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Four Stages of the Thermal Evolution of Eclogites from the Maksyutov Complex (South Urals)

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Abstract—Based on a detailed electron probe microanalysis of the composition and zoning of coexisting minerals (garnet, clinopyroxene, and plagioclase), we have studied the *P–T* conditions of formation of high-pressure (HP/UHP) rocks of the Maksyutov eclogite–blueschist complex in the South Urals. We have established its periodic evolution and have determined the specific thermodynamic parameters of mineral formation at each stage of its geodynamic history, from the conditions of crystallization of the protolith to the final stages of retrograde greenschist metamorphism. The new analytical data on the composition of coexisting phases confirm the high-pressure formation of eclogites present as numerous lenses, boudins, and interlayers among blueschist and feldspar–mica schists in the lower part of the complex. Thermobarometric calculations of metamorphism parameters were performed for the Grt + Cpx ± Pl + Qz paragenesis using a Grt–Cpx geothermometer and a Pl–Cpx–Qz geobarometer. Garnet in eclogites of the Maksyutov Complex, being conservative to changes in the *P–T* conditions, has a direct, reverse, or inverse chemical zoning. Under equilibrium of garnet with omphacitic clinopyroxene, this zoning records conjugate progressive and regressive *P–T* paths reflecting the thermodynamic conditions at the certain stages of the terrane evolution. Based on the data obtained, we have recognized at least four *P–T* stages of progressive metamorphic transformations of the Maksyutov Complex: (1) >800–910 °C/~2.5–3.5 GPa; (2) 540–790 °C/2.0–3.5 GPa; (3) 410–690 °C/1.1–2.5 GPa; and (4) 310–520 °C/1.0–1.2 GPa. The estimated *P–T* parameters of the conjugate regressive stages of metamorphism are as follows: (1) 870–625 °C/3.5–2.5 GPa; (2) 745–615 °C/3.5–2.0 GPa; (3) 690–550 °C/1.5–1.0 GPa; and (4) 590–460 °C/1.2–0.6 GPa, respectively. The age data for the certain stages, along with the parameters of metamorphism, form a single *P–T–t* path of the complex, which determines the position of the gradient of the metamorphic field during the complex exhumation.

Keywords: Maksyutov Complex, eclogite, HP/UHP metamorphism, garnet–clinopyroxene equilibrium, geothermobarometry

INTRODUCTION

The Maksyutov eclogite–blueschist complex in the South Urals is a typical plate-tectonic structure (terrane) in the zone of junction of large crustal tectonic structures: East European Platform and Magnitogorsk intraoceanic island arc.

Such complexes are usually localized in convergent suture zones and bear evidence for high (HP) or ultrahigh (UHP) pressure. Typical UHP phases (quartz pseudomorphs after coesite, graphite cuboid after diamond, and diamond microinclusions in garnet and other minerals) are well known in the rocks of the Maksyutov Complex (Chesnokov and Popov, 1965; Dobretsov and Dobretsova, 1988; Leech and Ernst, 1998, 2000; Bostick et al., 2003). There are numerous publications with different interpretations of the geodynamic settings (Puchkov, 1993; Beane et al., 1995; Lennykh et al., 1995; Dobretsov et al., 1996; Leech and Stockli, 2000; Beane and Leech, 2007; Valizer et al., 2013; Kovalev et al., 2015), age (Shatsky et al., 1997; Beane and Connelly, 2000; Valizer et al., 2015), and *P–T* conditions of its formation (Lennykh et al., 1995; Lennykh and Valizer, 1999; Leech and Ernst, 2000; Volkova et al., 2001; Lepezin et al., 2006; Valizer et al., 2011). Despite the long history of investigation of the complex, a number of issues regarding its geodynamic history, the conditions of its formation, the geochemical composition of its primary rocks (the protolith), and the evolution of rock metamorphism are still debatable and must be refined. In particular, the age of the peak of metamorphism and of the HP rocks of the complex and the *P–T* conditions of subduction process are controversial; the plate-tectonic setting of formation of the UHP rock protolith and the geochemical parameters of this process are not clear either. The estimated *P–T* conditions of formation of some major mineral assemblages of the Maksyutov Complex rocks are considered in literature, but there was no systematic study of the complex evolution from the protolith crystallization to the final stages of retrograde greenschist metamorphism.

The goal of this work is to solve one of the above key problems, namely, to study the physicochemical conditions of formation of the UHP rocks of the Maksyutov Complex,

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establish the cycles and stages of its metamorphism and geodynamic evolution, and estimate the thermodynamic parameters at each stage. The studies were carried out based on a detailed electron probe microanalysis of the composition and zoning of coexisting minerals, primarily garnet and clinopyroxene, the most informative phases in terms of mineralogical geothermobarometry. The obtained data and calculated physicochemical parameters give an insight into the *P–T–t* evolution of the Maksyutov Complex and permit evaluation of the heat flow at the UHP stage of its subduction and the so-called geothermal gradient of the metamorphic field (Spear, 1993) during its exhumation.

GEOLOGIC SETTING

The Maksyutov Complex is located in the southeastern part of the western slope of the South Urals in the Sakmara River basin and is a narrow terrane 15–20 km in width, 180–200 km in length (Lennykh et al., 1995), and ~5–10 km in thickness (Dobretsov, 1974). It is part of the South Urals Orogenic Belt; its geotectonic position is shown in Fig. 1. The complex has tectonic contacts with adjacent geologic structures. In the west it borders upon the underlying Paleozoic Suvanyak Complex of the East European Platform (Zonenshain et al., 1984, 1990; Puchkov, 1993; Matte, 1995; Scarrow et al., 2002). In the east, its tectonic boundary runs along the Main Uralian Fault, where it joins lower Paleozoic metabasalts of the Kimpersai belt, which is part of the Magnitogorsk island arc (Sengör et al., 1993; Berzin et al., 1996).

Three lithologic/tectonic units form a HP–UHP plate within the Maksyutov Complex (Valizer and Lennykh, 1988; Lennykh et al., 1995; Dobretsov et al., 1996; Lennykh and Valizer, 1999):

(1) lower “subcontinental” eclogite–blueschist unit formed by blueschists, feldspar–mica schists, and quartzites with lenses, boudins, and interlayers of eclogites and garnet–pyroxene and, more seldom, olivine–enstatite rocks;

(2) upper metaophiolitic unit made up of oceanic-crust rocks and associated graphite schists and metagreywackes with serpentinite, marble, and metabasalt bodies and lenses;

(3) intermediate Yumaguzin unit formed by metasedimentary rocks (eclogite-free quartzites and mica schists).

The complex protolith is of Precambrian age; the oldest dates (obtained by dating of detrital zircons from ancient provenances) cover the interval from 1.10–1.40 to 2.35–2.84 Ga (Valizer et al., 2011). Protolithic zircon from eclogites is dated at 581–533 Ma (Valizer et al., 2015). There are two viewpoints of the main stage of eclogite metamorphism: early Paleozoic (~550 Ma) (Coleman et al., 1993; Dobretsov et al., 1996) and late Paleozoic (390—375 Ma) (Shatsky et al., 1997; Lepesin et al., 2006). Some researchers assume a two-stage evolution of the complex, but most geologists believe that the peak of metamorphism fell on the Devonian (~390 Ma) (Lennykh and Valizer, 1999; Beane and Connelly, 2000; Hetzel and Romer, 2000; Glodny et al., 2002;

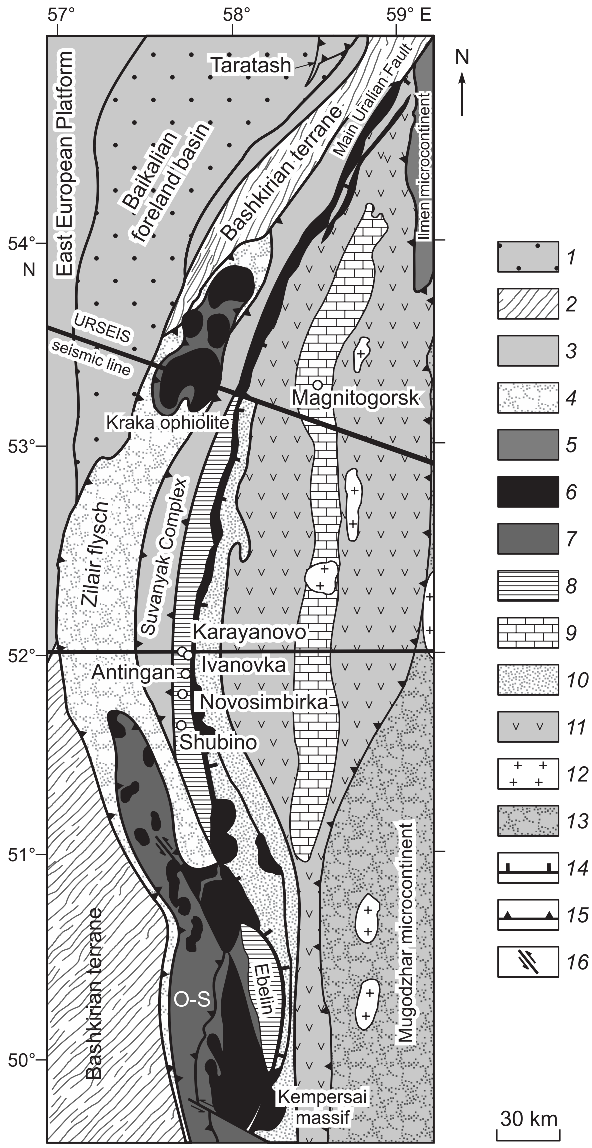

Fig. 1. Geotectonic map of the position of the Maksyutov Complex in the South Urals, adapted from Leech and Stockli (2000) and supplemented with the URSEIS (Urals Reflection Seismic Experiment and Integrated Studies) profile. *1–3*, parautochthonous units: *1*, Permian–Baikalian foreland basin, *2*, Bashkirian terrane, *3*, East European Platform; *4–8*, accretionary complexes: *4*, Zilair flysch (O–C), *5*, Suvanyak Complex (S–D), *6*, ophiolite complex and mélange zone, *7*, Uzian nappe, *8*, Maksyutov Complex; *9–11*, Magnitogorsk Zone: *9*, Carboniferous deposits, *10*, D–C deposits, *11*, Magnitogorsk volcanic arc (S–D); *12*, *13*, East Uralian Zone: *12*, granitoid intrusions (C–P), *13*, Precambrian microcontinental block; *14*, Main Uralian Fault, *15*, thrusts, *16*, other faults.

