantle peridotites may be the chemical decomposition of orthopyroxene, caused by plastic deformation. In particular, the works (Saveliev et al., 2017; Saveliev, Sergeev, 2018) described petrographic facts indicating that the angular moments of bending large enstatite crystals and related real transformations were fixed in samples of peridotite: 1) the formation of pargasite lamellae in the inner parts of the crystal and more intense precipitates on the bend line, as well as the complementary inclusions of high-Mg olivine, was recorded; 2) in the most stressed areas of the crystal, numerous neoblasts of enstatite depleted in impurities, forsterite, diopside, pargasite, and Cr-spinel are formed; these regions are zones of intense manifestation of syntectonic recrystallization.

The comparison of the compositions of large deformed enstatite crystals and neoblasts showed the presence of systematic differences consisting in a decrease in the impurity concentrations of aluminum and chromium in the newly formed grains. Such grains
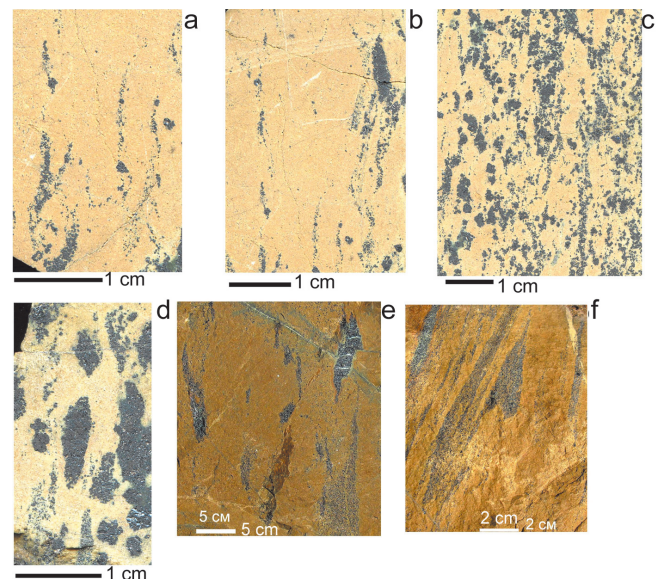

Fig. 7. Typical textures of Kraka's chromite impregnations

are usually found in association with fine newly formed grains of Cr-spinels, which were probably formed due to the release of these elements during deformation of the primary pyroxene.

In addition, in many samples, we identified petrographic evidence of the processes of formation and growth of new Cr-spinel grains during plastic deformation of olivine crystals and orthopyroxene. Fig. 8 (a, b) demonstrates the formation of spinel rod-shaped precipitates parallel to the direction of translational slip in olivine, at large angles to the plastic fracture bands, which bend near the precipitates. Fig. 8 (c, d) shows fine precipitates of Cr-spinels inside olivine and orthopyroxene crystals, moreover, in Fig. 8 (d), closely spaced secretions vary considerably in composition: the higher-Cr of them is confined to orthopyroxene ($CrSp_2$). Fig. 8 (e,f) shows an example of the decay of orthopyroxene caused by plastic deformation. Due to impurity components dissolved in the primary crystal, the lamellae of diopside, pargasite, and chromospinelide are formed on the slip planes. On the low-angle border separating the misoriented enstatite blocks, pargasite and Cr-spinel are also released.

