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ANCIENT AGE OF ZIRCONS AND ISSUES ASSOCIATED WITH THE GENESIS OF DUNITES FROM GABBRO-ULTRABASITE COMPLEXES OF OROGENIC AREAS AND CENTRAL-TYPE PLATFORM MASSIFS

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The determination of ancient ages of zircons in dunites from the orogenic regions and central-type platform massifs raised a number of issues: 1) the equilibrium of zircon with dunite material and, as a result, the possibility of determining the age of dunite using zircon; 2) polychronic zircons in dunites and the mechanism for the formation of zoned zircon crystals; 3) the origin of the oldest dunite material dated at more than 2500 Ma; 4) mechanism for the formation of zoned zircon crystals in dunite. The article presents results of studying phase equilibrium in the system $MgO–SiO_2–ZrO_2$, which confirmed the possibility of zircon crystallisation in equilibrium with olivine and pyroxene. It was found that zircon is stable in dunite up to 1450°C, whereas at higher temperatures zircon is replaced by baddeleyite. It is shown that zoned zircon crystals can be formed in dunite as a result of the gradual transformation of zircon into baddeleyite and vice versa. Drawing on the experimental data, the authors proposed a mechanism for the accumulation of dunite material in the form of restite, which forms during the partial melting of mantle peridotite, as well as the possible way for dunite resitite to raise to the surface in the form of diapir. The difference between the Ural alpine-type ultrabasites and the ultrabasites of the Platiniferous Belt is discussed. It is proposed that the alpine-type ultrabasite occur closer to the surface where they actively interact with water.

Keywords: *dunite, zircon, age, phase equilibrium, baddeleyite, restite, origin*

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INTRODUCTION

Ultrabasite formations are the main components of Earth's orogenic systems. In addition, they constitute the earliest intrusive formations showing the initial stage in the development of linear tectonic-magmatic systems [Kuznetsov, 1964; Pinus et al., 1973; Velinskii, 1979]. However, despite a long history of studying ultrabasite massifs, their genesis is still debatable [Kuznetsov, 1964; Pinus et al., 1973; Pushkarev, Ferstater, 1995; Ivanov, 1997; Efimov, 2010; Malitch et al., 2012]. The most problematic issues associated with ultrabasite formations are as follows: how and where ultrabasic material accumulated, its state of matter upon introduction into the upper levels of the Earth's crust, as well as the mechanism of its introduction. The following views on the genesis of ultrabasites are expressed in the literature [Velinskii, 1979].

1. According to the first view, ultrabasites were formed through the introduction and crystallisation of ultrabasic melt or the crystallisation differentiation of basaltic magma in magmatic chambers. It is believed that the ultrabasic melt was formed during the melting of the upper mantle substance. A high (more than 1500°C) temperature of the ultrabasite melt [Hiroshi, Kushiro, 1993] is not consistent with the chill margins of ultrabasite massifs, as well as with the absence of evidence of the effect of this temperature on the host rocks [Kuznetsov, 1964; Pinus et al., 1973]. In addition, ultrabasite melt heated to this temperature cannot reach the surface without assimilating the material of the surrounding rocks and thus changing its composition. Despite these contradictions, this view continues to be discussed in the literature [Ivanov, 1997; Saltykov et al., 2008; Simonov et al., 2011].

2. According to the second view, the variety of rocks in the ultrabasite formation is explained by metasomatic processes in the rocks of the upper mantle [Moskaleva, 1959]. The research work of V. Velinskii [1979] and A. Efimova [1995] showed that metasomatism is widespread in ultrabasite massifs; however, being superimposed, it cannot be involved in the formation of primary rocks of ultrabasite massifs.

3. The third view, which considers refractory residue formed from the upper mantle material during the production of basalt melt to be the source of ultrabasites, in our opinion, is the most justified [Pinus et al., 1973; Velinskii, 1979].

GEOLOGICAL STRUCTURE OF ULTRABASITE MASSIFS

One of the most comprehensive works on the study of ultrabasites is the monograph by V. Velinskii [1979], which describes in detail the geological structure and petrography of alpine-type ultrabasite massifs of the

Cenozoic Kamchatka-Koryak orogenic region. Due to young age, these massifs have preserved many structural features that cannot be observed in more ancient orogenic zones where they were erased or deformed by superimposed processes. Studies conducted by V. Velinskii allow us to draw the following conclusions.

1. Ultrabasite massifs are commonly associated with the formations of orogenic systems in their early stage of development, represented by siliceous-volcanogenic deposits.

2. Ultrabasites are predominantly shaped as plates or lenses of various thickness, occurring concordantly within the host rocks. Most often they are introduced into the central parts of anticlinal structures. The position of bodies is determined by the dip angle of the fault, which they are associated with.