Leech and Willingshofer, 2004; Beane and Leech, 2007; Kovalev et al., 2015). Several younger isotopic ages (up to ~315–300 Ma) were obtained for the rocks cooled during the complex exhumation (Leech and Stockli, 2000; Lepesin et al., 2006).

The mineralogical and petrographic data on the parageneses of eclogites and on the host Grt–Cpx and Gln–mica schists show that they formed in the wide range of pressures and temperatures. Abundant boudins, lenses, and interlayers of mafic eclogites in garnet–glaucophane–mica schists and the presence of olivine–enstatite, quartz–jadeite, and lawsonite parageneses testify to rock metamorphism at 550–700 ºC/ 0.8–2.4 GPa (Lennykh et al., 1995; Dobretsov et al., 1996; Lennykh and Valizer, 1999; Beane and Connelly, 2000; Leech and Ernst, 2000). However, the observed quartz pseudomorphs after coesite (Chesnokov and Popov, 1965; Dobretsov and Dobretsova, 1988), graphite cuboids after diamond (Leech and Ernst, 1998), and diamond microinclusions in garnet (Bostick et al., 2003), which are mineral indicators of high and ultrahigh pressure, imply a lithostatic pressure of at least 2.8–3.2 GPa at the above temperatures at the early mineral formation stage. These data are supported by finding of jadeite eclogites in contact with ultramafic (Ol–Enst) UHP rocks, which suggests that the peak of eclogite metamorphism was at ~3.1–3.4 GPa/~633–740 ºC (Valizer et al., 2013, 2015).

Later, these rocks were exhumed and recrystallized under decompression and temperature decrease (300–400 ºC/0.6–0.8 GPa) to form glaucophane–greenschist parageneses. Thus, the lower unit of the Maksyutov Complex has preserved features of metamorphism of three stages: HP–UHP peak eclogite metamorphism, retrograde HP blueschist metamorphism of the decompression cooling stage, and greenschist metamorphism of the later deformation stage (Beane and Leech, 2007).

THE OBJECT OF STUDY

The lower lithologic/tectonic unit of the Maksyutov Complex is of the greatest petrological interest. It is a polymetamorphic complex of mafic eclogite, greenschist, and blueschist rocks. The unit is composed of garnet-glaucophane-mica, garnet-glaucophane, and feldspar–mica schists alternating with quartzites and contains numerous lenses, boudins, and interlayers of eclogites, garnet–pyroxene rocks, and scarcer olivine–enstatite rocks. This group of rocks was subjected to HP–UHP metamorphism and, later, low-pressure metamorphism of glaucophane–greenschist facies. The rocks of the lower structural unit host the following HP–UHP parageneses: (1) coesite (quartz pseudomorphs) + garnet + omphacite + rutile + zoisite; (2) jadeite + quartz + garnet + kyanite + paragonite; (3) garnet + omphacite + barroisite; and (4) garnet + glaucophane + lawsonite (Dobretsov et al., 1996; Lennykh and Valizer, 1999). Their formation conditions are generally estimated at 550–650 °C/15–25 GPa (Beane and Connelly, 2000; Leech and Ernst, 2000; Valizer et al., 2013). At the retrograde stage, garnet + glaucophane paragenesis formed in the unit rocks under blueschist and, then, greenschist facies metamorphism, forming a clockwise *P–T–t* path (Beane et al., 1995).

The upper structural unit is formed by mafic metaophiolites overlying eclogite–blueschist rocks of the lower complex. It consists of oceanic crustal rocks and associated graphite schists and metagreywacks, which formed before the metamorphic stage of the Ordovician–Silurian spreading. Metaophiolites of the upper structural unit sometimes contain bodies and lenses of serpentinites, marbles, and metabasaltic rocks. The unit was subjected to blueschist and, then, greenschist metamorphism and has a serpentinite mélange with lawsonite rodingites and gabbroid amphibolites. The conditions of metamorphism in the upper structural unit vary greatly, from 550–760 °C/2.2–2.5 GPa for Lws–Omp parageneses to 380–460 °C/~0.7–1.0 GPa for rocks with replacement of lawsonite by clinozoisite pseudomorphs and other low-temperature phases (Dobretsov et al., 1996; Valizer et al., 2013). The metamorphosed mélange rocks contain lithologic blocks of ultramafic rocks, blueschist metabasalts, and metasedimentary quartz–jadeite rocks.

The lower and upper structural units are separated by **the intermediate Yumaguzin unit**. It consists of metasedimentary rocks of the unclear degree of metamorphism, with a predominance of quartzites and quartz–mica schists and without eclogites. The rocks of the Yumaguzin unit underwent recrystallization under blueschist and greenschist facies conditions at 350–600 °C/0.5–1.7 GPa (Lennykh and Valizer, 1999).

A comprehensive study of eclogites of the Maksyutov Complex was carried out at the best studied informative areas in its southern part, from Shubino Village in the south to Karayanovo Village in the north (Fig. 1). Some information about the *P–T* conditions of formation of these eclogites was given elsewhere (Dobretsov et al., 1996; Lennykh and Valizer, 1999; Valizer et al., 2013, 2015), but these data were not compared and generalized in terms of thermobarometry.

METHODS

Eighteen representative samples of UHP rocks from the lower lithologic/tectonic unit of the Maksyutov Complex were analyzed for major, trace, and rare-earth elements by XRF and ICP MS in the Geoanalytical Laboratory of Washington State University (Table 1). By the recommendation of the Geoanalytical Laboratory, one sample was analyzed twice as two independent samples (158 and 158R), which confirmed the high reproducibility of analyses. The results of XRF and ICP MS analyses of rocks and the normative compositions of minerals are given in supplementary materials (http://sibran.ru/journals/Supplementary.pdf).

To study the physicochemical conditions of metamorphism and formation of the HP eclogite associations of the Maksyutov Complex, we used cation exchange thermobarometry, a common method for a petrological research (Perchuk et al., 1983), proceeding from the principle of mosaic (domain) equilibrium (Korzhinsky, 1973). This principle is based on the hypothesis that the centers and edges of the growing phases and the mineral inclusions in them were

Table 1. Mineral assemblages of rocks from the Maksyutov Complex and temperatures of their formation according to different geothermometers

Sample	Location	Rock	Paragenesis	Temperature of formation	
				T, °C*	*T*, °C**
88–16	Shubino	Grt–Cpx eclogite	Grt + Cpx + Gln + Act + Brz + Wnc + Ep + Ms + Rt + Qz	575–915	605–915
88–17	Shubino	Grt–Cpx eclogite	Grt + Cpx + Gln + Act + Brz + Wnc + Ep + Ms + Qz	785–815	780–820
154a	Shubino	Grt–Gln eclogite	Grt + Cpx + Gln + Amp + Ep + Ms + Chl + Qz + Ttn + Rt + Ab	425–560	455–610
158	Shubino	Grt–Gln schist	Grt + Cpx + Gln + Act + Ep + Ms + Chl + Qz + Ttn + Rt + Gr	535–605	565–745
159	Shubino	Grt–Gln eclogite	Grt + Cpx + Gln + Act + Ep + Ms + Chl + Rt + Qz	675–825	710–835
161	Shubino	Grt–Gln–Rt eclogite	Grt + Cpx + Gln + Amp + Ep + Ms + Chl + Qz + Ttn + Rt + Gr	680–750	765–790
163	Shubino	Grt–Ep–Act rock	Grt + Cpx + Gln +Act + Ep + Ms + Chl + Qz + Ttn + Rt	–	–
185v	Antingan	Altered eclogite	Grt + Cpx + Gln + Amp + Ep + Ms + Qz + Ttn + Rt	405–555	445–595
200–I	Karayanovo	Grt–Gln eclogite	Grt + Cpx + Gln + Ms + Qz + Ttn + Rt + Opq	590–655	560–630
200–II	Karayanovo	Grt–Cpx eclogite	Grt + Cpx + Gln + Ms + Qz + Ttn + Rt + Opq	550–750	545–695
200–III	Karayanovo	Qz–Cpx–Gln interbed	Qz + Cpx + Gln + Grt + Opq	525–510	495–720
207	Karayanovo	Grt–Gln eclogite	Grt + Cpx + Gln + Ep + Ms + Qz + Ttn + Rt	585–825	630–820
213	Karayanovo	Eclogite	Grt + Cpx + Gln + Act + Ms + Qz + Ttn + Rt	–	–
216	Karayanovo	Grt–Gln eclogite	Grt + Cpx + Gln + Act + Amp + Ep + Ms + Qz + Rt + Ab	615–670	640–690
219	Karayanovo	Altered eclogite	Grt +Cpx + Gln + Act + Ms + Qz + Rt	645–720	690–735
230	Novosimbirka	Altered eclogite	Grt + Cpx + Gln + Act + Ep + Czo + Rt + Chl + Qz + Ttn + Ab	485–530	515–565
231	Novosimbirka	Altered eclogite	Grt + Cpx + Gln + Act + Ep + Chl + Qz + Ttn + Ab	605–675	595–705
235	Novosimbirka	Altered eclogite	Grt + Cpx + Gln + Act + Ep + Chl + Qz + Ttn + Ab	470–555	500–610
236	Novosimbirka	Chl–Ep rock	Grt + Cpx + Act + Ep + Czo + Chl + Qz + Ttn + Rt + Opq + Ab	300–415	395–480
238	Novosimbirka	Grt–Gln schist	Grt + Gln + Act + Ep + Chl + Qz + Ttn + Rt + Opq + Ab	500–670	545–720
239	Novosimbirka	Grt–Ep–Amp rock	Grt + Cpx + Gln + Ep + Czo + Qz + Ttn + Rt + Ab	415–675	470–715
267	Karayanovo	Grt–Omp eclogite	Grt + Cpx + Gln + Ep + Qz + Ttn + Opq + Ab	570–770	590–785
271	Karayanovo	Grt–Gln–Omp eclogite	Grt + Cpx + Gln + Act + Amp + Ep + Ms + Chl + Qz + Rt + Cal	860–925	875–920
273	Karayanovo	Grt–Gln–Rt eclogite	Grt + Cpx + Gln + Act + Ms + Chl + Qz + Pl	515–725	525–760
288	Ivanovka	Grt–Gln schist	Grt + Cpx + Gln + Act + Ep + Ms + Chl + Qz + Ttn + Rt + Ab	445–510	505–565
289	Ivanovka	Grt–Act–Ep–Chl rock	Grt + Act + Ep + Ms + Chl + Qz + Ttn + Ab	545–930	570–915

N o t e . Mineral abbreviations are after Whitney and Evans (2010). Samples 88–16 and 88–17 were kindly donated by P.M. Valizer (Il'meny State Reserve).
* Temperatures were calculated for P = 2.5 GPa (Krogh and Ravna, 2000).
** Temperatures were calculated for P = 2.5 GPa (Powell, 1985).

in thermodynamic equilibrium at different times of their crystallization and that their compositions reflected the thermal conditions of the successive stages of metamorphism. The compositions of coexisting phases and mineral inclusions were used to reconstruct the thermal evolution of these polymetamorphic rocks. The chemical composition, heterogeneity, and zoning of the minerals were examined by electron probe microanalysis at the Korzhinsky Institute of Experimental Mineralogy (IEM), Chernogolovka. We analyzed both large porphyroblastic grains of contacting minerals and newly formed crystals in the rock matrix, grains with direct and reverse zoning, and various types of inverse zoning. Electron probe microanalysis for a number of elements (from Be to U) was carried out with a Tescan Vega II XMU (Tescan, Czech Republic) scanning electron microscope equipped with an INCA Energy 450 X-ray microanalysis system with an INCAx-sight (Oxford Instruments, England) energy dispersive X-ray spectrometer. Operating conditions: accelerating voltage of 20 kV, Co beam current of 0.3 nA, and measurement time of 70 s per point. Measurements were made along the analytical lines and with the use of the IEM standards employed for electron probe microanalysis of minerals.