Fig. 8 (g-j) shows an example of a growing complex Cr-spinel crystal capturing fragments of neighboring olivine grains (g,h), and enstatite (j) contains Cr-spinel lamellae in the slip plane. The images in fig. 8 (k-m) demonstrate the final stages of the capture of silicate inclusions by growing chrome spinel crystals. The given examples illustrate the successive stages of the syndeformation of new Cr-spinel grains, comparable to the stages of impurity segregation, coalescence and spheroidization well known in materials science, the driving force for which is minimization of grain-boundary free energy.
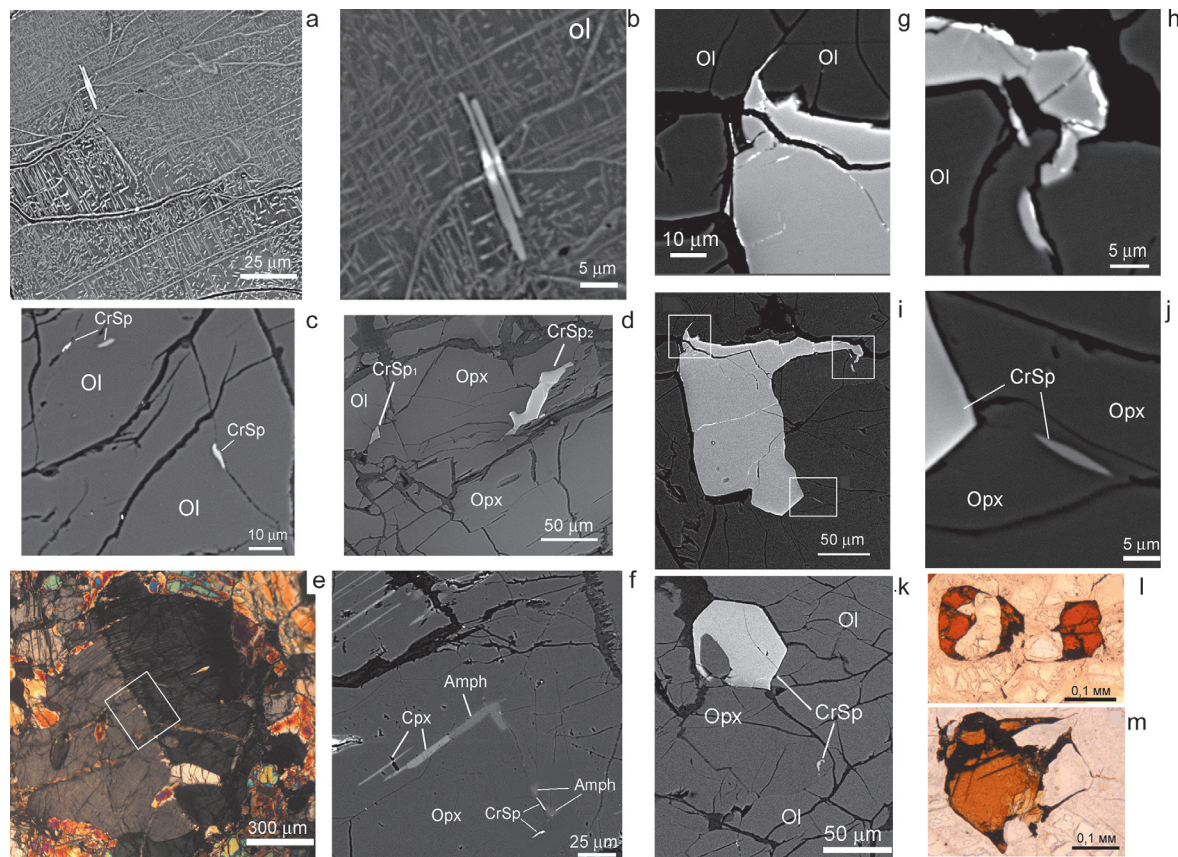
Fig. 8. Formation of new grains of Cr-spinels in a plastically deformed silicate matrix: a, b – rod-like precipitates of chromspinelides along the slip direction [100] in olivine; near the precipitates, a bend of plastic fracture bands is fixed (b – enlarged fragment of a), c – thin precipitates of chromspinelides inside the crystals of plastically deformed olivine, d – closely spaced chromospinel precipitates in olivine (CrSp1) and orthopyroxene (CrSp2), differing in composition, e, f – enstatite disintegration caused by plastic deformation, newly formed diopside, pargasite and Cr-spinel localized on sliding planes and a strip of plastic fracture within the host mineral; g-j – syndeformational coalescence of a complex Cr-spinel crystal with a capture of a silicate matrix (i – overview image, g,h,j – details; j – lamella of Cr-spinel in the plane of slip of enstatite); k – coalescence and spheroidization of the Cr-spinel crystal, accompanied by the capture of an enstatite fragment; l,m – coalescence and spheroidization of Cr-spinel crystals, accompanied by the capture of a fragment of olivine; a, b – BSE images of polished edged sections previously subjected to oxidative annealing (holding for 1 hour at T = 850 °C); c, d, f-k – BSE images of polished thin sections and polished sections, l, m – micrographs of thin sections in transmitted flat-polarized light.

Physical model of chromite segregation in dunite bodies

Stratification of multiphase and multicomponent flows is observed in dispersed and colloidal systems of different scales. Observations indicate the existence of stable particle distributions in the flow and multiphase flow regimes (Nigmatulin, 1987). Their character is influenced by many factors, which include the shape, speed, compressibility, density of particles and medium, concentration of dispersed particles, the influence of neighboring particles, etc.