3. Well exposed contacts of ultrabasites with host rocks possess a pronounced tectonic character.

4. Eclogite-like garnet-containing rocks were found in the axial part of a number of elongated lentoid ultrabasites.

5. Gabbroid outcrops are associated with all large ultrabasite massifs. Plagiogranite intrusions are also associated with ultrabasites and gabbroids. Gabbro intrusions break through and metamorphose ultrabasic rocks.

A number of important conclusions made drawing on the study of the geological structure of the ultrabasite massifs of the Ural Platiniferous Belt are given in a review paper by A. Efimova [2010].

1. The internal structure of large ultrabasite massifs was formed in the course of high-temperature plastic flow and dynamic metamorphism, which led to the formation of huge volumes of hot tectonites around ultrabasites.

2. The clearly manifested metamorphism of the granulite and amphibolite facies is confined to the contours of the massifs, being absent outside of them.

3. Tectonic-metamorphic evolution (not generation) of the initial ultrabasite material from the Platiniferous Belt could take place in a zone whose depth did not exceed 25 km (about 10–15 km).

4. Dunites are always surrounded by a pyroxenite shell and never come into contact with gabbro.

AGE OF ULTRABASITE MATERIAL

The age of the material composing ultrabasite massifs constitutes one of the most important characteristics exhibited by ultrabasites, the issue of whose genesis is impossible to solve without its determination. In recent years, absolute age has been determined for a number of dunites through U-Pb dating of zircon crystals. This was made possible by using SHRIMP-II – a secondary ion mass spectrometer [Ireland, Williams, 2003]. The results of these studies were quite unexpected. Firstly, it was found that zircons in dunites are polychronic and their age in the same massif can vary from 140 to 2400–2850 Ma. Secondly, ancient zircons dated at 2850–2400 Ma were discovered in the five studied massifs: the Kytlym and Nizhny Tagil massifs in the Urals, the Kondyor and Inagli massifs in the Aldan Province), as well as the Galmoenansky Massif (South Koryakia), [Bea at al., 2001; Knaupf, 2009; Malitch et al., 2009; Krasnobaev et al., 2011; Anikina et al., 2012; Malitch et al., 2012; Ibragimova et al., 2015] (Fig. 1).

Ancient zircons dated up to 3000 Ma are also found in the gabbro-ultrabasite complex of the Mid-Atlantic Ridge [Bortnikov et al., 2008; Shulyatin et al., 2012; Simonov et al., 2013]. This indicates that 3.0–2.5 Ga ago dunites accumulated in the upper mantle or at the base of the lithosphere, which served as material for the formation of ultrabasite massifs of the orogenic system during subsequent activation. The obtained results also indicate that before being introduced into the upper layers of the Earth's crust ultrabasite material underwent a long evolution, which was accompanied by the resetting of the U-Pb zircon chronometer. These results can be considered as a fundamental contribution to studying the history of Earth's geological development, if we prove that zircons in dunites are not xenogenic, engulfed by dunites from other, more acidic rocks, and the ages of zircons correspond to real events that took place during the formation and evolution of dunite materials.

It is traditionally believed that zircon is a mineral present in acidic rocks and that it is unstable if surrounded by dunite material. For this reason, a number of researchers consider zircons in dunites as foreign material engulfed by dunite from host rocks or hypothetical acidic magmas in the process of its formation and introduction [Bea at al., 2001; Bortnikov et al., 2008; Malitch et al., 2012]. Thus, the xenogenicity of zircons in dunite requires a more detailed discussion. Clearly, xenogenic zircon crystals must be present in

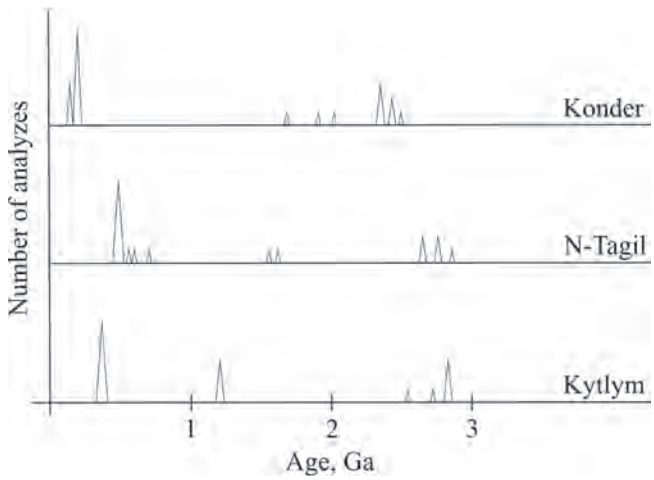

Fig. 1. Absolute ages of zircons from the Nizhny Tagil and Kytlym massifs (Urals) and the Kondyor Massif (Aldan Shield).

dunite as part of rock fragments enveloped by dunite, whose composition is different from that of dunite. The sampling of dunite material from Ural ultrabasite massifs to determine the absolute age revealed no material other than dunite in all the massifs. Figures 2 and 3 show the photographs of zircon crystals from the dunite of the Kytlym Massif. Obviously, if these crystals originate from more acidic rocks and are not in equilibrium with dunite, then they must undergo intense corrosion. However, the beautiful faceting of crystals and the brilliant lustre of facets are not consistent with the assumption about their xenogenic nature.