Garnet–pyroxene mineral thermobarometry of mafic rocks. Garnet and clinopyroxene in the HP–UHP metamafic rocks are treated as well-preserved and most informative phases for the estimation of mineral equilibrium temperatures. We tested different Grt–Cpx thermometers (Råheim and Green, 1974; Ellis and Green, 1979; Ganguly, 1979; Powell, 1985; Ai, 1994; Krogh and Ravna, 2000) and chose the most common Powell garnet–clinopyroxene geothermometer (Powell, 1985) and its last version, the Krogh–

Ravna geothermometer (2000) (Table 1). The systematic discrepancy in the temperatures of the two thermometers is within the accuracy of their measurements, ±30–40 °C, which is not significant for a relative comparison of the crystallization temperatures of zoned phase crystals during their growth in equilibrium with other minerals. Therefore, we used a Powell (1985) thermometer for subsequent constructions of the *P–T–t* paths of the metamorphism evolution, focusing attention on the relative temperature differences between different zones of garnet during its crystallization and between individual garnet grains in the rock matrix.

P–T CONDITIONS OF FORMATION OF ECLOGITES OF THE MAKSYUTOV COMPLEX

Minerals for the estimation of the parameters of eclogite metamorphism. The physicochemical conditions, cycles, and stages of metamorphism of the Maksyutov Complex were determined by a comprehensive study of the composition and zoning of coexisting minerals, namely, garnet, clinopyroxene, and plagioclase. We studied host-rock samples with different degrees of retrograde metamorphism and with different phase morphologies and structures.

Garnet is present as large porphyroblasts and as small, often euhedral, crystals in the rock matrix in almost all samples. It is chemically and morphologically inhomogeneous. The large porphyroblasts are cracked and disintegrated, with unclear uneven outlines. They often abound in quartz, epidote, titanite, rutile, and, less often, clinopyroxene and plagioclase inclusions. Sometimes they are totally replaced by an assemblage of secondary minerals, which can fill box or framework mineral structures. Such grains usually show a regressive zoning: They have high-temperature cores, whereas their rims are similar in composition to the matrix garnet. The examined garnet porphyroblasts show different (progressive or regressive) zonings, thus marking opposite temperature trends of metamorphism. Sometimes, traces of opposite metamorphic processes are present in the same sample or even in the same garnet grain. The representative and most typical compositions of the cores and rims of garnet porphyroblasts and of matrix garnet are given in (http://sibran.ru/journals/Supplementary.pdf).

Clinopyroxene is present in the rock matrix as small (0.1–0.4 mm) short-prismatic crystals (sometimes, up to 40–55%) together with glaucophane, epidote, chlorite, muscovite, and quartz. The crystals often have rims of glaucophane, chlorite, or small-grained aggregate of these minerals. Pyroxene inclusions in garnet do not differ in composition from clinopyroxene grains in the rock matrix, which are also used for the estimation of the *P–T* parameters of the Grt–Cpx–Ab–Qz equilibrium. The composition of clinopyroxene in the rocks is similar to that of omphacite and changes insignificantly within the samples (Supp. Matl. 4). The mole fraction of jadeite (X_{Jd}) in clinopyroxene contacting with large porphyroblastic garnet grains, in clinopyroxene inclusions in garnet, and in matrix clinopyroxene is ~0.2–0.40; but X_{Jd} within a clinopyroxene grain does not exceed 0.30–0.35. The maximum mole fraction of jadeite in some samples is 0.60–0.65. The analyzed omphacites are rich in an Eskola–Tschermak component, which confirms their HP genesis (Lennykh and Valizer, 1999).

Plagioclase coexisting with garnet and clinopyroxene is found only in low-pressure rocks that underwent regressive secondary alterations. Usually it occurs as small untwinned crystals (0.1–0.2 mm) composing (along with chlorite, muscovite, and quartz) the rock matrix. Sometimes, plagioclase grains are localized near spots of secondary chlorite. Plagioclase inclusions in large garnet grains significantly facilitate the interpretation of the metamorphism conditions during the rock formation. By optical properties (estimation of the composition according to symmetrical extinction), plagioclase varies in composition from nearly pure albite to Ab_{5-7}. The microprobe-measured content of Na in the mineral is underestimated because of its loss during the analysis; therefore, the measured composition of plagioclase does not exceed An_3 (Supp. Matl. 5). Surely, this error results in the underestimated equilibrium pressure for the Grt–Cpx–Pl–Qz paragenesis, 0.1–0.2 GPa. These deviations in Pl composition do not affect seriously the relative pressure values; therefore, in Table 2 we present the *P* values calculated from the measured composition of plagioclase. For a relative comparison of minor changes in the composition of plagioclase during its formation, we used the mole fraction of anorthite, Pl_X = An/ (Ab + An + KFs) ·100%, which is a more sensitive and precise value in this case.

The *P–T* parameters of formation of the Maksyutov Complex eclogites, calculated from the Grt–Cpx ± Pl–Qz equilibrium, are given in Table 2 as temperature and/or pressure trends during the crystallization of coexisting garnet and pyroxene at their contact in the cores and rims of large grains, in mineral inclusions, and in the rock matrix. The calculation was made from data of probe microanalyses of the coexisting phases (http://sibran.ru/journals/Supplementary.pdf).

Shubino Village area. According to petrological and Grt–Cpx thermometry data, the maximum degree of prograde metamorphism of the Maksyutov eclogites was reached in the Shubino Village area. High-Ti high-Fe eclogites outcropping in several small quarries here bear predominantly a Grt + Cpx + Gln + Ep + Qz + Rut paragenesis (Shubino type), in which large (up to 5–10 mm) euhedral garnet grains have preserved a progressive zoning. The maximum *P–T* parameters estimated with a Grt–Cpx thermometer are 800 → 900 °C/~3.5 GPa (Table 2, samples 88-17 and 161), which corresponds to the UHP stability conditions of diamond and coesite found earlier in mafic eclogites of the complex (Chesnokov and Popov, 1965; Dobretsov and Dobretsova, 1988; Leech and Ernst, 1998; Bostick et al., 2003).

In sample 159, the composition of garnet varies from $Alm_{59}Prp_{14}Grs_{27}Sps_1$ in the grain core to $Alm_{64}Prp_{12}Grs_{23}$

Table 2. Physicochemical conditions of formation of HP rocks of the Maksyutov Complex and their *P*–*T* trends