Assuming that the general patterns are also characteristic in the case of solid-phase mantle flows, an assumption was made about the role of stratification in the formation of chrome ore deposits in mantle ultramafic rocks. A qualitative correspondence was found between the results of modeling distribution of components and the structure of real systems – the chromite-bearing

sections of the Kraka massifs (Saveliev, Fedoseev, 2011; 2014).

The thermodynamic description of stratification of laminar flows with the redistribution of particles of the dispersed phase used in (Saveliev, Fedoseev, 2011, 2014) is presented in a general form (Fedoseev, 2015; 2016). In these works, the main regularities of the behavior of dispersed systems and individual bodies in the flow and the observed types of multiphase flows are reproduced. The proposed approach allows generalizing the results of numerical modeling and experimental observations for systems of different composition and scale.

The thermodynamic approach is based on the minimization of the free energy of a multicomponent system, which takes into account the kinetic energy of the flow components. The stationary flow is considered, in which the cross section, the average velocity and the

velocity diagram are constant. The coordinate system is associated with a fixed boundary of the flow. The x axis is directed along the flow, the z axis is perpendicular to the walls.

The velocities profile is described by the expression:

$$v(z) = az + bz^2,\qquad(1)$$

where a and b are parameters. When b = 0, equation (1) describes the Couette shear flow with a shear rate a = dv/dz. When b ≠ 0, expression (1) describes the Poiseuille flow. When the flow width is H = −a/b, the flow is symmetric about the center. This variant of the Poiseuille flow is discussed further (Fig. 9).
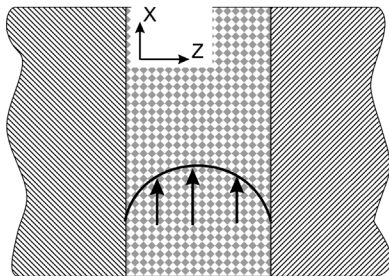

Fig. 9. Scheme of the upward flow of Poiseuille between fixed blocks

The form of dispersed particles is represented by cubes with an edge L with a base parallel to the walls of the flow. More complex forms are discussed in (Fedoseev, 2015). Particles move in a laminar flow parallel to the walls. The velocities of particles movement $v_b(z_b)$ and medium $v(z_b)$ may differ in magnitude:

$$v_b(z_b) = v(z_b) + \Delta v,\qquad(2)$$

where Δv is the velocity of the particle relative to the medium. In vertical flows, it can be identified with the rate of sedimentation, when the density of particles is different from the density of the medium.

The equilibrium distribution of dispersed particles over the flow cross section in the approximation of a dilute dispersed system has the form (Fedoseev, 2016):

$$n_b(z, z_0) = n_b(z_0)\exp\left\{ -\frac{\rho_b V_b \Delta v_b^2(z, z_0)}{2kT}\left[1 - \frac{\rho_0}{\rho_b L_z}\int_{z-\frac{1}{2}L_z}^{z+\frac{1}{2}L_z}\frac{\Delta v^2(q, z_0)}{\Delta v_b^2(z, z_0)}dq \right]\right\},\qquad(3)$$

where the indices 0 and b correspond to the dispersion medium and the dispersed phase, respectively, V_b is the particle volume

The main limitations and approximations that

determine the applicability of expression (3) should be noted. Laminar flows of free-dispersed dilute systems with low shear rates are considered; dispersed particles have the same size and shape; particles incompressible and non-deformable. These conditions make it possible to exclude the influence of friction forces and forces depending on acceleration from consideration (Magnus, Saffman, Basse-Bussinesq, Stokes) and neglect the corrections associated with the non-uniform flow in the vicinity of particles.

Ascending flows with a width H (distance between fixed walls) from 1 to 10 meters were simulated. As noted in (Fedoseev, 2016), the distributions (3) have properties of self-similarity. This is manifested in the fact that almost identical distributions are obtained if the particle size decreases with increasing flow rate. Similar distributions for particles of different sizes can be obtained by varying the flow width. The behavior of small particles in fast narrow flows is similar to the behavior of large particles in slow wide flows. Therefore, below are estimates only for H = 10 m.