The host rocks of the Kondyor ultrabasite massif in the Aldan Province are composed by Middle Riphean sedimentary rocks and Early Archean metamorphic rocks, whereas the youngest zircons in dunites are dated at 140–180 Ma old [Malitch et al., 2012].

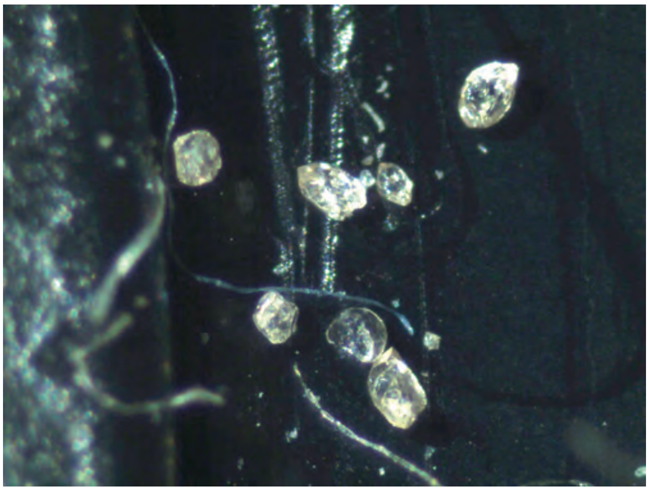

Fig. 2. Zircon crystals from dunites of the Kytlym Massif (Northern Urals).

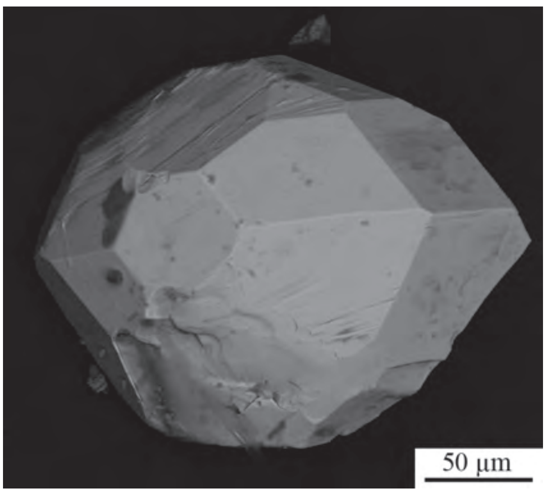

Fig. 3. A zircon crystal from the dunite of the Kytlym Massif, a backscattered electron image.

This brings up the question, where and from which rocks dunite could engulf zircons of this age. There is a point of view that ancient zircons were engulfed by the mantle melt from the rocks of the continental crust, which descended into the mantle during paleosubduction [Bea at al., 2001]; however, according to O. Shulyatin et al. [2012], it is completely incomprehensible how isotopic geochronological data could be stored in zircon crystals at temperatures of 1500–1600°C. In addition, it is difficult to explain why xenogenic zircons dated at more than 2.5 Ga are present in all the studied massifs located in different tectonomagmatic provinces.

PHASE EQUILIBRIA IN THE SYSTEM $MgO–ZrO_2–SiO_2$

The issue associated with the equilibrium between zircon and dunite, which largely determines the correctness of ages yielded by zircons, can only be solved experimentally drawing on the study of phase equilibria in the system $MgO–SiO_2–ZrO_2$, which is the basis for determining the stability field of zircon in equilibrium with olivine and pyroxene.

The reference literature [Toropov et al., 1969] gives a diagram showing phase equilibria in the system $MgO–SiO_2–ZrO_2$ (Fig. 4); however, its correctness raises serious doubts. The area of zircon crystallisation forms a closed field inside the diagram. The position of this area suggests the presence of the ternary compound $mMgO–nZrO_2–qSiO_2$ – which is absent in this system – rather than zircon. The $SiO_2–ZrO_2$ side of the diagram is adjacent to the area of two liquids, which