Sample	Location	Temperature of formation, from the Grt–Cpx equilibrium (Powell, 1985), °C			Pressure, GPa		Temperature trends from core to rim of zoned grain, °C	Classification of *P*–*T* trends, *T*, °C
		Core, inclusions	Middle zone, inclusions	Rims and contacts	Petrological data	Pl–Cpx–Qz barometer (Perchuk, 1992)		
88-16	Shubino	875	786	770–626	3.5–2.5	–	875–625	Retr. 1, **875**–630
88-17	Shubino	805–830	849	881–892	3.5	–	805–890	Progr. 1, **>800–900**
154a-pr	Shubino	448–511	–	518–620	1.5	1.19–1.26	450–620	Progr. 3b, 400–**630**
154a	Shubino	406–519	–	511–628	1.5	1.19–1.26	405–630	Progr. 3b, 400–**630**
158	Shubino	563–585	–	622–708	2.5	–	565–710	Progr. 2, 560–**790**
159	Shubino	866–788	–	781–731	3.5	–	865–730	Retr. 1, **875**–630
161	Shubino	801–816	802	892–899	3.5	–	800–890	Progr. 1, **>800–900**
230B-1	Novosimbirka	544–459	509–433	385–313	1.0	1.19–1.17–1.04	545–315	Retr. 4, 545–310
230B-2	Novosimbirka	493–498	528	545	1.0	1.11–1.16	495–545	Progr. 4, 385–545
231	Novosimbirka	562–581	587	601–679	1.5	1.20–1.33	560–680	Progr. 3a, **470**–690
235	Novosimbirka	470–522	484–541	548–575	1.0	0.74–1.26	470–575	Progr. 4, 385–545
236-1	Novosimbirka	384–419	372	423–453	1.0	0.96–1.16	385–455	Progr. 4, 385–545
238-1	Novosimbirka	490	526	693	1.5	–	490–695	Progr. 3a, **470**–690
238-2	Novosimbirka	513	549	639–741	2.5	–	515–740	Progr. 2, 560–**790**
238-2-2	Novosimbirka	665	690	817	3.5	–	665–815	Progr. 1, **>800–900**
239-1	Novosimbirka	650	624	560	1.5	1.37–1.10	650–560	Retr. 3, **690**–450
239-2	Novosimbirka	692–569	451	381	1.5	1.34–1.03	690–380	Retr. 3, **690**–450
239-3	Novosimbirka	593–541	531	514–450	1.5	1.31–1.13	595–450	Retr. 3 and 4, **590**–450
185b-1	Antingan	473–496	517	526–657	1.5–2.0	–	475–655	Progr. 3a, **470**–690
185b-2	Antingan	594	573	546–498	1.5	–	595–500	Retr. 4, 595–450
185v-1	Antingan	427–479	521	571–595	2.5	–	425–595	Progr. 3b, 400–**630**
200-I c	Karayanovo	622–627	–	677–680	3.5	–	620–680	Progr. 3a, **470**–690
200-II m	Karayanovo	619–637	677	770	3.5	–	620–770	Progr. 2, 560–**790**
200-III r	Karayanovo	744–704	691	673	3.5	–	745–675	Retr. 2, 750–610
200-IV mx	Karayanovo	473–516	487	564–627	3.0	–	475–625	Progr. 3b, 400–**630**
207-I inn	Karayanovo	568	599–608	625–751	1.5	1.37–1.40	570–750	Progr. 2, 560–**790**
207-II out	Karayanovo	689	–	789	1.5	–	690–790	Progr. 2, 560–**790**
207-III	Karayanovo	559	615–639	649–688	1.5	–	560–690	Progr. 3a, **470**–690
216-inn	Karayanovo	727–694	715	663–613	1.5	1.43–(1.60)	725–615	Retr. 2, 750–610
216-out	Karayanovo	629	631	635–658	1.5	(1.66)–1.46	630–660	Progr. 3a, **470**–690
219	Karayanovo	591–597	676	766	3.0	–	590–765	Progr. 2, 560–**790**
219-2	Karayanovo	671	708–714	751	3.0	–	670–750	Progr. 2, 560–**790**
219-3	Karayanovo	544–580	694	773	3.0	–	545–775	Progr. 2, 560–**790**
219-3-1	Karayanovo	523–556	718	843	3.5	–	525–845	Progr. 1, **>800–900**
267-1	Karayanovo	591–598	646	726–784	2.5	–	590–785	Progr. 2, 560–**790**
267-2	Karayanovo	475–561	610	617–667	2.0	–	475–665	Progr. 3a, **470**–690
267-2-pr	Karayanovo	463–488	486–508	566–605	2.0	–	465–605	Progr. 3b, 400–**630**
271	Karayanovo	661	681–716	793–907	3.5	–	660–910	Progr. 1, **>800–900**
273	Karayanovo	534–545	574	700–776	3.0	–	535–775	Progr. 2, 560–**790**
288	Ivanovka	464–485	586	520–670	1.5	1.04–1.42	465–670	Progr. 3a, **470**–690
289-1 r	Ivanovka	627–592	525	484–474	1.5	–	625–475	Retr. 3, 690–470
289-2 c	Ivanovka	638	–	721	2.0	–	640–720	Progr. 2, 560–790
289-3-1	Ivanovka	564	480	475–449	2.0	(1.04–1.14)	565–450	Retr. 4, 590–450
289-4 m	Ivanovka	728	584	440	2.0	(1.30–1.08)	730–440	Retr. 2 and 3, 745–450
289-4-1sg	Ivanovka	470–492	559–605	709	1.5	–	470–710	Progr. 2, 560–**710**
289-5 c	Ivanovka	536	564	698–712	2.0	–	535–710	Progr. 2, 560–**710**

Note. The hyphenated numbers and letters denote particular sites of the same sample. pr, profile; inn, inner zone of grain; out, outer zone of grain; sg, small grain; c, core; m, middle zone; r, rim. Hereafter, Progr. is a prograde *P*–*T* trend, and Retr. is a retrograde *P*–*T* trend. The critical (most significant) values of the final temperature trends are bold-typed. Parenthesized pressure is given tentatively.

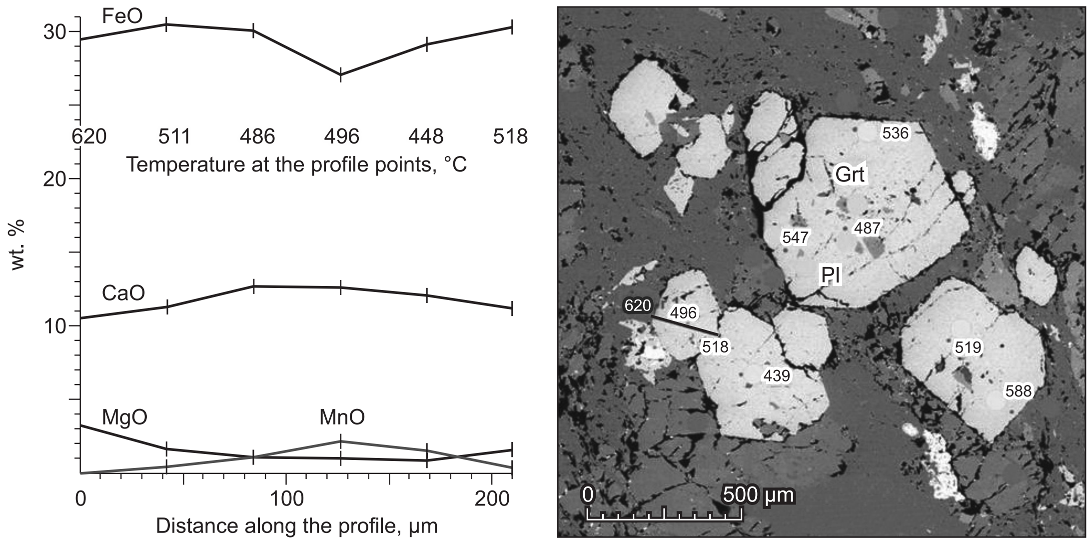

Fig. 2. Progressive zoning in garnet (sample 154a, Shubino Village) in equilibrium with clinopyroxene records a prograde temperature trend of the third stage of metamorphism (448–620 °C). The composition of plagioclase inclusions in the core of euhedral garnet grain reflects the pressure at the beginning of its crystallization, 1.19–1.26 GPa. Numerals in the photo mark a temperature, °C.

$Sps_{0.7}$ in the rim, with the temperature of the Grt–Cpx equilibrium decreasing from 866–788 to 781–731 °C and then to 626 °C and the pressure decreasing from 3.5 to 2.5 GPa (Table 2, sample 88-16). Eclogites with such a significant difference in the *P–T* parameters of the retrograde stage are rare; however, we revealed them at the Novosimbirka area in the vicinity of Ivanovka and Karayanovo villages (Table 2, samples 239-2, 289-4m, and 219-3-1).

Other eclogite samples from the Shubino area bear evidence for two more stages of prograde metamorphism, at 406–628 and 563–708 °C and ~1.5–2.5 GPa (Table 2, samples 154a and 158). One of these samples is shown in Fig. 2. The progressive zoning in garnet in equilibrium with clinopyroxene records its progressive temperature trend from 439–487 to 588–620 °C. The cores of well-faceted euhedral garnet crystals contain plagioclase inclusions. Based on the composition of plagioclase, we have estimated the equilibrium *P–T* parameters of the beginning of crystallization of the Grt–Cpx–Ab–Qz assemblage, 440–450 °C/1.2–1.3 GPa. These values mark one of the stages of progressive blueschist facies metamorphism. One more prograde metamorphism trend, 563–708 °C, is records in the composition of zoned garnet in sample 158. This rock is free of plagioclase, which confirms its high-temperature formation.

The Novosimbirka and Antingan areas located north of Shubino Village are characterized by a decrease in the *P–T* parameters of metamorphism. Most of the rock samples from these areas contain small grains of secondary plagioclase similar in composition to albite. Its presence indicates the rock alteration under retrograde metamorphism at a relatively low pressure (in the stability region of the Ab–Jd–Qz paragenesis). Nevertheless, garnets from these areas show both progressive and regressive zonings. In relatively fresh eclogites, without plagioclase, well-faceted euhedral garnet crystals have a progressive zoning, with the maximum temperatures of the Grt–Cpx equilibrium varying from 490–513 to 740–817 °C (Table 2, sample 238). It is one of the best preserved eclogite samples; the garnet grains in it are characterized by the widest range of compositions, from $Prp_{1.9}Alm_{53}Sps_{32}Grs_{13}$ in the core (http://sibran.ru/journals/Supplementary.pdf) to $Prp_{8.4}Alm_{62}Sps_{30}Grs_0$ in the rim (http://sibran.ru/journals/Supplementary.pdf). The composition of this garnet reflects the *P–T* changes at three prograde stages of metamorphism: 490 → 693 ºC/~1.5 GPa, 513 → 741 ºC/~2.5 GPa, and 665 → 817 ºC/~3.5 GPa. The rock (Grt–Cpx–Gln eclogite) has a porphyroblastic texture and contains large grains of brownish-red garnet unevenly distributed throughout the rock as broken chains. The grains are 1–2 mm in size, with cracks filled with quartz and muscovite. The grain cores contain inclusions of small quartz, glaucophane, chlorite, titanite, and rutile grains. The rock matrix is composed of a small-grained diverse acicular glaucophane aggregate (up to 70%) and actinolite developed after it. There are also preserved scarce short prisms of pale green pyroxene of relatively stable composition (http://sibran.ru/journals/Supplementary.pdf). Most of primary pyroxene has preserved only the grain shape, but the mineral has been completely replaced by a small-grained aggregate of amphibole, glaucophane, and epidote. The rock contains much (2%) titanite with inclusions of small rutile grains. The texture, mineral composition, and three *P–T* paths of the rock are very similar to those of the Shubino eclogites.

All other studied rock samples from the Novosimbirka area contain plagioclase and are low-temperature diaphthorites. They also bear evidence for progressive *P–T* paths of metamorphism but of low grade (greenschist facies): from 384–453 ºC/1.0–1.2 GPa to 650–680 ºC/1.2–1.4 GPa. Sometimes, the sample contains garnet grains with both direct and reverse zonings (Table 2, sample 230B). The maximum temperatures of the prograde stage recorded in it (495–545 ºC) coincide with the temperature of the beginning of the retrograde stage (545–315 ºC), when heating of the rock was changed by its cooling, i.e., two conjugate processes ran, marking a change in the temperature regime of metamorphism. This indicates the cyclic character of crystallization of the Maksyutov rocks, on the one hand, and its incomplete character in equilibrium systems, on the other. The compositions of coexisting minerals in six studied samples from the Novosimbirka area records four progressive temperature trends — 384→453 ºC (sample 236-1), 470→575 ºC (samples 230B-2 and 235), 562→679 ºC (sample 231), and 665→817 ºC (sample 238-2-2) — and three regressive trends — 650→560, 593→450, and 544→313 ºC (Table 2), which successively change each other, sometimes in similar temperature ranges. The widest range of the temperatures of retrograde metamorphism (more than 310 ºC) is established in sample 239-2. The temperature drop in this sample is due to the varying composition of pyroxene, whose mg# value changes from grain to grain in the interval $X(Fe^{2+}/Mg)$ = 0.064–0.447 and mole fractions of jadeite and aegirine are X_{Jd} = 0.25–0.36 and X_{Aeg} = 0.13–0.0, respectively. At the same time, the composition of garnet contacting with this pyroxene is almost constant, $Prp_{13.4–14.3}Alm_{60.6—59.3}Sps_{3<0.2}$ $Grs_{26—26.2}$ (Supp. Matl. 3).