The two-phase flow is formed by a polycrystalline olivine (dunite) medium, in which Cr-spinel crystals are distributed. Since the components of the flow have different densities, in the vertical flow the velocity of the Cr-spinel crystals with a higher density may differ from the flow rate due to sedimentation. The rate of sedimentation depends on the particle size and viscosity of the dispersion medium. Accounting for sedimentation changes the distribution of the dispersed phase in the flow. In the ideal case, the rate of sedimentation is proportional to the square of the particle size. Therefore, for fairly large chrome spinel crystals (1-5 mm) for modeling upflows, the results that take into account the "lag" of dispersed particles from the medium are more interesting.

Fig. 10 shows the distribution of chromite particles in a plastic stream 10 m wide at a shear rate $a = 5 \cdot 10^{-8}$. The rate of sedimentation is inversely proportional to the viscosity of the medium:
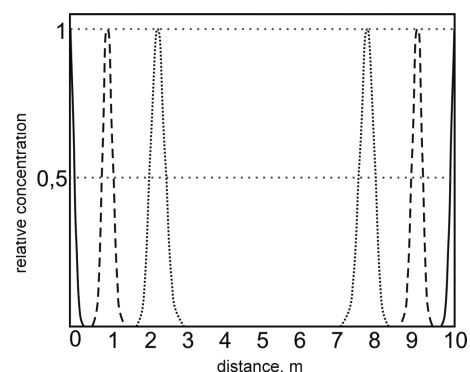

Fig. 10. The distribution of chromite particles in the upward flow of dunite with L = 5 mm at the shear rate $a \approx 5 \cdot 10^{-8}\ s^{-1}$ and sedimentation rate Δv = 0, 40, 80 cm/year – solid, dashed and dotted lines, respectively (medium viscosity ~ $10^8\ Pa \cdot s$)

$$\eta \sim \frac{(\rho_b - \rho_0)L^3 g}{4\pi L \Delta v},$$

where g is the acceleration of gravity. According to a rough estimate for particles with L = 5 m ~ 40 m, a sedimentation rate of ~ 40 cm year can be observed at a viscosity of the medium of ~ 10^9 Pa·s. With the same viscosity, the sedimentation rate of millimeter-sized particles should be ~ 25 times less, and the rate of sedimentation of smaller particles can be neglected.

As shown in Fig. 10, chromite distributions in plastic flow are characterized by the presence of distinct layers symmetrical with respect to the flow center. Distributions are normalized to the maximum value. For larger particles (5 mm), sharper maxima and a more noticeable shift toward the center of the stream with increasing sedimentation rate are characteristic.

When the flow rate is comparable to the rate of sedimentation, a different type of distribution may occur (Fig. 11).
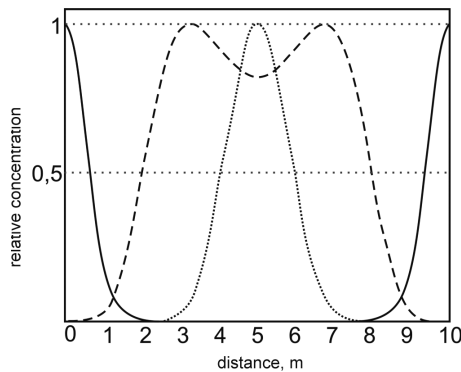

Fig. 11. The distribution of chromite particles in the upward flow of dunite with L = 5 mm at the shear rate a ≈ 10^{-8} s^{-1} and sedimentation rate Δv = 0, 20, 40 cm/year – solid, dashed and dotted lines, respectively (medium viscosity ~ 10^8 Pa·s)

For particles with an average linear size of 1 mm, modeling yields chromite distributions that describe wider layers that are symmetrical about the center of the stream. However, their formation requires higher flow rates and sedimentation (Fig. 12).

For the segregation of small particles (L = 0.1 mm) to occur, even higher shear and sedimentation rates are needed (Fig. 13). According to the model, near-wall segregation of chromite particles with an average linear size of 0.1 mm is observed at shear rates of ~ 10^{-6} s^{-1}. In order to maximize the distribution of these particles from the wall, high sedimentation rates are necessary, which can hardly be implemented in a solid-phase medium.

In non-planar channels, additional convective flows may occur (Abakumov, Fedoseev, 2010) and more complex distributions may occur, leading to a more substantial separation of components (Abakumov, Fedoseev, 2003).