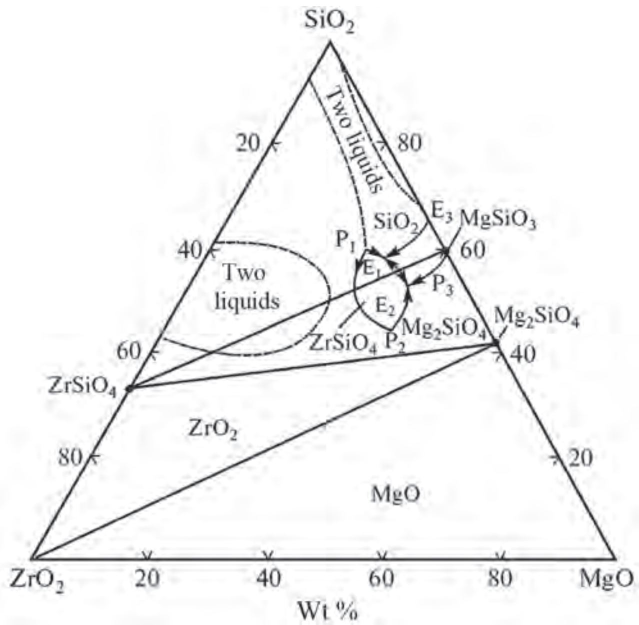

Fig. 4. Diagram of phase equilibria in the system $MgO–ZrO_2–SiO_2$ [Toropov et al., 1969].

is absent in the binary diagram of SiO_2–ZrO_2 [Toropov et al., 1969]. This was the basis for the experimental verification of the diagram of the system MgO–SiO_2–ZrO_2 and for the determination of the real area of zircon crystallisation in equilibrium with Mg_2SiO_4, $MgSiO_3$, and SiO_2. The experiment results were published in [Ryzhkov et al., 2016].

The diagram showing the phase equilibria that we obtained is shown in Figure 5. This diagram contains 6 fields: I – $MgSiO_3$ + SiO_2; II – $MgSiO_3$ + ZrO_2; III – $ZrSiO_4$ + SiO_2; IV – $MgSiO_3$ + Mg_2SiO_4; V – ZrO_2 + + MgO; VI – $ZrSiO_4$ + ZrO_2. The four upper fields, especially fields II and IV, are of interest for solving the issue associated with the stability of zircon in dunite. In field II, zircon is in equilibrium with pyroxene. Along the line separating fields II and IV, zircon is stable in the presence of pyroxene and olivine. With an increase in the MgO content and a compositional transition of the system into field IV, olivine interacts with zircon forming baddeleyite:

$$ZrSiO_4 + Mg_2SiO_4 = ZrO_2 + 2MgSiO_3. \quad (1)$$

Reaction (1) exhibits two important features: 1) the change in free energy in the reaction at a temperature of 1400–1500°C, calculated according to the data given in [Robie at al., 1978], is close to zero; 2) total molar volumes of phases in the left and right sides of the equation are equal. Given these features, the equilibrium (1) will depend only on the composition of the system. At point P, baddeleyite appears on the liquidus curve (see Fig. 5). The presence of field II in the diagram solves one of the most important issues – the possibility of zircon crystallisation in dunite at a very low concentration of ZrO_2.

