Mineral equilibria at high PT-parameters

The equilibrium demonstrates formation of yimengite with variations of the ilmenite composition (it becomes more magnesian). The excess of Cr_2O_3 and TiO_2 demonstrates possible non-stoicheometry of titanates or formation of additional non-detectible oxides in the run products. No titanates are observed at lower $K_2CO_3/(H_2O+CO_2)$ ratios (table 1).

Conclusions. The dependence of crystallization intensity and appearance of K-Cr titanates on the amount of K₂CO₃ in the system was investigated. Based on the obtained experimental data, the reactions of mantle metasomatism describing the process of formation of K-Cr titanates are derived. In the experimental study of the reaction of chromite and ilmenite with aqueous potassium-carbonate fluid (melt) phases of the pair of titanates (piderite, vimengite and vimengite, mathiasite) - indicator minerals, mantle metasomatism, which directly confirms the possibility of formation of yimengite, mathiasite and K-Cr-priderite and other titanates, the result of mantle metasomatism of upper mantle peridotite under conditions of the highest activity of potassium (Safonov, Butvina, 2016).

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Fedkin V.V.¹, Shchipansky A.A.². Subduction initiation of the maksyutov eclogiteglaucophane schist complex (South Urals) UDC 549.6+552.16:552.48

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Abstract. The new geodynamic concept of the "Subduction initiation rule" (SIR) (Whattam and Stern, **2011**) connects the processes of formation of collision zones of lithospheric plates with the formation of ophiolitic complexes, pre-arc basins and the processes of initiation of subduction (SI). This concept predicts that most ophiolites were formed during SI and the diagnostic chemostratigraphic progression for SIR ophiolites is from less to more HESE-depleted and LILE-enriched compositions. The Maksyutov eclogite-glaucophane highpressure complex in the Southern Urals (MC) is a unique object for studying the phenomenon of subduction initiation. The main reason is related to the fact that along with the diagnostic magmatic chemostratigraphic sequence of SI and ophiolites, the reconstructed HP-UHP subduction channel, which is the Maksyutov complex, was also discovered here. To understand the geodynamics of the SI process, this is of paramount importance, since the time of HP-UHP metamorphism of the MC coincides with the appearance of the Magnitogorsk intra-oceanic island arc in the early Devonian. In this work, on the basis of precision XRF and ICP MS, analyzes of bulk composition of representative samples of garnet-bearing mafic rocks of the MC attempted to identify the temporal, tectonic and geochemical features (indicators) of the SI process and assess their role in the geodynamic development of the complex. The issues of the chemical composition and genesis of the protoliths of the complex, the geodynamic setting of their source, the participation in the subduction process of the mantle-plume mechanism and crustal contamination, as well as the role and importance of boninite-bearing ophiolites in the subduction initiation of are considered.

Keywords: Maksyutov complex, Ural Mountains, UHP metamorphism, protolith, eclogite, subduction, XRF and ICP MS bulk-rock chemistry

A new geodynamical concept 'The subduction initiation rule' (SIR) recently introduced by **Whattam and Stern (2011)**, creates seductive prerequisites for revising a large amount of factual material on geology, geochemistry, petrology, geochronology and geodynamics of the Maksyutov eclogite-glaucophane schist HP/UHP complex in the Southern Urals. The subduction initiation rule considers the processes of subduction nucleation in conjunction with the formation of ophiolite complexes, the development of forearcs basins and allows to establish patterns of the subduction process

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based on geochemical indicators, to evaluate its parameters: temporal, spatial, petrological. The Maksyutov eclogite-glaucophane schist complex is a unique object for studying the phenomenon of subduction initiation, because along with the diagnostic magmatic chemostratigraphic sequence and ophiolites, the restored HP/UHP subduction channel, which is the Maksyutov complex, is found here, and the time of HP/UHP metamorphism of the Maksyutov complex coincides with the appearance of the Magnitogorsk intra-oceanic island arc in the early Devonian (Brown et al., 2006; Puchkov, 2010).