The Antingan area is located between the Novosimbirka and Karayanovo villages. Weakly altered eclogites from this area lack plagioclase. In **sample 185b-1**, euhedral porphyroblastic garnet of fresh appearance with the minimum number of inclusions has slight cracks parallel to the rock schistosity. In equilibrium with clinopyroxene it records a progressive temperature trend in the interval 473–657 ºC (Table 2). The above sample also contains less altered garnet grains. They are cracked and abound in glaucophane, epidote, muscovite, chlorite, and titanite inclusions and small rutile grains. Their cracks are not parallel to the rock schistosity. Glaucophane grains encircle garnet porphyroblasts and are intergrown with epidote grains. Quartz, titanite, and glaucophane accumulated around the garnet grains as bending jets make a shadow structure of their rotation and transition (Table 2). These garnet grains show a regressive zoning recording a regressive temperature trend from 594 to 498 ºC, which is almost the same as the regressive trend in the Novosimbirka Village area (Table 2, sample 239-3). The temperature interval of the prograde–retrograde metamorphism of the Antingan eclogites, from 427–496 to 595–657 ºC at 1.5–2.5 GPa, determined the *P–T* conditions at the third stage of metamorphism in all studied areas of the Maksyutov Complex. High-temperature (>620–660 ºC) rocks are almost free of plagioclase (Table 2, samples 238, 185, 200, 219, and 267), and its presence in some other samples is due to its later formation during diaphthoresis.

The Karayanovo Village area is easily accessible and thus has been studied in more detail. Eclogites of this area were repeatedly subjected to prograde and retrograde metamorphism, and the temperatures of their formation vary greatly, from 310–400 to 780–900 °C (Table 2). The maximum temperatures have been established for the freshest samples from the cores of eclogite boudins: from 680–700 to 800–900 °C at ~3.5 GPa. They are close to the parameters of formation of eclogites from the Shubino area and, most likely, correspond to the peak of eclogite metamorphism in the Maksyutov Complex as a whole. Other samples of mafic rocks from the Karayanovo area show a significant scatter of the *P–T* parameters of metamorphism depending on the structural position of eclogite bodies (boudins, lenses, and interlayers) and the degree of their secondary alteration. The morphology of garnet grains and their zoning depend on these parameters.

In Grt–Gln eclogite (sample 216), large porphyroblastic garnet grains are cracked rhombic dodecahedron crystals. In the cores, the cracks are filled with quartz, glaucophane, muscovite, and finest rutile grains. Some garnet grains have altered completely, except for the edges. The core of the garnet grain shows a regressive zoning, and the rim formed under conditions of a slight temperature increase (Fig. 3). Plagioclase in the rock has a contrasting composition: At the contact with the rim of garnet grain, a small plagioclase grain is almost pure albite ($Pl_{0.23}$), and plagioclase in the rock matrix has a composition $Pl_{2.89}$ (Supp. Matl. 5). Nevertheless, both compositions of plagioclase at its contacts with garnet and pyroxene show similar pressures of eclogite formation, 1.43–1.46 GPa. According to the *P–T* paths of this eclogite sample, only the edges of the inner zone and rim of garnet grains fall in the stability field of the Cpx–Pl–Qz paragenesis, ≤620–650 °C/≤1.5 GPa. The phase compositions of the two zones indicate the following *P–T* conditions of their formation: (1) inner zone: core — $Prp_{15}Alm_{57}Sps_2$ $Grs_{26}/Jd_{50}/(Pl_{2.89})$/694 °C/(1.6) GPa, edge — $Prp_{14}Alm_{61}Sps_2$ $Grs_{23}/Jd_{44}/Pl_{2.89}$/613 °C/1.43 GPa; (2) overgrown rim: core — $Prp_{19}Alm_{59}Sps_{1.2}Grs_{20}/Jd_{45}/Pl_{0.23}$/629 °C/1.44 GPa, edge — $Prp_{26}Alm_{60}Sps_2Grs_{12}/Jd_{42}/Pl_{0.23}$/658 °C/1.46 GPa. At 694 °C, plagioclase in the core of the inner zone is metastable; therefore, the pressure estimated with the Cpx–Pl–Qz geobarometer (Table 2, parenthesized value) is tentative.

The same case is with sample 207, in which the composition of a large zoned garnet grain records a successive increase in its crystallization parameters from 570–750 °C/1.37–1.40 GPa in the core to 690–790 °C in the rim (Fig. 4; Table 2). The two progressive *P–T* paths form a single trend of the peak of eclogite metamorphism. The presence of acid plagioclase ($Pl_{0.05}$–$Pl_{0.86}$) in the core of the garnet grain indicates a low pressure at the beginning of its crystallization, 1.35–1.40 GPa, and a high temperature at the end of this process, 690–790 °C, when the plagioclase became unstable. During the growth of the high-temperature rim, the core of the garnet grain was replaced by the low-temperature Chl + Gln + Qz paragenesis, recording a change in the conditions of mineral formation at the last stage. Relict garnet grains in the core (Table 2, sample 207-II), like coarse-grained garnet with pyroxene inclusions in the rock

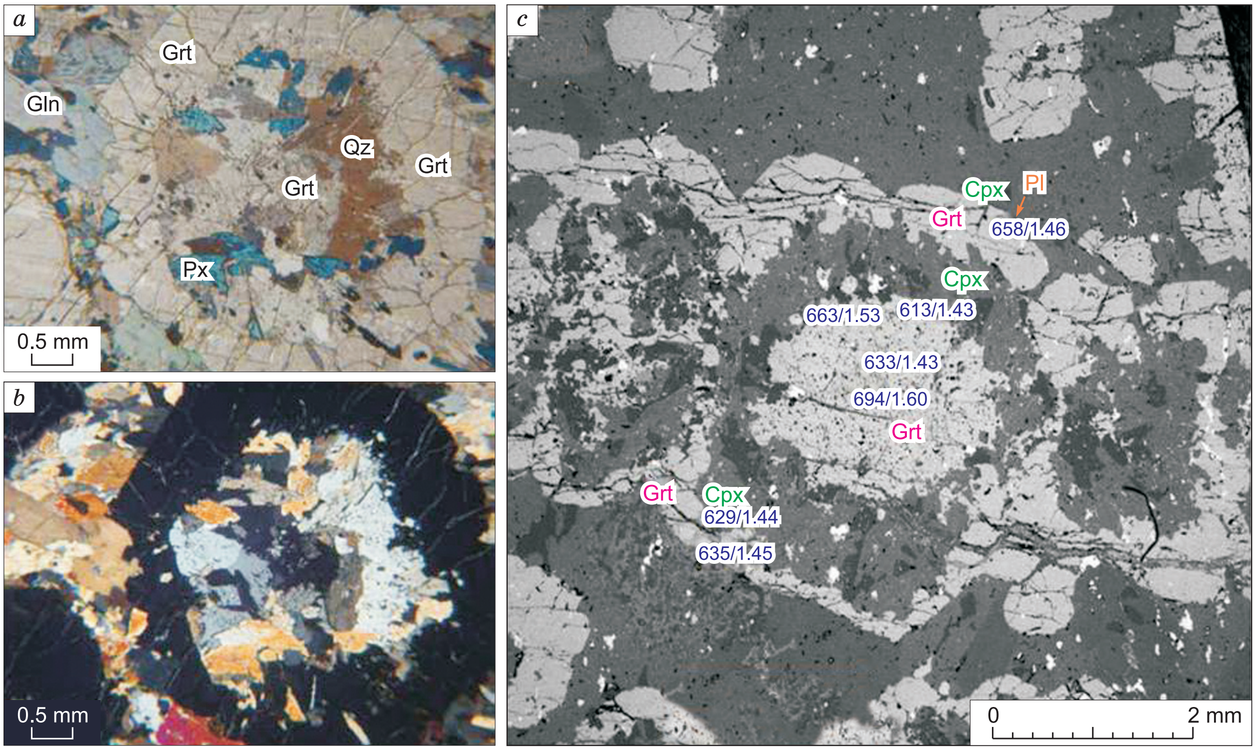

Fig. 3. Garnet porphyroblasts in Grt–Cpx–Gln eclogite (sample 216-1): *a*, Without an analyzer, *b,* with an analyzer, *c*, large garnet crystal with an inverse zoning (regressive zoning in the core and weakly progressive zoning in the rim). The structure of garnet grain reflects its successive and cyclic growth and the mosaic thermodynamic equilibrium. Here and in Fig. 4, numerals mark temperature (°C)/pressure (GPa).

matrix (Table 2, sample 207-III), show higher temperatures of formation (up to 688 °C) as compared with the beginning of crystallization.

Porphyroblastic garnet grains in large eclogite boudins hosted by Grt–Gln–Ms schists usually show a stable progressive zoning; in equilibrium of garnet with pyroxene, it records different progressive *temperature* trends. The composition of pyroxene varies insignificantly both within a sample (X_{Jd} = 0.299–0.345) and within the whole rock (X_{Jd} = 0.22–0.38) (Supp. Matl. 4, sample 267-2). In such samples, some grains of zoned garnet in equilibrium with relatively homogeneous clinopyroxene record different temperature trends at 2.0–2.5 GPa: 475 → 610, 515 → 655, and 610 → 665 °C. A similar temperature trend, 445 → 605 °C, has been established along the profile of a large pyroxene grain. Modeling of mineral equilibria in the system Na_2O–CaO–K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O–TiO_2 (NCKFMASHTO), performed for this sample with the use of the PERPLE_X software (Burlick et al., 2014), also yielded high *P*–*T* parameters of the multiequilibrium ("pseudosection") at the certain compositions of coexisting phases: 650–675 °C/2.4–2.5 GPa at X_{H_2O} = 4% and 740 °C/2.6 GPa at X_{H_2O} = 1%. Thus, the pseudosection modeling of mineral equilibria in this sample shows maximum thermodynamic parameters at the final stages of its formation. These data are confirmed by the composition of omphacite with X_{Jd} = 0.49 (Supp. Matl. 4, an. 5c) found in sample 267-1. This composition of pyroxene in paragenesis with zoned high-Mg garnet records an additional high-temperature trend, 590 → 785 °C, typical for the Karayanovo area and also established at the Shubino and Novosimbirka areas (Table 2).