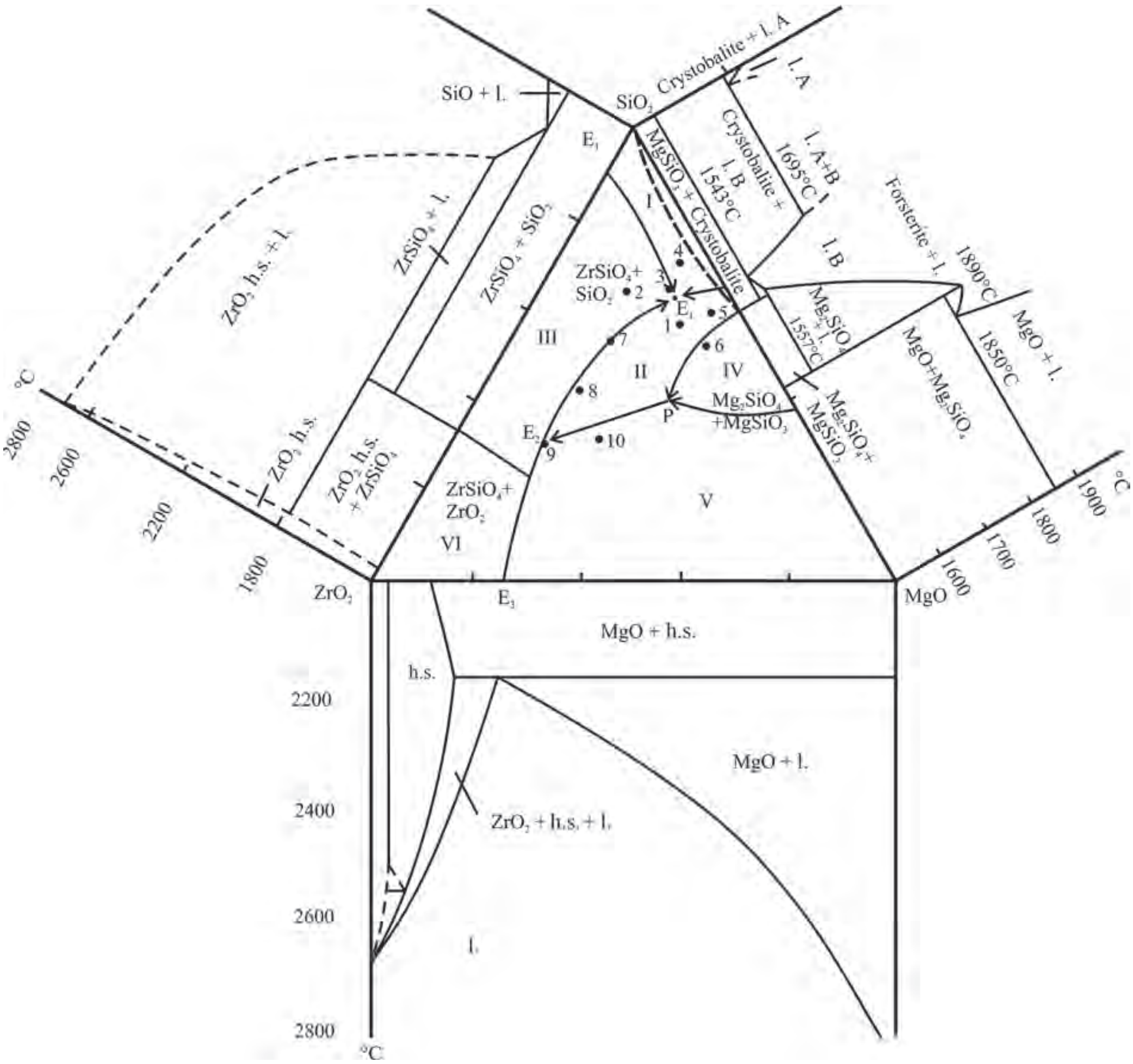

Fig. 5. Diagram of phase equilibria in the system MgO–ZrO_2–SiO_2 (experimental data).

The formation of baddeleyite in zircon should be considered as acid-base interaction. In this process, a strong base (MgO) takes silica from a weak base (ZrO_2). In accordance with the principle of acid-base interaction, baddeleyite rims around zircon grains appear during the interaction of zircon with olivine, as well as upon introduction of any strong base into the system (for example, CaO in the form of $CaCO_3$). Such processes are observed in rodingites and kimberlites [Corfu et al., 2003; Mitsyuk et al., 2005; Kuznetsov, Mukatova, 2013]. Conversely, in komatiite rock series zircon replaces baddeleyite [Kulikova et al., 2010].

In addition to studying phase equilibria in the system $MgO–SiO_2–ZrO_2$, a series of experiments was carried out to test the stability of zircon in natural dunite. Olivine powder selected from dunite was used as model dunite material [Anfilogov et al., 2015]. It was found that at temperatures above 1450°C a rim (an aggregate of baddeleyite and pyroxene) is formed around the zircon grain (Fig. 6). Note that the model composition of the mixture in the experiments was in field IV (see Fig. 5). Therefore, the interaction of olivine with zircon led to the formation of baddeleyite and pyroxene according to reaction (1). Thus, experiments have shown that zircon remains unchanged in dunite when heated to 1400°C. The results of above-mentioned experimental studies suggest that the absolute age determinations made using zircon reflect the time of real events occurring during the formation and transformation of dunite material.

The second issue associated with determining the age of ultrabasites consists in the need to explain the mechanism for the formation of zircon generations and zoned zircon crystal in dunite yielding different ages. At the initial stage, when dunite material is generated in the mantle as refractory restite, zoned zircon crystals can form during their growth in the melt; however ultrabasite massifs show several ages, each corresponding to its own generation of zircon crystals or a new zone in a zoned crystal. The problem is that these generations, zones, are formed in solid dunite material, where the introduction of ZrO_2 from the outside is impossible.