The more than 50-year history of studying the complex and a large amount of factual material accumulated over this time creates a good basis for testing new geodynamic ideas, analyzing the causes of the emergence and conditions for the development of subduction structures. The mineralogical criteria and characteristic phases of ultrahigh pressure are well known: quartz pseudomorphs in coesite, graphite cuboids after diamond, diamond microinclusions in garnet and other minerals. There are numerous publications reflecting various interpretations of the geodynamic conditions, age, geochemical composition of rocks, and PT conditions for the formation of the complex. Nevertheless, some geodynamic aspects of the development of the terrane remain controversial due to the complexity of the subduction process and the diversity of the geochemical characteristics of its rocks. In this paper, an attempt is made to identify the temporal, tectonic and geochemical features (indicators) of the process of subduction initiation and to evaluate, taking into account the new concept, their role in the geodynamic development of the complex. This work is carried out on the basis of precision analyzes of the bulk composition of representative samples of garnet-containing mafic rocks MC.

The Maksyutov complex is located in the zone of the Main Ural fault, in the junction zone of the East European Platform and the western margin of the Siberian Craton, at the boundary of the Riphean rocks of the Suvanyak complex in the west and the Kempirsai hyperbasite belt, as a part of the Magnitogorsk island arc, in the east. Three structuralmaterial (lithological-tectonic) units are distinguished within the complex (Lennykh et al., 1995, Beane, Leech, 2007):

(1) the lower "subcontinental" eclogiteglaucophane schist unit: glaucophane and feldsparmica schists, quartzites with lenses, boudins, bodies and interlayers of eclogites, Grt-Cpx and less often Ol-En rocks;

(2) upper metaophiolitic unit, consisting of rocks of the oceanic crust, associated graphite crystalline schists and metagreywacks, sometimes including bodies and lenses of serpentinites, marbles and metabasalt rocks;

(3) and an intermediate Yumaguzin unit - metasedimentary rocks (quartzites and mica schists, without eclogite).

Of greatest petrological interest is the lower unit of the complex, in which, in addition to numerous lenses, bodies, boudins and layers of eclogitic rocks, there are described phases of ultrahigh pressure: diamond and coesite, as well as other mineralogical and petrological indicators of HP/UHP metamorphism: lawsonite associations, jadeite with quartz, olivine-enstatite ultramafites (Dobretsov et al., 1996; Lennykh et al., 1995; Beane, Connelly, 2000; Leech, Ernst, 2000; Valizer et al., 2015).

1. The chemical composition of the protolith. Previous works on the geochemistry of the rocks of the Maksyutov complex (Volkova et al., 2004; Beane and Sorensen, 2007; Valizer et al., 2015, Kovalev et al., 2015) have shown a wide variety of their bulk composition. Taking into account these data, 18 representative samples of mafic eclogites were analyzed by XRF and ICP MS, in the analytical laboratory of the University of Washington for rockforming, rare, scattered and rare-earth elements. For the main rock-forming components, most of the studied samples show a wide variation of compositions, but generally fall into the area of lowpotassium basalts with SiO₂ content of ~ 47-52 wt. %, And only one of them corresponds to basalt and esite with SiO₂ content of ~ 61 wt. % According to the Mg# = Mg/(Mg+Fe2+) index, mafic differences show strong fractionation in the range from 0.37 to 0.59-0.65. The calcium index Ca#=Ca/(Ca+ Na) of eclogitic rocks shows that the ratios of modal quantities of igneous clinopyroxene and plagioclase were approximately in equal proportions, around the mode of 50%. On the AFM diagram, Maksyutov eclogites form a single trend of the tholeitic and calc-alkaline series, including both depleted and enriched compositions. This emphasizes the origin of their protoliths from various mantle sources — N-MORB and OIB, respectively. However, a simple FeO*/MgO - SiO₂ diagram (Miyashiro, 1974) records changes in composition from tholeitic basalts to calc-alkaline basalts, basaltic andesites and andesites. It is extremely important to note that a shift in the composition occurs even in one eclogite block, 5 m \times 30 m, studied in detail by Volkova et al. (2004). However, this chemical pattern is more characteristic of volcanic island arc series or tectonic environments OIB, but not in MORB or BAAB (Zimmer et al., 2010). Bulk-rock composition does not show noticeable fractionation trends, and a variety of their composition does not allow identifying uniquely a single magmatic source of protolith. Thus, protoliths constituting HP/UHP mafic rocks of complex were originated either in contrast plate-tectonic environments, or from a common source, but under the influence of metasomatic processes of variant degree.