Although the model described above does not consider kinetic effects, they can also affect the distribution of the
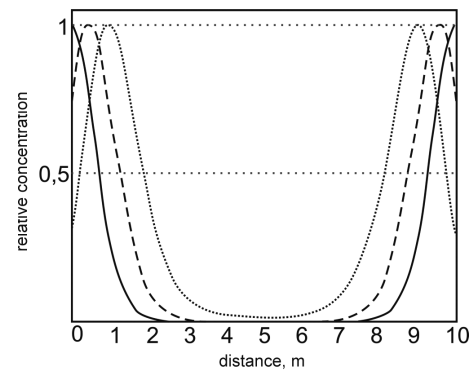

Fig. 12. The distribution of chromite particles in the upward flow of dunite with L = 1 mm at the shear rate a ≈ 10^{-7} s^{-1} and sedimentation rate Δv = 0, 40, 80 cm/year – solid, dashed and dotted lines, respectively (medium viscosity ~ 10^6 Pa·s)
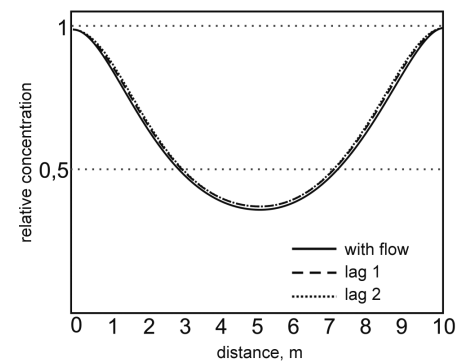
Fig. 13. The distribution of chromite particles in the upward flow of dunite with L = 0.1 mm at the shear rate a ≈ 10^{-6} s^{-1} and sedimentation rate Δv = 0, 40, 80 cm/year – solid, dashed and dotted lines, respectively (medium viscosity ~ 10^6 Pa·s)

dispersed phase. In particular, in a vertical expanding channel, the laminar flow rate decreases with height. According to the simulation results, this should lead to the erosion of narrow distributions. In the expanding or tapering flows, the sedimentation flow j, remaining vertical, becomes non-collinear to the flow of the medium (Fig. 14). In this case, in the expanding vertical

Fig. 14. Scheme of the upward laminar flow with non-parallel walls and sedimentation flow j

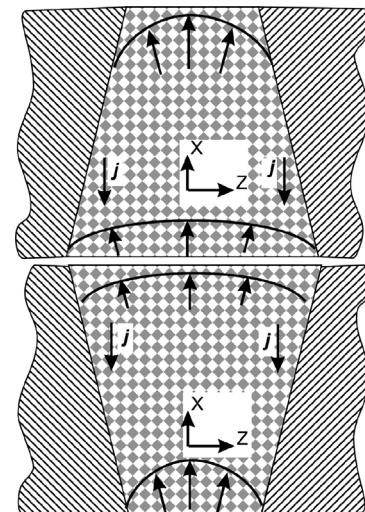flows, the sedimentation flow is directed towards the walls, in the narrowing direction, away from the walls, and at a constant sedimentation rate, the concentration maxima of the dispersed phase should shift. For example, in an expanding flow, the velocity of the medium, decreasing with height, will have a horizontal component directed to the nearest wall. One of the consequences may be the acceleration of segregation of components, the shift of the particle maximum to the walls, as well as the appearance of reverse wall currents of the dispersed phase. In a narrowing stream, the maximum concentration of particles will shift to the center. Thus, the shape of the channel will affect the position of the distribution maxima of dispersed phase. A numerical simulation confirms the well-known experimental effect of increasing the effective sedimentation rate of a dispersed impurity when the vessel walls deviate from the direction of gravity (Acrivos, Herbolzheimer, 1979; Nevsky, Osiptsov, 2009).

Another dynamic effect is associated with the instability of the flow of dispersed systems, which occurs as a result of the dependence of viscosity on the concentration of dispersed particles (Boronin, 2008). Viscosity increases with increasing concentration of dispersed particles. This leads to the fact that the velocity of layers with a high concentration of particles will differ from the Poisson flow (3), the condition for the existence of which is a constant viscosity over the cross section.

The collective behavior of particles can also be described with the thermodynamic approach using various equations of the state of a real solution. The existing models allow describing the distribution of components for true solutions with allowance for chemical and phase transformations (Abakumov, Fedoseev, 2002). For dispersed systems, such models are currently not available. When considering mantle flows, of particular interest could be equations of state similar to those that allow describing the behavior of stratified mixtures.