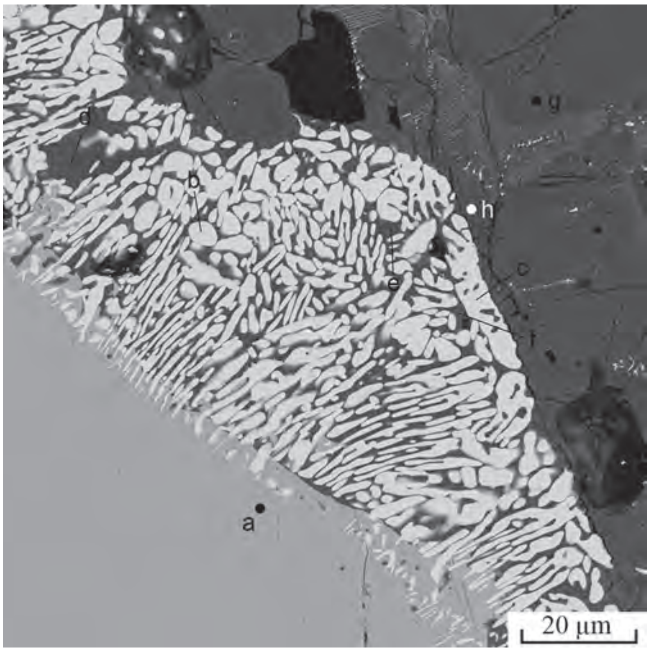

Fig. 6. Rim of baddeleyite lamellae (white) in zircon grain (grey). T = 1550°C.

New zircon generations are most likely to form in solid dunite if zircon transforms into baddeleyite and vice versa, which occurs according to reaction (1) [Anfilogov et al., 2017]. Given that the concentration of ZrO_2 in solid dunite is constant, the composition of the equilibrium association, which is formed in the course this reaction, will depend only on the concentrations of MgO and SiO_2 in the system.

Baddeleyite rims in zircon grains were found in the zircons of the Kondyor Massif [Ronkin et al., 2013]. The replacement of baddeleyite with zircon was established by A. Davidson and O. van Breemen [1998] in the Greville metagabbro province (Ontario). The zircon, which replaced baddeleyite, was found to be 75 million years younger than baddeleyite.

POSSIBLE MECHANISM UNDERLYING THE FORMATION AND EVOLUTION OF DUNITE MATERIAL

The distribution of zircon ages in ultrabasite massifs (see Fig. 1) allows us to distinguish three stages of their evolution:

1) 3000–2400 Ma – formation and accumulation of dunite in the area of basalt melt production;

2) 2000–1250 Ma – metamorphism of dunite in deep intermediate foci;

3) 500–150 Ma – the introduction of dunite as part of ultrabasites into the upper layers of the Earth's crust. For Ural ultrabasites, the last stage dated at 430–450 Ma corresponds to the early stages in the formation of the Ural orogenic system.

The first stage is of greatest interest. If we proceed from the model according to which ultrabasite material constitutes restite accumulated during the production of basalt melt from the mantle peridotite, then the interval 3000–2400 Ma should correspond to the time when powerful outflows of basalts took place. This period of Earth's geological history was marked by the formation of granite-greenstone belts, which indeed contain large volumes of volcanites of the basic and ultrabasic composition [Glikson, 1980]. The age interval during which these belts were formed is shown in Fig. 7.

Using the restite model to describe the formation and accumulation of dunite, it is necessary to consider at what depth and under what P-T conditions dunite restite is formed. Given that the geothermal gradient

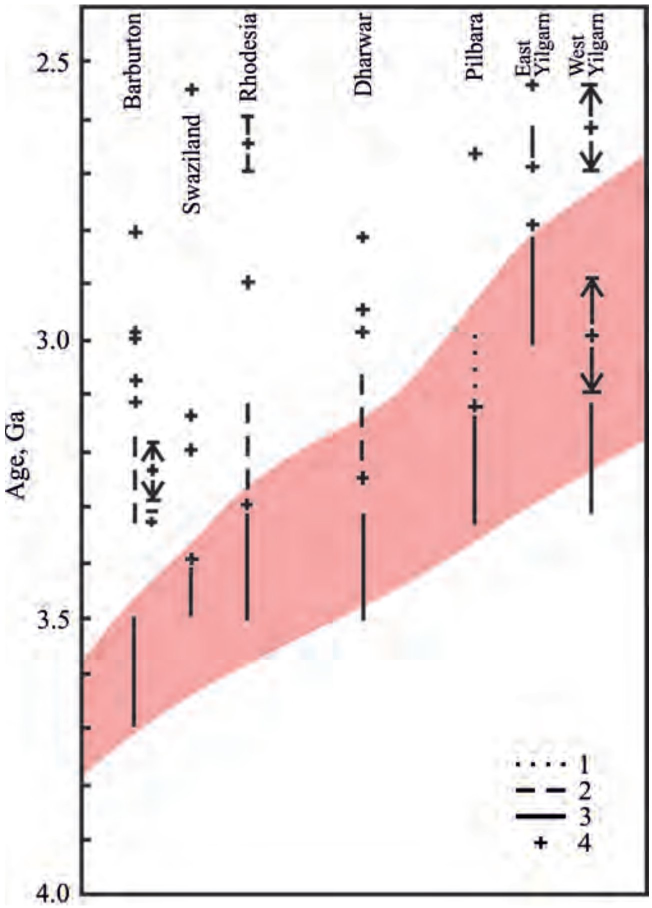

Fig. 7. Formation time of granite-greenstone belts [Glikson, 1980].

