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U-Pb DATING OF NIOBIUM MINERALS FROM THE PYROCHLORE GROUP (ILMENY-VISHNEVOGORSKY CARBONATITE-MIASKITE COMPLEX, SOUTH URALS)

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The article covers the U-Pb dating of minerals belonging to the pyrochlore group from the rare-metal ore deposits of Ilmeny-Vishnevogorsky carbonatite-miaskite complex (South Urals). Individual pyrochlore crystals were dated through a new technique of in-situ U-Pb dating using SHRIMP-II, which was developed at VSEGEI (St.Petersburg). The U-Pb dating of high-uranium pyrochlore (more than 2.5 wt % UO_2) was carried out employing laser ablation and ICP-MS. The U-Pb systems of studied pyrochlore samples indicate a multi-stage formation of rare-metal niobium mineralisation. The earliest age of ore formation (378 ± 4.9 Ma) is yielded by the U-Pb systems of U-bearing pyrochlores from the carbonatites of the Potanino deposit. This period of ore formation is probably associated with the final stages in the crystallisation of the alkaline-carbonatite magmatic system. The next periods of ore formation (230 ± 1.5 Ma) are widely manifested in the Vishnevogorsky and later in the Potanino deposit (217.2 ± 1.9 Ma), which is probably associated with the remobilisation and redeposition of alkaline-carbonatite and rare-metal substances at the post-collision stage in the evolution of Ural carbonatite complexes.

Keywords: *U-Pb dating, pyrochlore-group minerals, Ilmeny-Vishnevogorsky complex, Urals*

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INTRODUCTION

The dating of ore mineralisation and genesis remains a challenge despite the development of analytical methods of isotope geochronology. It is known that zircon is the best geochronometer; however, the origin of zircon – if it is present in ores – is not always definite; sometimes it is of xenogenic origin. Minerals of the pyrochlore group (Ca, Na, U, Th, REE, Sr, Ba, vacancy)$_2$ (Nb, Ti, Ta)$_2$O$_6$ (F, OH, O), as minerals bearing rather high concentrations of uranium and thorium, are a geochronological alternative to zircon and can be used for dating ore-formation processes. Pyrochlores were not widely used as geochronometers due to their highly metamict crystal structure [Lumpkin and Ewing, 1995], as well as various secondary changes and the instability of the uranium-thorium-lead system [Pöml et al., 2007]. Nevertheless, thanks to modern methods for the in situ analysis of isotopic systems, it has become possible to solve the problem of dating various generations of pyrochlore and to use pyrochlore as a geochronometer mineral. Thus, in situ isotope analysis of individual phases and domains of mineral grains reveals sections of pyrochlore crystals suitable for performing dating [Wetzel et al., 2010]. In international practice, works on dating pyrochlore are rare; however, they exist. Dating can be performed through several analytical methods – using a secondary-ion mass spectrometer (SIMS) [Wetzel et al., 2010] or laser ablation combined with ICP [Millonig et al., 2012, 2013; Bracciali et al., 2013; Deng et al., 2013].

Given that, unlike zircon, pyrochlore has divalent cations (including calcium and lead) occupying crystallographic position A, all minerals from to the pyrochlore group contain a relatively high proportion of ordinary (non-radiogenic) lead (Pb$_c$), as compared to radiogenic one (and, accordingly, low $^{206}Pb/^{204}Pb$ isotope ratios). The proportion of ordinary lead in pyrochlores sometimes constitutes tens of per cent, which is extremely high and not typical of the used intralaboratory and international geochronological standards when employing in situ methods of analysis. Thus, it is easier to find standards having a minimum content of ordinary lead among the most common dating minerals – zircon, baddeleyite, monazite, apatite. In addition, with accurate and careful measurement of Pb isotopic composition, as well as the right correction for the composition of ordinary (non-radiogenic) Pb, the resulting reproducibility of the obtained geochronological data reaches ± 2% and provides a satisfactory agreement between SIMS age estimates and data obtained using other isotope-geochronological methods (ID-TIMS, LA-ICP-MS).

In order to assess the age and duration of rare-metal mineralisation, we performed U-Pb isotopic dating of niobium ore minerals from the Vishnevogorsk and Potanino niobium deposits associated with the Ilmeny-Vishnevogorsky carbonatite-miaskite complex which is located within the Ural orogen.

The Ilmeny-Vishnevogorsky complex is a prototype of linear carbonatite complexes – an independent type of carbonatite formations associated with the linear zones of alkaline metasomatism and syenite-nephelinesyenite magmatism. Their origin is still debatable [Levin et al., 1997; Mitchell, 2005; Rass et al., 2006; Nedosekova et al., 2009, 2010, 2012, 2016; Ivanov et al., 2010; Ivanov, 2011; Rusin et al., 2012; Nedosekova et al., 2013; Bagdasarov, 2014]. The least studied issues include the age and origin of rare-metal (Zr-Nb-REE) ore mineralisation, as well as its relation to various magmatic phases, post-magmatic evolution and metamorphic processes.