The samples from eclogite interlayers in the host garnet–mica, Grt–Cpx, and Grt–Gln–mica rocks show similar but varying temperatures of the Grt–Cpx equilibrium. One of such samples, an eclogite interlayer in the Grt–Cpx–Gln–Qz matrix (sample 200), is shown in Fig. 5. Large garnet grains in the central zone of the eclogite interlayer preserve a progressive zoning, recording a high-temperature trend 620 → 680–770 °C in their composition. At the boundary with the host rock (Grt + Cpx + Gln + Ms + Qz), the Grt–Cpx assemblage shows a general tendency to a temperature decrease, and the garnet grains acquire a reverse zoning indicating a decrease in equilibrium temperatures: 745 → 675 and 690 → 545 °C. Small euhedral garnet crystals in the schist matrix usually show a weak progressive zoning. They are almost free of inclusions and demonstrate progressive low-temperature trend 487 → 564 °C (Fig. 5; Table 2). The presence of garnet grains with both progressive and regressive zonings and with different temperature gradients in the sample testifies to the cyclic formation of the host rocks in quasi-equilibrium conditions. Note that clinopyroxene at all sites of the eclogite interlayer and in the rock matrix preserves a stable composition, X_{Jd} = 0.34–0.41 (Supp. Matl. 4, samples 200-I, 200-II, 200-III, and 200-IV), and only the

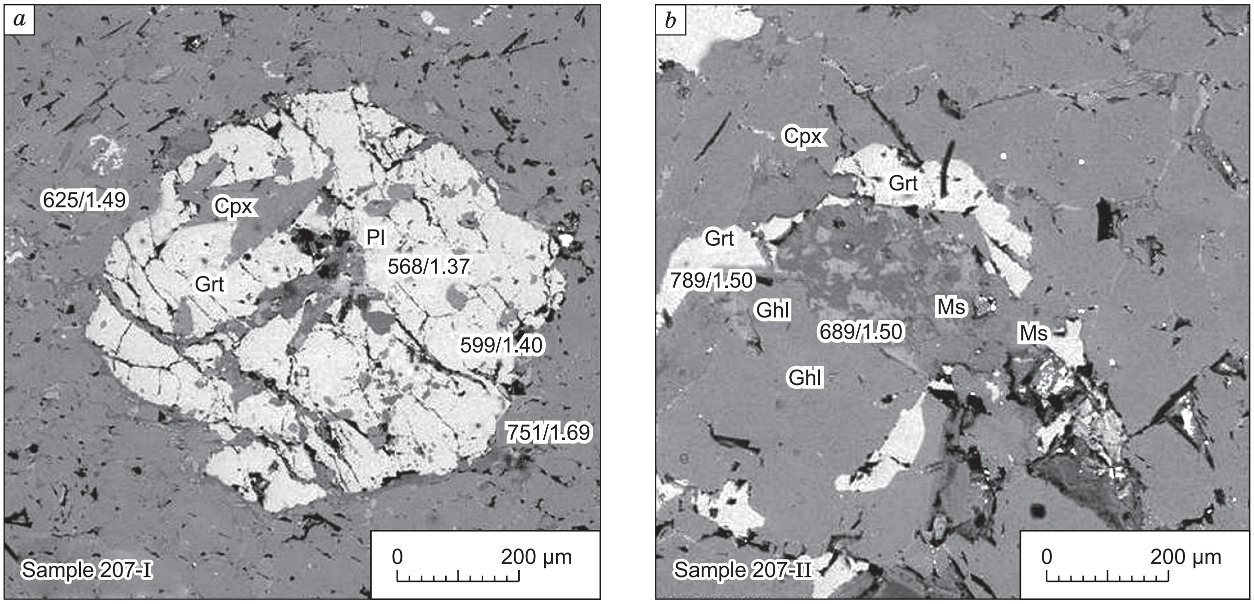

Fig. 4. Progressive zoning in garnet (*a*) and its replacement by secondary minerals at the stage of retrograde metamorphism (*b*). The *P*–*T* parameters of the Grt–Cpx–Pl equilibrium in the garnet core ((568 → 751 °C, 1.37–1.69 GPa) are inherited by the rim of the growing crystal (689 → 789 °C, 1.5 GPa) and correspond to the peak of metamorphism (Karayanovo area).

garnet zoning, from $Prp_{11.6}Alm_{60.8}Sps_{1.2}Grs_{26.4}$ in the core to $Prp_{21.4}Alm_{64.6}Sps_{2.4}Grs_{11.6}$ in the rim (Supp. Matl 3), records the maximum difference in temperatures (~150 °C) during the rock formation.

As seen from the above data, the structural diversity of eclogites from the Karayanovo area does not significantly change the relation between the progressive and regressive temperature trends. The combination of these trends and the temperature level do not depend on the type and texture of rock and its mineral assemblage. Table 2 presents *P*–*T* parameters for other eclogite samples from the Karayanovo area, which were calculated with regard to the temperatures and pressures of their formation. Sample 219 shows two trends of the maximum *P*–*T* parameters of prograde metamorphism. One of them, 545–590 → 750–775 °C/3.0 GPa, is repeated at three spots of the sample. The other, 525–

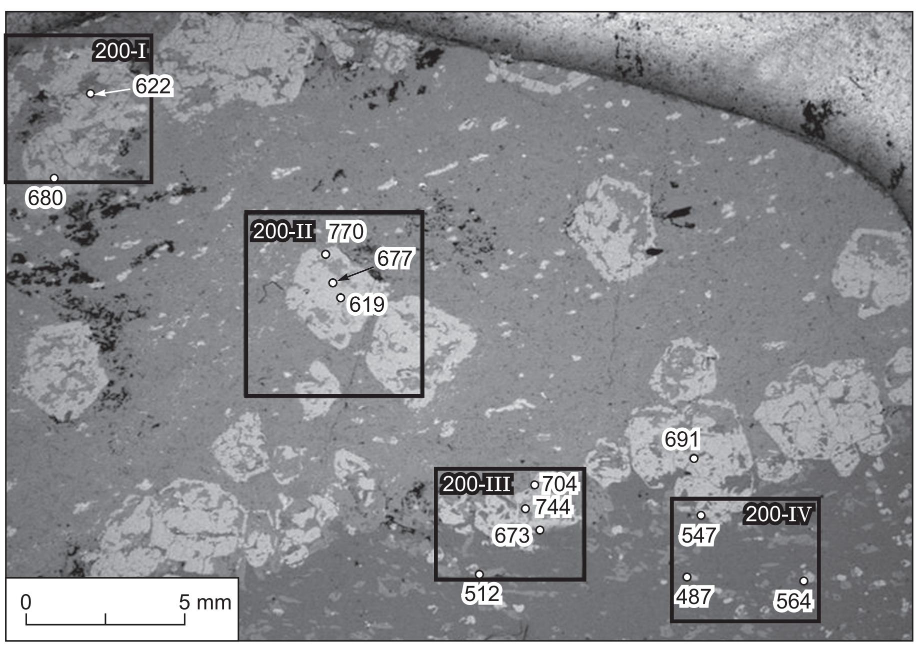

Fig. 5. Temperature variations (°C) in eclogite interlayer at its boundary with the host Grt–Cpx–Gln–Mu–Qz matrix (sample 200), according to the Grt–Cpx equilibrium. Rectangles mark the sites of electron probe microanalysis (Table 2).

845 °C/3.5 GPa, is close to the peak of metamorphism in the entire Maksyutov Complex. The maximum temperatures and pressures, 660–905 °C/3.5 GPa, are also reflected in the composition of the Grt–Cpx assemblage in sample 271. Samples 219 and 271 were taken almost at the same point as the earlier described association of ultrabasic rock (Ol–En) and Jd–Grs eclogite (Valizer et al., 2013). Our new data confirm the thermodynamic parameters reported in the above publication (≥700 °C/≥4.4 GPa at the prograde stage and 635–740 °C/3.1–3.4 GPa at the retrograde stage) and mark the upper bound of the UHP conditions of formation of the Maksyutov Complex (Table 2). Sample 273 from the Karayanovo area is characterized by lower *P–T* parameters: The hosted garnet and pyroxene record a progressive high-temperature trend 535–545 → 700–775 °C at 3.0 GPa. Most of the samples from this area lack plagioclase, which indicates a high grade of rock metamorphism in this area. Plagioclase is present only in samples 207 and 216 and permits evaluation of the *P–T* parameters of the transitional stage of metamorphism. In sample 207, relict plagioclase grains have been preserved only in the core of a garnet crystal almost completely replaced by secondary minerals; they mark the beginning of garnet crystallization. The crystal rim formed at higher temperatures and pressures, beyond the stability conditions of the Cpx–Pl–Qz paragenesis. In sample 216, plagioclase, on the contrary, crystallized only at the end of the retrograde stage at the decreased *P–T* parameters of metamorphism.

The Ivanovka Village area is composed mostly of eclogites altered under blueschist and greenschist facies conditions. The rocks have a porphyroblastic texture (garnet porphyroblasts are rounded or irregular-shaped) and contain small inclusions of clinopyroxene, quartz, glaucophane, epidote, chlorite, titanite, and rutile. Plagioclase present in the rocks makes it possible to estimate the pressure of the final stage of metamorphism, 1.0–1.4 GPa (sample 288). Garnet often shows an inverse zoning. The opposite *P–T* paths fit with each other and sometimes coexist in the sample. We thoroughly studied the core and rim of one of such samples, which clearly demonstrate a dependence of the mineral composition and type of zoning on the degree of diaphthoresis and secondary rock alterations (Table 2, sample 289). The rock was repeatedly subjected to varying *P–T* conditions; traces of these alterations have been preserved in different parts of the sample. In the cores, the freshest parts of the rocks (samples 289-2, 289-4, and 289-5), the compositions of the Grt–Cpx assemblage record the maximum equilibrium temperatures, up to 710–800 °C, and their progressive trend. The disintegrated large garnet grains with unclear outlines and the outer zones of the rock samples (Table 2, samples 289-1, 289-3, and 289-4) show, on the contrary, a regressive zoning in nearly the same temperature intervals, from 860–730 to 570–440 °C (Fig. 6*a*). The composition of garnet varies from $Prp_{13.2}Alm_{51.5}Sps_{3.0}Grs_{32.3}$ in the grain cores to $Prp_{3.0}Alm_{58.7}Sps_{1.4}Grs_{36.8}$ in the rims. The larger the garnet grain, the higher the temperature recorded in its core. Smaller euhedral garnet crystals abound in clinopyroxene inclusions and show an opposite trend in the same temperature interval, 470 → 710 °C/2 GPa (Fig. 6*b*). The opposite *P–T* paths recorded in samples 288 and 289 from the Ivanovka area form a single cycle of the progressive–regressive evolution of eclogites, marking the main stages of formation of the Maksyutov Complex.