1 – sedimentary rocks, 2 – basic-acidic volcanites, 3 – ultrabasic-basic volcanites, 4 – formation of granites.

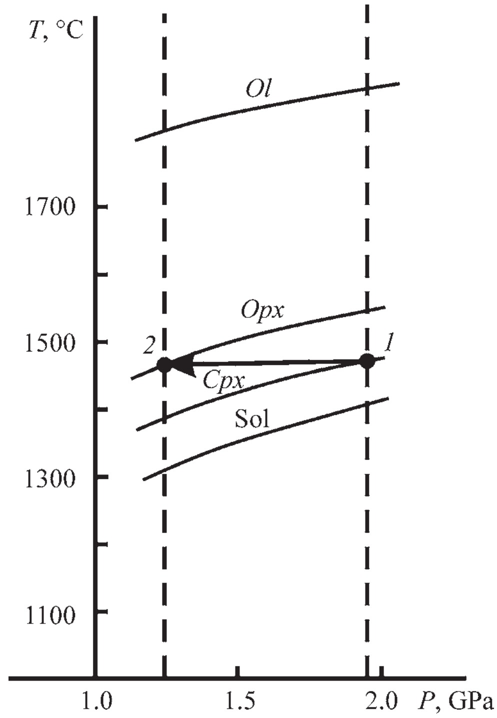

Fig. 8. Fragment of the diagram showing the melting of peridotite at a pressure of up to 2 GPa [Takahashi, 1986].

Sol – solidus line, *Cpx* – melting of clinopyroxene, *Opx* – melting of orthopyroxene, *Ol* – transition to olivine melt; point 1 – *P-T* conditions for the melting of peridotite at a depth of 60 km, point 2 – *P-T* conditions at a depth of 40 km. The arrow indicates the change in the restite composition associated with the isothermal rise of diapir from a depth of 60 km to a depth of 40 km.

was significantly higher during the formation of granite-greenstone belts than the modern one [Savel'eva et al., 2013], it can be assumed that the basalt melt was produced from the mantle peridotite at a depth of not more than 60 km and at a pressure of $P \leq 2$ GPa. A fragment of the diagram showing the melting of spinel lherzolite KLB-1 can be seen in Figure 8 [Takahashi, 1986]. The solidus temperature of lherzolite at a depth of 60 km and at a pressure of 1.9 GPa is 1400°C. At a temperature of 1460°C, clinopyroxene passes into the melt; olivine and orthopyroxene accumulate in restite. Further changes in the composition of the melt and restite occur according to the following scheme. At temperatures above 1300°C, spinel lherzolite becomes ductile. The shear stress in it decreases from 5 kbar at 1000°C and to 0.5 kbar at a temperature of more than 1300°C [Carter, Ave'Lallement 1970; Anfilogov, Khachai, 2007]. The emergence of melt in lherzolite reduces shear stress by an order of magnitude. This creates conditions for the rise of partially molten lherzolite in the form of diapir. When the diapir is rising, the degree of its melting increases and the melting temperature of pyroxene decreases due to a decrease in pressure. At a depth of 40 km pyroxene melts at a temperature of 1450°C. Only olivine remains in restite, with restite acquiring dunite composition (see Fig. 8). Moreover, the melt fraction in diapir reaches 40% [Takahashi, 1986]. During the movement of diapir, the basalt melt is separated from restite, with the latter, due to its high density, accumulating in the form of a dunite layer at the base of the lithosphere at a depth of 30–40 km. The question arises about the source of ancient zircons in dunite. The most likely source of zircon crystals is mantle peridotite, whose partial melting results in the formation of dunite restite. The possible existence of zircon in mantle peridotite, which was generated during the Earth's formation, is confirmed by the presence of zircon in meteorite material [Lizuka et al., 2015], finds of zircon crystals in kimberlites [Mitsyuk et al., 2005] and xenoliths of mantle peridotites [Salop, 1982]. In the course of partial melting of peridotite, zircon crystals remain in ultrabasite restite and thus get into dunite.

With the subsequent activation of the magmatic process, dunite in the form of diapir can be pushed to the surface. Clearly, there are two ways to bring dunite to the surface. One of them is realised during the formation of small concentrically zoned massifs such as the Kondyor and Inagli massifs. The rise and introduction of dunite material in these massifs occurred simultaneously with the manifestations of alkaline magmatism represented by alkaline gabbroids, syenites and carbonatites [Karetnikov, 2006; Malitch et al., 2012; Ibragimova et al., 2015]. The formation of these rocks involves the active participation of volatile components, including water. The introduction of dunite could be preceded by its partial serpentinisation, which led to a sharp decrease in shear stress and contributed to the formation of a small ductile diapir. A similar mechanism for the formation of the Kondyor Massif was proposed in [Burg at al., 2009].