Discussion
Rheomorphic model
The textures and structures of ultramafic rocks of the ophiolitic association show signs of plastic flow, which was one of the main factors of petrogenesis and mineralization. The stratification of the mantle substance, accompanied, in particular, by the formation of bodies of chromitites, occurred during the solid-phase redistribution of minerals in the rocks, which are a dispersion system. The primary cause of plastic flow and structuring could be a decompression rise of the mantle material within the riftogenic structures and a seismic effect. Further complication of the internal structure and a deeper separation of matter probably occurred in a compression environment, which is probably

comparable with the current geodynamic settings in the mantle of forearc basins.

Olivine and orthopyroxene – the main rock-forming minerals of the mantle peridotites – have different "rheological strength". Indications can be found in a number of works (Carter, 1976; Hirth, Kohlstedt, 1996; Nicolas et al., 1971; Saveliev et al., 2008; Saveliev, Fedoseev, 2011, etc.). Characteristics of olivine are as follows: 1) fragmentation (polygonization) over the entire volume of protograins with the formation of a developed substructure; 2) relatively easy activation of secondary slip systems. In some cases, the misorientation of blocks within large grains leads to the formation of pseudopoikilitic inclusions of the type "olivine-in-olivine", which is known as intragranular (Carter, 1976) or rotational (Poirier, 1985) recrystallization.

Characteristics of orthopyroxene are as follows: 1) bending of unfavorably oriented grains with the formation of kink-bands, 2) intense nucleation – the formation of numerous recrystallization centers in areas of the greatest distortion of the crystal lattice; 3) inside the grains subject to bending, the formation of mechanical twins or lamellae of new phases (clinoenstatite, diopside) occurs; 4) in some cases, a transverse rupture of the grains occurs, and the gap is filled with an olivine aggregate. Recrystallization consists in the growth of new grains with a minimum of defects; the latter also include impurity components. The formation of dispersed phases of Cr-spinels is observed mainly in areas composed of a fine-grained aggregate – neoplasts of orthopyroxene.

In addition to structural evidence of more weakness of olivine compared with orthopyroxene, which is imprinted in mantle ultramafic samples, there is experimental evidence. In particular, the study of fluid inclusions in minerals from xenoliths in basalts and kimberlites shows a steady decrease in internal pressure in inclusions in the order of spinel $\geq$ orthopyroxene $\approx$ clinopyroxene $>>$ olivine, which indicates the uneven depressurization of inclusions on the way to the surface (Frezotti et al., 1992 Schwab, Freisleben, 1988; Yamamoto et al., 2002; et al.). It was suggested that a decrease in fluid pressure should be observed in the softest mineral, and an increase in the hardest mineral.

The literature describes studies of the relative "strength" of mantle minerals across the width of X-ray diffraction reflections as a function of pressure, temperature, and time (Yamamoto et al., 2008). The results obtained confirmed the conclusions made earlier on pressure measurements in fluid inclusions, and allowed us to conclude that olivine is the "weakest" of the mantle minerals of ophiolite peridotites considered. In addition, in the same work (Yamamoto et al., 2008), it was concluded that at temperatures above 800°C in the upper mantle conditions, the yield strength of ultramafic

rock-forming minerals approaches zero. At the same time, an increase in shear rate can be accompanied by a decrease in viscosity typical of pseudoplastic materials. The difference in the rheological behavior of minerals under these conditions results in the formation of more mobile (plastic) layers composed of monomineral olivine (dunites), which can be considered as "weakened" zones of the upper mantle, in which the plastic flow is localized.

At present, the rates of movement of mantle material estimated using remote sensing methods are lower. However, first, it should be noted that the data obtained are an "integrated" result for the mantle as a whole, which does not take into account the details of the structure of the mantle flows. The structural, mineralogical and geochemical features of ultramafic rocks discussed above indicate that dunite bodies can be weakened zones of the upper mantle, in which the movement of large mantle masses to the surface is localized. Second, there is reason to believe that the formation of ophiolitic ultramafic rocks, as well as their removal to the earth's surface from the mantle depths, could be due to more "rapid", catastrophic events in the past.

The features of the deformation process could be determined by the action of various physical fields: gravitational, hydrodynamic and hydrostatic, acoustic (vibrational, seismic). The above simulation results show that the hydrodynamic field arising inside the mantle flow, even in the absence of other factors, contributes to the redistribution of mineral phases in accordance with their physical properties.

Most likely, we deal with the result of a complex effect (superposition) of various factors in natural objects. In all options of the above effects, the determining parameter is the particle size; for gravitational, acoustic and hydrodynamic fields, density is an important factor; for a hydrostatic field, the elastic moduli of the rock components also become a significant factor.