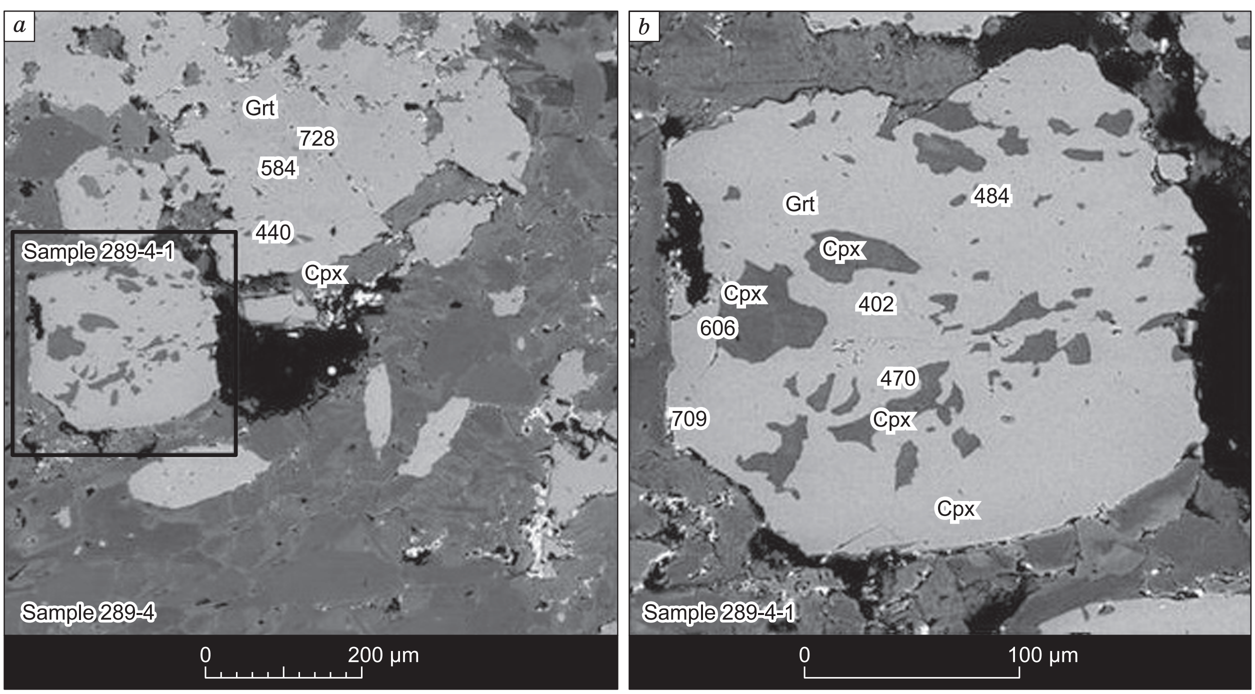

Fig. 6. Regressive (*a*) and progressive (*b*) temperature trends (°C) of metamorphism recorded in the composition of garnet grains in eclogite.

DISCUSSION

The *P–T* parameters of the studied samples from five areas of the Maksyutov Complex are listed in Table 2. The compositions of coexisting minerals in almost each sample record conjugate pairs of the progressive and regressive *P–T* paths of UHP rock metamorphism. These pairs apparently reflect the cycles (stages) of the complex evolution. To identify significant thermal events and classify the *P–T* paths, we chose the starting temperature of a particular (progressive or regressive) process. The initial calculated temperatures in the samples and in the classification trend intervals were rounded up to 5 and 10 °C, respectively (Table 2). Based on the generalized data, we have established at least four stages of the thermal evolution of the Maksyutov eclogites, whose traces are revealed in all the studied areas (Table 3).

The UHP eclogite metamorphism of the Maksyutov Complex is indicated by HP minerals, namely, quartz pseudomorphs after coesite, graphite cuboids after diamond, and diamond microinclusions in garnet and other minerals (Chesnokov and Popov, 1965; Dobretsov and Dobretsova, 1988; Leech and Ernst, 1998, 2000; Bostick et al., 2003), which mark the *P–T* conditions at the early stage of mineral formation: 2.7–3.2 GPa/600–700 °C. These parameters are confirmed by our data on eclogites from the Shubino, Novosimbirka, and Karayanovo areas (Table 2). Nearly the same temperature intervals of the prograde and retrograde stages in these areas determine the *P–T* conditions of the first prograde–retrograde cycle of metamorphism: >800–910 °C/2.5–3.5 GPa at the prograde stage and 870–625 °C/~3.5–3.0 GPa at the retrograde stage (Table 3). Similar parameters of mineral formation (≥700 °C/≥4.4 GPa at the prograde stage and 635–740 °C/3.1–3.4 GPa at the retrograde stage) were established in jadeite eclogites from the Karayanovo area, where these rocks are spatially associated with UHP (Ol–En) ultramafic rocks (Valizer et al., 2013, 2015).

The established maximum temperatures (>800 °C) are somewhat overestimated, because the Maksyutov Complex lacks adakites (indicators of slab melting) or other rocks typical of the final stage of subduction process. Nevertheless, we do not ignore these temperatures, because temperatures above 800 °C were estimated from the Grt–Cpx equilibrium in rocks from three of the five studied areas and temperatures above 730–760 °C were reported in the literature (Valizer et al., 2013; Kovalev et al., 2015). The possibility of adakite formation in the Maksyutov Complex is determined by the parameters of the second critical point (770 ± 50 °C/~3.4 ± 0.2 GPa) in the experimental basalt–H_2O system (Mibea et al., 2011). Therefore, the estimated T > 800–820 °C and P > 3.2–3.4 GPa should be considered tentative and approximate. The regressive thermal stage of the first cycle begins nearly at the maximum temperature of the prograde stage, 875–740 °C; then, the temperature decreases to 625–615 °C (Table 2), and the second cycle of the Maksyutov Complex evolution begins.

Eclogites of the second cycle are usually free of plagioclase; the latter appears only at the retrograde stage at <620–650 °C. Most of the studied rock samples from the Karayanovo area and Jd–Grs eclogites considered earlier (Valizer et al., 2013) belong to this group. Our samples from nearly the same exposures as described in the above publication also show high *P–T* parameters of formation (Table 2, samples 200, 219, 267, and 273) and mark the second cycle of the Maksyutov Complex evolution in the temperature interval from 540–580 to 750–790 °C and in the pressure range 2.0–3.5 GPa. Two groups of temperature trends with a 40 °C difference between the starting and final temperatures are recognized at the second stage of prograde metamorphism (Table 3). Both groups show two or three anomalous values of starting temperatures, but most of the studied samples are characterized by the temperature interval 540–790 °C. The presence of plagioclase in these rocks testifies to retrograde alteration at reduced temperatures and to the transition to the third cycle of the prograde–retrograde evolution of Maksyutov rocks.

The third cycle of the Maksyutov Complex evolution included a prograde stage at 410–690 ºC and a retrograde stage at 690–550 ºC; thus, the starting and final alterations took place at temperatures below 500–700 ºC. These alterations are observed at all studied areas and, as in the second cycle, are subdivided into two groups of trends with a temperature difference of 50–60 ºC. A distinctive feature of this cycle is the beginning of the prograde stage of metamorphism at lower temperatures, 410–460 ºC, and its completion at <680–700 ºC. These are limiting temperatures of the active phase of the complex exhumation. At the retrograde stage, the temperatures of mineral formation again decreased to 475–550 ºC at a pressure of 1.1–1.5 GPa.

In the Antingan area, the regressive garnet zoning records a temperature decrease from 594 to 498 ºC, almost the same as in the Novosimbirka area (Table 2, sample 239-3). The temperature interval of prograde/retrograde metamorphism of the Antingan and Novosimbirka eclogites, from 427–496 to 595–655 ºC at 1.5–2.5 GPa, marks the conditions of the third stage of metamorphism in all the studied areas of the Maksyutov Complex.

The final fourth cycle of the complex evolution is established in few samples. It proceeded under conditions of greenschist facies metamorphism: at 310–520 ºC at the prograde stage and at 590–460 ºC at the retrograde stage, with a pressure within 0.6–1.2 GPa (Table 3).

The age ranges of the thermal cycles of evolution of the Maksyutov Complex. Among the numerous dates of minerals and rocks of the Maksyutov Complex (Shatsky et al., 1997; Lennykh and Valizer, 1999; Beane and Connelly, 2000; Hetzel and Romer, 2000; Glodny et al., 2002; Lepezin et al., 2006; Valizer et al., 2011; Kovalev et al., 2015), there are several significant age ranges close to the stages of its metamorphic evolution. These ages and related *P–T* parameters of particular events or objects can be used as bench-

Table 3. Parameters of metamorphic evolution (stages) of eclogites of the Maksyutov Complex

Cycle (stage)	*P–T* path[1]	Parameters of *P–T* paths, *T*, °C / *P*, GPa	Parameters of *P–T* paths in the studied areas of the complex, *T*, °C / *P*, GPa					Assumed age, Ma
			Shubino	Novosimbirka	Antingan	Karayanovo	Ivanovka	
I	Progr. 1	>800–910/2.5–3.5	800–900/3.5 805–890/3.5	665–815/3.5	–	660–910/3.5 525–845/3.5	–	545–533[1] 485–392[1]
	Retr.1	870–625/3.5–2.5	875–625/3.5	–	–	–	–	
II	Progr. 2a	580–790/2.0–3.5				690–790/3.5 590–785/2.5 575–775/3.0	–	399–378[2,3]
	Progr. 2b	540–750/2.0–3.4	565–710/2.5	515–740/2.5	–	670–750/3.0 630–740/3.1–3.4 [2]) 570–750/1.5	640–720/2.0 535–710/2.0	
	Retr.2	745–615/3.5–2.0	–	–	–	740–633/3.1–3.4 [2]) 740–680/3.5–1.5 725–615/1.5	730–440/2.0	
III	Progr. 3a	460–690/1.5–2.5	–	560–680/1.2–1.3 490–695/0.7–1.5	475–655/2.0	610–690/1.5 560–690/1.5–3.0 475–665/2.0	465–670/1.2–1.4 – –	360 ± 3[1,2] 335[2]
	Progr. 3b	410–630/1.1–2.0	450–620/1.2–1.5 405–630/1.2–1.5	495–545/1.1–1.2 470–575/0.7–1.3	425–595/2.5	465–605/2.0 450–550/1.1–2 [1]	– –	
	Retr.3	690–550/1.5–1.0	–	690–560/1.4–1.0	–	690–550/1.5	625–475/1.5	
IV	Progr. 4	310–520/1.0–1.2	–	385–455/1.0–1.2	–	310–515/0.4–0.7[3]	–	335–315[2]
	Retr.4	590–460/1.2–0.6	–	595–450/1.3–1.1	595–500/1.5	–	565–450/1.3–1.1	

N o t e . Data after: [1] (Valizer et al., 2013); [2](Leech and Ernst, 2000); [3](Beane and Leech, 2007).

marks for the construction of the age scale of the thermal evolution of the Maksyutov Complex (Lennykh and Valizer, 1999; Leech and Willingshofer, 2004; Beane and Leech, 2007; Valizer et al., 2013, 2015).