2. Genesis of the protolith. Most of the analyzed eclogite rocks of the Maksyutov complex do not reveal coherent positive anomalies of Eu and Sr in the REE spectra characteristic of middle crust gabbro intrusions that have undergone metamorphism of the eclogite facies, which proves their origin through the transformation of basalt. The behavior of rare and scattered elements (Sr / Sr *, Eu / Eu *, Gdpm, (La / Sm) pm), normalized to the primitive mantle, also confirms the volcanogenic origin of protoliths from the basalt melt. The increased Sr/Sr* values relative to the Eu/Eu* values in the eclogites of the Maksyutov complex indicate that their protoliths originated from a volcanogenic igneous source in the setting of island arcs IAB, and not during the fractional crystallization of the intrusive rocks MORB (Niu and O'Hara, 2009). The bulk of the points on the Gdpm - MgO and (La/Sm)pm - MgO diagrams fall on the trend of fractional crystallization of MORB, or in the field of enriched mantle melts. The only exception is one sample (235/236) with the highest Mg#, 0.65 and Ca#, 0.57, which indicates the most primitive composition derived from a mantle melting column. The REE spectrum of this sample shows a well-pronounced positive Sr anomaly $(Sr/Sr^*=1.8)$, which is more characteristic of the IAB situation than for the MORB. In combination with the highest possible magnesia and calcium levels, this may indicate the cumulative nature of the original gabbro or diabase.

3. Sources of protolith. For a long time, it was believed that the Maksyutov complex was formed during the subduction of the continental margin of the East European Plate to the east (Beane and Connelly, 2000; Brown et al., 1998; Brown et al., 2006; Puchkov, 2010) when it collided with the Magnitogorsk volcanic arc. However, the distribution of high-charging small elements in the eclogites of the complex shows that their compositions show depleted (La/YbN ~0.5-1.5) and enriched (La/YbN \sim 2-4.7) differences, indicating the origin of their protoliths from different mantle sources: N-MORB and OIB, respectively. In addition, most of the eclogites MK was very unusual in geochemistry - the so-called Nb-enriched basalts (NEB). This factor is an indicator of the subduction of oceanic ridges and the interpretation of eclogites as sills and dyke bodies in a reef basin on the edge of a craton requires at least clarification.

On the MnO*10 - P_2O_5*10 - TiO₂ diagnostic diagram, the bulk composition of UHP MC rocks overlaps the fields of basalts of oceanic islands, island-arc tholeiites, N-MORB and E-MORB basalts. Practically at each studied site of the complex two groups of samples are distinguished, the REE profiles of which are close to N-MORB or are clearly enriched relative to N-MORB with the elements LREE, MREE and HFSE. However, half of the samples of the first group that have similarities with N-MORB. detect negative Nb anomalies (Nb/Thpm=0.5-0.7 ppm), which indicates that they belong to the IAT plate-tectonic condition, and not to the N-MORB. In addition, many of them show positive Sr peaks, also typical of IAT. The second group of eclogites, with steeper REE spectra (La/Ybpm \sim 2-5), has negative Sr anomalies characteristic of MORB, and negative peaks of Ti, elements of the HFSE group: Nb, Zr, characteristic of the supersubduction zones (SSZ).

A very similar separation of REE spectra into two groups is also observed for high-Nb samples: (1) a group close to the OIB standard, with positive Nb anomalies, without signs of anomalous behavior of Zr and Ti, and (2) a group intermediate between OIB and E -MORB, with negative Nb peaks and weak Zr and Ti disturbances.

Thus, various geochemical indicators show at least the dual source of Maksyutov mafic eclogites' protoliths: the depleted basalts of the mid-oceanic ridges of the E-MORB type and the enriched basalts of the OIB oceanic islands and the subtle geochemical characteristics of their composition according to HFSE, rare and scattered elements allow to distinguish between the geodynamic features of sources of protolithic magmas.