Comparison with the existing views

At present, the widely accepted ideas about the formation of chromite in ophiolites are reaction-magmatic, fluid-metasomatic, as well as magma mixing models. The main reason for the rebirth of hypotheses, in which the leading role is played by deep fluids, is the numerous facts of the discovery of submicron inclusions in Cr-spinel crystals not only typical for ultramafic rocks of olivine, pyroxenes and PGM, but also "fluid-containing" minerals – amphibole, chlorite, serpentine, carbon-containing phases (Borisova et al., 2012; Pushkarev et al., 2015; Johan et al., 2017, etc.).

Undoubtedly, the discovery of mineral phases containing fluid components indicates the presence of fluids at the time of crystallization of Cr-spinels. At the same time, the question of the leading role of fluids in the formation of chromitites as geological bodies cannot be

positively resolved, relying only on such findings, since the fraction of fluids estimated from the inclusions found is hundredths of a percent. To substantiate such views, it is necessary to indicate the physicochemical mechanisms of the chromium transport by fluids in the required quantities and its deposition only in dunites. The fact is that "fluid-containing minerals" are present in even larger quantities in peridotites surrounding ore-bearing dunites, but accumulations of chromite are not formed in them. On the other hand, small amounts of fluid could be captured during syndeformational crystallization of Cr-spinels, and its role in the formation of dunites and chromitites may consist in a rheologically weakening effect on mantle ultramafic rocks (Saveliev, 2012).

The following arguments can be made against the ore-forming role of serpentinization processes. First, there is no dependence between the intensity of serpentinization and the scale of chromitite formation; deposits of massive ores are also found in weakly serpentinized dunites. Second, the primary structural features of chromite-bearing dunites are interrelated with those of surrounding peridotites (Denisova, 1989; Saveliev, 2013, etc.). Third, in ophiolite chromitites, textures are commonly observed, expressed in the fragmentation of chromite grains by transverse cracks that do not continue into the serpentinized enclosing dunite. This suggests that serpentinization superimposed on the already formed dunite-chromitite association: olivine, reacting with water, formed serpentine with an increase in volume, while chromite reacted to this change with brittle breaks. At the same time, it should be recognized that serpentinization, associated with the tectonic movement of blocks of ultramafic rocks in the upper levels of the Earth's crust, played a certain role in the regrouping of ore material in zones of serpentinite melange (Saveliev 2012).

The basis of reactionary magmatic ideas is the thesis that since mantle melts are not in equilibrium with residual peridotites, they had to move to the surface through isolated conduits, which are currently represented in the ophiolite complexes by dunite bodies (Kelemen et al., 1997; Spiegelman et al., 2001). In this case, it is believed that harzburgites and dunites of ophiolite complexes are not simple refractory residues from partial melting of pyrolite, but are the result of the reaction of restite with melts penetrating through it, generated at a greater depth. The melts dissolve pyroxenes and crystallize additional olivine, which leads to the formation of dunites in the extreme case. In some interpretations, dunites are considered to be isolated conduits through which basalt melts are transported to the surface (Kelemen et al., 1997). The formation of chromitites is associated exclusively with the transport of boninite melts through peridotites, the reaction of boninites with peridotites, the dissolution of pyroxenes,

the precipitation of olivine and high-Cr spinels (Zhou et al., 1996, etc.). To confirm the validity of this thesis, the authors of numerous publications (e.g. Gonzalez-Jimenez et al., 2011; 2014; Arai, Miura, 2015)) provide mainly geochemical data that are poorly or not at all related to the characteristics of the internal structure of rocks.

As noted above, in the fluid-metasomatic and reaction-magmatic models, there are no mechanisms for the formation of chromitites as geological bodies. Understanding this fact forces many researchers, supporters of the "melt-rock interaction model", to use various other mechanisms in explaining the genesis of chrome ores (e.g. Zhou et al., 2001, Miura et al., 2012)). In the cited works, previously developed models of magma mixing are proposed (Ballhaus, 1998; Lago et al, 1982; Leblanc, Ceuleneer, 1992), along with the "reactionary hypothesis". However, the application of mantle ultramafic models of magma mixing to form chrome ores is faced with the problem of "empty space", which is necessary for the deposition of large volumes of ores, but which is absent in a very low-porous crystalline upper mantle.