The most ancient age estimates obtained for eclogite metamorphism with *P–T* parameters in the field of diamond and coesite stability are 550–600 Ma (late Precambrian) (Coleman et al., 1993; Dobretsov et al., 1996). The more precise ages of the first-cycle HP rocks (Table 3) were estimated from zircon from Jd–Grs eclogite spatially associated with the UHP ultramafic rocks (Ol + En) of the lower unit of the complex: 533 ± 4.6 Ma for rocks of the prograde stage and 485–392 ± 4 Ma for rocks of the retrograde stage (Valizer et al., 2015). The above researchers treat these rocks as early Paleozoic mantle–crust inclusions of the ancient protolith. The parameters of their formation (>4.4 GPa/>700 ºC for UHP metamorphism and 3.4–3.1 GPa/740–635 ºC for the retrograde stage) are close to the *P–T* conditions of the first cycle of the Maksyutov Complex evolution (Table 3). As mentioned above, the maximum temperatures of the first-cycle metamorphism (>800–910 ºC) are tentative because of no signs of slab melting. Therefore, the question arises as to whether the estimated age of protolith (533 ± 4.6 Ma) corresponds to this stage or the peak of metamorphism was at 380–400 Ma (Beane and Connelly, 2000; Hetzel and, Romer, 2000; Leech and Willingshofer, 2004).

At the boundary between the first and the second cycles, the subduction of the complex is changed by its exhumation. There are almost no data on the ages of the Maksyutov Complex rocks within 533–400 Ma (Lennykh and Valizer, 1999; Lepezin et al., 2006; Beane and Leech, 2007), which is remarkable, because the marble lenses in the upper unit of the complex contain late Silurian–Early Devonian conodonts (Puchkov, 1993). This fact suggests a global change in the geodynamic and physicochemical settings and the two-stage formation of mafic–ultramafic rocks of the complex.

Thermomechanical modeling shows that the exhumation of the Maksyutov Complex proceeded in several stages in the period 393–310 Ma (Leech and Willingshofer, 2004). At the initial stage (393–385 Ma), the process ran quickly; in the time interval 10–12 Myr, the complex raised from UHP depths to the Earth's crust (30 km), thus having recorded the boundary between the second and the third cycles (Table 3). This period (360 ± 3 Ma) was characterized by pressures of >1.1–2.2 GPa and temperatures of >450–550 ºC (Valizer et al., 2015), which correspond to the conditions of the third prograde cycle (Table 3). There are numerous chronological data on the Maksyutov Complex minerals and rocks formed in this period (Lennykh and Valizer, 1999; Lepezin et al., 2006; Beane and Leech, 2007; Valizer et al., 2015). These data include the ages of various events related to prograde and retrograde metamorphism (Table 3). The most significant of them are as follows:

399–378 Ma — the peak of metamorphism (>3.1–3.4 GPa / >635–740 ºC) of UHP eclogites and the host rocks (Beane and Connelly, 2000; Hetzel and Romer, 2000; Leech and Willingshofer, 2004; Valizer et al., 2015), the second cycle of the complex evolution;

377–357 Ma — retrograde cooling metamorphism (450–350 ºC) (Matte et al., 1995; Shatsky et al., 1997; Beane and Connelly, 2000; Glodny et al., 2002), the third cycle of the complex evolution;

370–344 Ma — retrograde metamorphism in the mélange zones (~1.1–2.5 GPa, 410–550 ºC) (Beane and Connelly, 2000; Hetzel and Romer, 2000; Valizer et al., 2013), the prograde and retrograde stages of the third cycle;

340–311 Ma — formation of lawsonite-containing HP pseudomorphs, potassic metasomatism, and retrograde greenschist metamorphism (Beane and Connelly, 2000; Beane and Leech, 2007), the fourth cycle of the complex evolution.

Then the process slowed down and continued at ~110 ºC at a depth of 3–4 km till the late Carboniferous (~315–300 Ma) (Leech and Stockli, 2000; Lepezin et al., 2006).

The assumed stages of the geodynamic evolution of the Maksyutov Complex should be refined and specified for the local objects. Nevertheless, we believe they give a general idea of the P–T–t evolution of the complex.

CONCLUSIONS

The thorough microprobe study of the composition and zoning of coexisting minerals (garnet, clinopyroxene, and plagioclase) of mafic rocks of the Maksyutov eclogite–blueschist complex has shown progressive and regressive P–T paths of their formation. Geothermobarometric study of the minerals has confirmed the ultrahigh-pressure formation of the complex under P–T conditions of diamond and coesite stability: ≤3.2–3.4 GPa/≤700–760 °C (presumably up to 800–910 °C). These parameters record a geothermal gradient in the subduction zone at the early stage of the complex formation and the P–T conditions of the transition from subduction to exhumation regime (Fig. 7).

Four cycles of conjugate prograde and retrograde metamorphism characterize the main events during the Maksyutov Complex exhumation and determine the position of the metamorphic gradient (Table 3).

The assumed ages of these cycles and additional petrological data (Leech and Ernst, 2000; Beane and Leech, 2007; Valizer et al., 2013) suggest the following main events of the Maksyutov Complex evolution:

(1) 533 ± 4.6 Ma — metamorphism of early Paleozoic mantle–crustal ultramafic inclusions of the ancient protolith and UHP eclogites of the Shubino, Novosimbirka, and Karayanovo areas under P–T conditions of diamond and coesite stability (>800 °C/≤3.5 GPa);

(2) 393–385 Ma — HP–UHP metamorphism of the eclogite facies in the subduction zone (750–790 °C/~3.2–3.4 GPa); transition to exhumation;

(3) 360 ± 3 Ma — retrograde and repeated prograde HP stages of metamorphism during the pulsed rise of the complex under blueschist facies conditions (~460–680 °C/~1.1–1.5 GPa), with exhumation/decompression and heating to a maximum temperature of 690–700 °C;

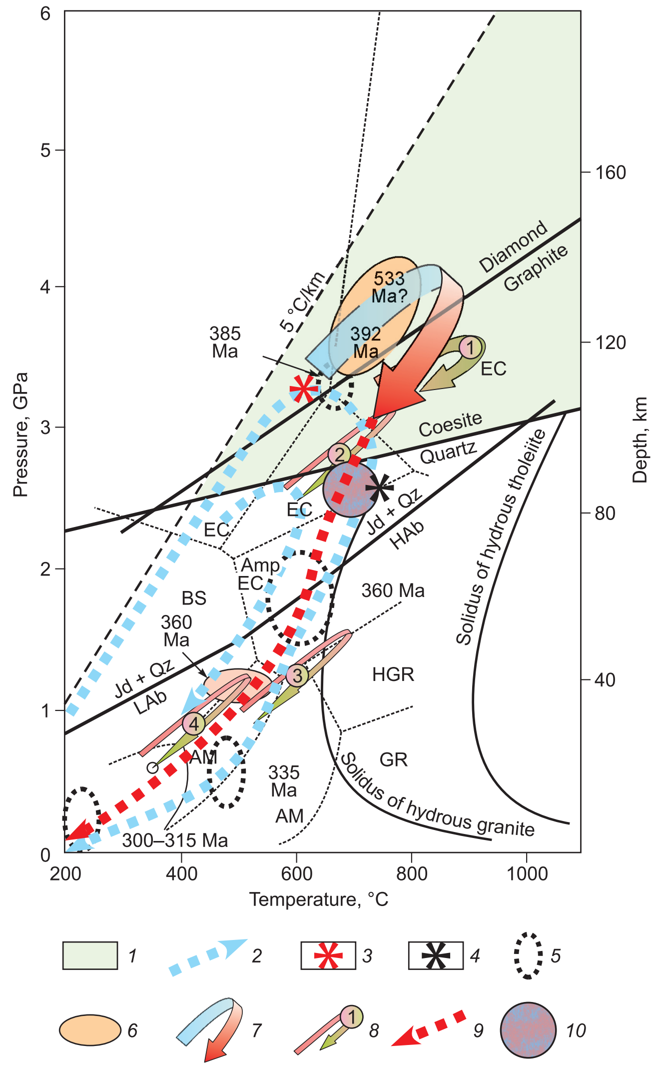

Fig. 7. Physicochemical conditions of formation of the Maksyutov Complex. *1*, ultrahigh-pressure (UHP) field, *2*, subduction P–T path, *3*, maximum pressure at the subduction stage, *4*, maximum temperature at the exhumation stage, *5*, retrograde-metamorphism field (Beane and Leech, 2007), *6*, P–T parameters of formation of ultramafic inclusions in Jd–Grs (Valizer et al., 2015), *7*, P–T field of subduction–exhumation transition, *8*, four cycles of evolution of the Maksyutov Complex at the exhumation stage (Table 3), *9*, P–T path of the complex exhumation, *10*, parameters of the Perple_X modeling of mineral equilibria. Petrogenetic fields of metabasic rocks (Liou et al., 1998): EC, eclogites, BS, blueschists, GR, granulites, HGR, high-pressure granulites, AM, amphibolites.

(4) 335–315 Ma — cooling and transformation of the complex rocks under greenschist facies conditions (~310–520 °C/~0.6–1.2 GPa) at the late stages of deformation, accompanied by Na-metasomatism.

These age data, along with the P–T parameters, form a single P–T–t path of the Maksyutov Complex evolution. The pulsed change in the thermodynamic regime of the complex formation, recorded in the compositions of coexisting minerals, indicates an irregular and slow exhumation process under quasi-equilibrium thermodynamic conditions, which is typical of thick continental subducted complexes (Hacker et al., 2013).

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