A different mechanism was active upon the introduction of large alpine-type massifs and massifs of the Ural Platiniferous Belt. These massifs were formed under the conditions of the Earth's crust stretching caused by the emergence of foci of the partial melting of mantle peridotite at a depth of about 100 km. The melting was accompanied by a pressure increase, which led to the formation of a stretch region and a dome-shaped elevation on the surface above the melting zone [Anfilogov, Khachai, 2007]. If there was a layer of dunite restite directly above the melting zone, accumulated during the previous magmatic activation, then as a result of heating and increasing plasticity, the dunite material will be extruded to the surface in the form of a large diapir. When the diapir is raising, a situation may arise when the excess pressure acting on the diapir is balanced by the lithostatic pressure. In this situation, a dunite diapir can change the direction of movement from vertical to horizontal. As a result, a horizontally occurring ultrabasite body will be formed. Such a transition from the vertical to the horizontal direction of movement has been established for the Kimpersay Massif (South Ural) [Savel'ev et al., 2008].

The rise of dunite diapir to the surface will precede the rise of basalt melt forming in the melting zone. Eventually, an age-related relationship between dunite and gabbro develops, which is characteristic of ultrabasite massifs: the age of gabbro associated with ultrabasites is several million years younger than that of ultrabasite.

In conclusion, it is necessary to consider the fundamental differences between alpine-type ultrabasites and ultrabasites from the Platiniferous Belt and central-type massifs. Research conducted by G. Pinus, E. Velinskii and et al. [Pinus et al., 1973] showed that for them, as well as for other ultrabasites, the 'restite' mechanism underlying the accumulation of ultrabasic material is the most justified one. The distribution of U-Pb zircon age turned out to be essentially the same. All types of ultrabasites contain ancient zircons yielding an age of more than 2500 Ma. The comparison of U-Pb ages, petrography, petrochemistry and geochemistry of rare elements born by alpine-type Ural ultrabasites with the ultrabasites of the Platiniferous Belt revealed no fundamental differences between them as well [Chashchukhin et al., 2007; Savel'ev et al., 2008]. The only significant characteristics of alpine-type ultrabasites from the Urals that distinguish them from the ultrabasites of the Platiniferous Belt are a high degree of serpentinisation and chromite content [Chashchukhin et al., 2007; Savel'ev et al., 2008].

These differences can be explained if we assume that upon introduction, the material of alpine-type ultrabasites rises closer to the surface than the ultrabasites of the Platiniferous Belt. As a result, it finds itself in the area of active pore fluid flow, which occurs in thermal fields around magmatic bodies [Lykov, 1954; Kadik, Stupakov, 1970; Anfilogov, Purtov, 1976; Anfilogov, 2010]. The interaction of intruded hot ultrabasites with the pore fluid will lead to their intense serpentinisation, redistribution of chromium and its concentration in the form of ore bodies.

Important results were obtained when determining the U-Pb age of zircons taken from the chromite-enriched dunite of the Voykar–Synya Massif in the Polar Urals [Savel'eva et al., 2013]. Five age groups of zircons have been established: 1) 2565 Ma, 2) 2304–2363 Ma, 3) 1873–2038 Ma, 4) 480–552 Ma, 5) zircons younger than 350 Ma. This indicates that the dunite material of chromite-bearing alpine-type ultrabasites underwent the same evolutionary stages as the massifs of the Platiniferous Belt and central-type platform massifs, with the differences between them arising after their introduction into the host rocks rather than in the mantle.

CONCLUSIONS

1. The studying of phase equilibria in the system $MgO–SiO_2–ZrO_2$ revealed that zircon can crystallise in equilibrium with pyroxene and olivine. This suggests that the U-Pb age of zircon in dunite determines the time when dunite material was formed and its subsequent evolution.

2. The distribution of zircon ages in ultrabasite massifs helps to distinguish three stages of their evolution: 1) 3000–2400 Ma – formation and accumulation of dunite material; 2) 2000–1250 Ma – metamorphism of dunite material in intermediate foci; 3) 500–150 Ma – the time of dunite introduction (established for different massifs) into the upper levels of the Earth's crust.

3. Drawing on the experimental data about the melting of garnet lherzolite, a mechanism is proposed for the formation of dunite material during the partial melting of mantle peridotite, its accumulation in the melting zone and subsequent displacement into the upper layers of the crust in the form of diapirs.

4. We examined the conditions leading to the formation of alpine-type ultrabasites, which explain their differences from the ultrabasites of the Ural Platiniferous Belt.

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