Within the framework of the reactionary hypothesis, it is difficult to explain the often observed sharp contacts of dunites and harzburgites, as well as an increase in the content of orthopyroxene in the near-contact parts of harzburgites, which is very often observed in ophiolites. Among the large number of publications devoted to the "melt-rock interaction" model, we did not find a description of the presence of incompletely dissolved pyroxenes, crystallization products of the components "extracted" from it, and crystallization products of the residual melt in the same area. At the same time, as a simple calculation shows, to convert even a small block of peridotite to a dunite (for example, 300*100*35 m with a volume of 10^6 m^3) requires a huge amount of reacted melt (300,000 tons), which must leave "petrographic traces" in one form or other (Saveliev, 2014).

In conclusion, some researchers, assuming the magmatic origin of dunites and chromitites, believe that they underwent a "moderate" tectonic effect later, which always led to the dilution and destruction of previously formed ore concentrations (Thayer, 1964; 1969; Greenbaum, 1977; Cassard et al., 1981 et al.). Foreign authors divide the deposits of chrome ores in ophiolite complexes into two types: podiform in the internal parts of the massifs and cumulative at the border with the gabbroid complex (Auge, 1987), suggesting different mechanisms of their formation. The latter are assumed to be, in particular, the crystallization of chromite in the supplying magmatic channels among restite and mixing magma of different composition (Ballhaus, 1998; Lago et al., 1982; Leblanc, Ceuleneer, 1992). The reality of all the proposed mechanisms is criticized by opponents

not without reason, and therefore, until now, almost all the hypotheses put forward "peacefully coexist", which indicates the lack of clear understanding of the processes of a matter differentiation in mantle ultramafic rocks.

The thermodynamic model proposed in this work demonstrates the possibility of the emergence of solid-phase flows under the conditions of the upper mantle and makes it possible to eliminate some of the difficulties and contradictions characteristic of magmatic and reactive-magmatic hypotheses. In particular, the implementation of the rheomorphic mechanism does not require additional sources of the substance and its transfer agents, since the material of the initial mantle peridotite is redistributed within the solid-phase flow. As noted above, the proposed model contains approximations and constraints, the failure of which can affect the concentration of the dispersed phase in the layers, the position of the density maxima of particles relative to the flow walls and the kinetics of formation. Further development and complication of the presented model in the long term will allow taking into account the collective behavior of chromite particles (aggregation) and its effect on sedimentation and flow structure.

Conclusion

In this work, a rheomorphic model is substantiated thermodynamically, it shows the possibility of the emergence of solid-phase flows under the conditions of the upper mantle and makes it possible to eliminate some of the difficulties and contradictions characteristic of magmatic, fluid-metasomatic and reaction-magmatic hypotheses. The developed model makes it possible to explain the regularities of the redistribution of the substance of the upper mantle in the process of the formation of ophiolite complexes and the formation of ore bodies.

The studies have shown that in ultramafic rocks of the ophiolitic assemblages, ubiquitous signs of plastic flow are recorded, which was one of the main factors of petrogenesis and mineralization. The main trend of changes in the composition and structure of mantle rocks is their stratification, accompanied by the separation of the weakest aggregates – dunite bodies, which are host rocks for chrome ores. One of the main factors of the mantle substance stratification could be the solid-phase redistribution of mineral particles in the rocks, which are a dispersion system.

The thermodynamic approach gives the most concise description of the phenomena. The result is a description of the most favorable state corresponding to the minimum free energy in the conditions considered. In the proposed model, these conditions are determined by the action of hydrodynamic and gravitational fields. The processes of mass transfer during the plastic flow of the mantle material can be associated with other

external fields, in particular, acoustic (vibrational, seismic), hydrostatic and temperature, as well as their superposition (Fedoseev, 2010). This work shows that the elastic properties of the components can also affect the distribution of the dispersed phase.

The proposed model allows us to state that the conditions arising from slow viscoplastic vertical flows of a multiphase material contribute to the stratification of the flow and the appearance of a layered structure in it. At the same time, the implementation of the described states can be affected by kinetic factors related to the duration of the process, temperature and viscosity of the medium, geometric configuration of the flow, short-term exposure to other factors, for example, seismic waves. If it is impossible to reproduce the actual conditions of the formation of the described geological structures in more detail, it is not necessary to complicate the model by taking into account additional factors. Although, in some cases, modeling of non-planar asymmetrical and non-vertical flows may be of interest.

Acknowledgements

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