4. The phenomena of the crustal contamination and the mantle-plume interaction make a certain contribution to the development of the subduction process, although perhaps to a lesser extent than the surrounding plate-tectonic situation. These processes are most clearly reflected in the ratios of high-field strength elements of the original rocks: TiO2 / Yb - Nb / Yb and Th / Yb - Nb / Yb, which were analyzed in detail by Pierce (2008). The compositions of Maksyutov eclogites are well interpreted by the interaction model of the OIB-type mantle-plume source and the MORB depleted mantle source. In the coordinates of TiO2 / Yb - Nb / Yb, the compositions of depleted mafic rocks lie within the MORB array, whereas enriched basalts, on the contrary, along the curve of polybaric melting from the deep garnet-bearing peridotite to much less deeper than spinel lherzolite mantle, being set the interval of baric conditions of possible magma generation for Maksyutov rocks from 3.5 to 1.5 GPa. The source of the mantle plumes - fragments of the Paleoproterozoic primitive mantle - could be deep magma chambers associated with hot spots. The presence of UHP ultramafic (Ol-En) rocks in the lithological-tectonic lower unit of complex structurally and spatially connected with eclogites (Valizer et al., 2015), confirms the participation of the ancient (Lower Cambrian - \geq 533 Ma) tectonic mantle-crust inclusions in the protolith substrate of the region.

5. Boninites as a sign of IP. Another important sign of the subduction initiation and mantle-crustal interaction is the occurrence of boninites or the ophiolite volcanites, a series of boninitic rocks that were formed in situ by partial melting of peridotite. In the structure of the South Ural Paleozoids, ophiolites are widely distributed, the composition of which rocks indicates that they were formed in a suprasubductive setting and belong to the boninite series. Such information is given for the Caledonian island-arc complex of the Sakmar zone, for the Buribay district in the west of the Magnitogorsk zone. The tectonic structure of the Maksyutov complex, the spatial connection and the temporal proximity of boninite-bearing ophiolites emphasize the influence of the activity of the mantle plume on the initiation of early Devonian subduction and indicate that Maksyutov ophiolites were formed in the suprasubduction environment.

6. Crustal contamination or contribution of a subduction component. The variable anomalies of Nb in the composition of the UHP rocks of the Maksyutov complex indicate both the absence of the crustal or subduction contamination (with Nb / ThN > 1) and its presence (with Nb / ThN < 1). The Th / Yb - Nb / Yb diagram is a sensitive indicator of crustal contamination (of contribution of the subduction component) to the petrogenesis of mafic volcanites (Pearce, 2008). The composition of eclogites of the Maksyutov complex for these components reveals another source of formation of protoliths. According to model calculations, most of the eclogite compositions, both depleted and enriched, fall into the MORB-OIB field, which, on the one hand, confirms their oceanic (not arc) and on the other, determines identity. the contribution of the subduction component, which ranges from 1 up to 4% and occurs due to the receipt of subduction material, not due to the mantle-crust interaction. This is probably due to the fact that the formation of the Early Devonian P-MORB range in the Southern Urals took place on the oceanic underwent suprasubduction lithosphere. which changes in Ordovician time (Ryazantsev et al., 2008).

Some conclusions and arguments.

The geochemistry of the basic eclogites of the Maksyutov complex shows that their protolith was tholeitic and sub-alkaline basalts, both enriched (of the OIB type) and depleted (of the N- and E-MORB types) with inherited signs of the subduction component and of subsequent metasomatic changes.

Most of the studied samples of eclogites of MK do not reveal coherent positive anomalies of Eu and

Sr, typical for intracrustal gabbro intrusions, which proves their origin through crystallization of basalt melt, and not transformation of crystalline gabbro.

Crustal contamination and an unusual (Nbenriched) composition of basalts are indicators of the subduction of oceanic ridges.

The presence of boninite-bearing ophiolites in the region implies participation in the subduction process of the mantle-plume mechanism, which developed in the supersubduction environment of the island-arc complex.

The geochemistry of the basic eclogites of the Maksyutov complex shows that the formation of their protoliths occurred with the participation of three different sources: the depleted mantle of the N-MORB type enriched by the OIB mantle, the inherited contribution of the subduction component, and possibly some mantle source.

As for the initiation of subduction, for its understanding of paramount importance:

1. A temporary combination of the formation of eclogites and ophiolites. The formation time of the HP-UHP channel and the metamorphism of the Maksyutov complex coincides with the appearance of the Magnitogorsk intra-oceanic island arc in the early Devonian;

2. Spatial combination. High-barreled (HP / UHP) subduction channel is actually combined with ophiolites into a single structural-tectonic terrane – the Maksyutov complex.

3. The necessary chemostratigraphic sequence is provided with a three-membered structure of MK: High-Pressure subcontinental part, with eclogites, the metaophiolitic upper unit consisting of oceanic crust rocks and flisch-like Yumaguzin metasedimentary sequence.

4. Finally, geochemical criteria for the composition of rocks that demonstrate various geodynamic settings of the complex formation in the process of its subduction.

Apparently, the most probable geodynamic settings, where processes of such mixing could be realized, could be pre-arc or back-arc areas of plate convergence, similar to those of the modern zone of convergence of the Pacific and Indo-Australian lithospheric plates.

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Khodorevskaya L.I. Experimental study of diopside-fluid H₂O-Na₂CO₃ interaction under pressure gradient conditions at 750°C.

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Abstract. High-temperature melanocratic metasomatism in basic rocks was simulated experimentally by transporting petrogenic components at a temperature of 750°C and a pressure of 500 MPa under pressure gradient conditions. Diopside (*Di*) in our experiments was a source of transported elements such as Si, Ca and Mg. The solution consisted of saturated Na₂CO₃. During the experiments under gradient conditions *Di* was partly dissolved and the dissolved components were redeposited as amphibole *Hbl*₅ on the surface. Normalizing *Hbl*₅ is accompanied by the removal of CaO and SiO₂. The experiments have shown that solutions containing Na and carbonate ions are not characteristic of basificate formation upon granitization.

Keywords: fluid , filtration, metasomatism, amphibole, granitization, basification.

The removal of Ca, Mg and Fe bases is essential for the construction of D.S. Korzhinsky's model of granitization which supplies alkalies and silica to host rocks. These elements are excessive for granite eutectics. As they are removed from host rocks, the rock approaches granite composition and is molten at corresponding P-T conditions. The components removed and redeposited are scattered or (less frequently) concentrated, giving rise to melanocratic metasomatic rocks called basificates. The addition and removal of components are largely controlled by the composition of the fluid phase which is filtered through the rock. The goal of the present study is to assess the transfer pattern of the above elements associated with the fluid $H_2O-Na_2CO_3$.

The directed flow of solution containing Ca, Mg, Fe, Si and Al under gradient conditions was reconstructed experimentally. Diopside (Di_{in}) was a source of the above elements, whose composition is given in table 1. Di_{in} was placed on the bottom of an ampoule. Saturated Na₂CO₃ (0.05-0.07 ml) solution was poured. A cylindrical amphibolite sample, prepared with regard for the internal diameter of the ampoule, was then inserted tightly into the ampoule. The amphibolite was a surface on which the elements removed from diopside were deposited. The amphibolite consisted of garnet, biotite, ilmenite and amphibole Hbl_{ucx} . (Table 1). The amphibole nomenclature, recalculation procedure of amphibole analyses to the crystal-chemical formula $AB_2C_5^{VI}T_8^{IV}O_{22}(OH)_2,$ and characteristics of isomorphism in the mineral follow recommendations by Leake et al. (1997). The distribution of cations between crystal chemical sites and the Fe3+/Fe2+ was calculated with the software of Schumaher (1997). The amphibolite corresponds to ferropargasite.

The distance between *Di* and the amphibolite was 15-20 mm, and they interacted only via a fluid phase. A thick-walled microchamber was mounted on the amphibolite. During the experiments an external pressure of 5 kbar spread into the lower portion of the ampoule because its walls are thin. Primary pressure in the upper portion of the ampoule was 1 atm because the walls of the microchamber are thick. Variations in pressure along the ampoule resulted in the directed flow of the solution between the ampoule walls and the sample (along the fractures in the samples, etc.) until the pressure in the upper and lower portions of the ampoule was levelled. These variations in pressure resulted in a small uncontrolled temperature gradient along the ampoule (throttling). Oxygen volatility in the experiments was not controlled because it was hard to fill the ampoules. The experiments were conducted for 240 h. The experimental temperature (750°C) was consistent with the conditions of formation of natural basificates upon granitization. A pressure of 400 MPa is typical of high-temperature metamorphic and metasomatic processes (Levitsky, 2005).

The composition of the initial phases and phases after the experiments are given in table 1.