GEOLOGICAL POSITION AND COMPOSITION OF THE ILMENY-VISHNEVOGORSKY MIASKITE-CARBONATITE COMPLEX

The Ilmeny-Vishnevogorsky miaskite-carbonatite complex is located at the junction of the South and Middle Urals, in the East Urals megazone, which, along with the Tagil-Magnitogorsk and Trans-Ural megazones, forms the Eastern (paleo-island arc) sector of the Urals, constituting a complex tectonic collage of oceanic, island-arc and collision complexes having micro-continental blocks [Puchkov, 2010]. The East Urals megazone is characterised by a wide distribution of granitoids and gneisses, as well as the presence of micro-continental blocks of Precambrian (?) crystalline crust (Taldyk, Murzinka-Aduy, Kayrakty, partly Sysert-Ilmenogorsky, etc.).

The Ilmeny-Vishnevogorsky complex occurs in the axial part of the Sysert-Ilmenogorsky anticlinorium, in the Lower Proterozoic rocks of the Selyankino, Ilmenogorsky and Vishnevogorsky strata (PR1), in the submeridional (collision) structure, stretching from north to south for over 100 km, with the maximum width of 4–6 km (Fig. 1). The complex includes two relatively large (20–25 × 6 km) intrusive miaskite massifs (Vishnevogorsky and Ilmenogorsky), numerous stratal and dyke-like bodies of miaskites, syenites and miaskite-pegmatites, stratal and vein-shaped bodies of carbonatites, as well as thick zones of fenitisation in the host rocks of Vishnevogorsky and Ilmenogorsky suites. Miaskite massifs are connected by the Central Alkaline Belt composed of fenites, feldspar metasomatites, small miaskite and syenite bodies, as well as melanocratic carbonate-silicate rocks and carbonatites.

Carbonatites characterised by ore niobium mineralisation are widely developed in the northern part of

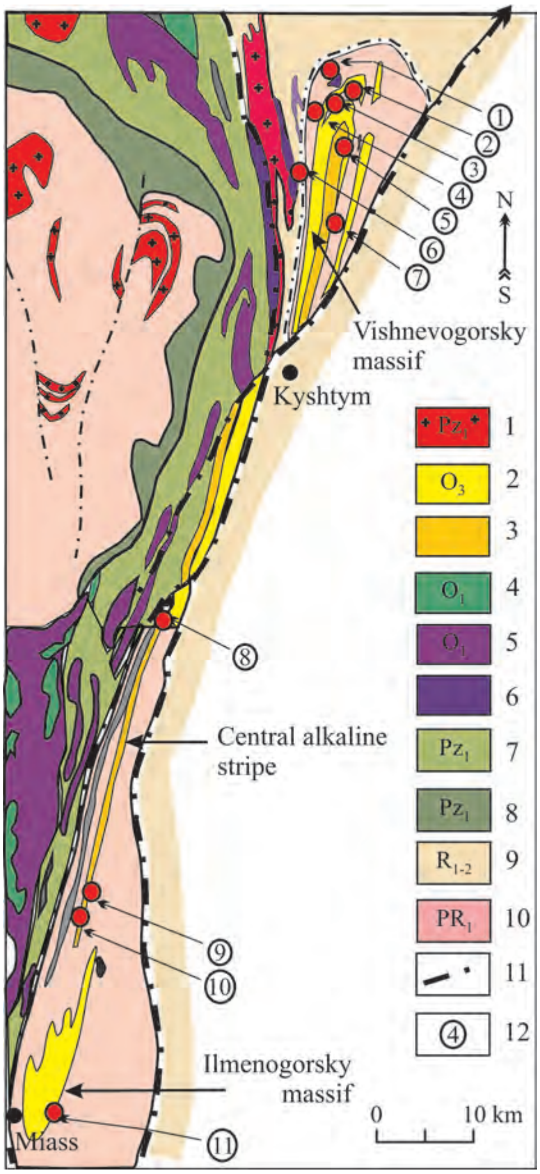

Fig. 1. Geological structure of the Ilmeny-Vishnevogorsky alkaline-carbonatite complex according to [Levin et al., 1997; Zoloev et al., 2004].

1 – granites (Pz_3); 2, 3 – Ilmeny-Vishnevogorsky complex (O_3): 2 – miaskites of the Vishnevogorsky and Ilmenogorsky massifs, 3 – metasomatites, carbonatites, silicate-carbonate rocks of the Central Alkaline Belt; 4 – ophiolite gabbro (O_1); 5 – ophiolite ultrabasites (O_1); 6 – Buldym meta-ultrabasites (PR?); 7 – volcanogenic-sedimentary rocks of the Tagil-Magnitogorsk megasynclinorium (Pz_1); 8 – garnet-mica schists and eclogites of the eastern margin of the Ufaley middle massif (Pz_1); 9 – plagioclase shists and quartzites of the Sysert-Ilmenogorsky middle massif (R_{1-2}); 10 – plagiogneisses, granite migmatites, crystalline schists, amphibolites, quartzites of the Sysert-Ilmenogorsky and Ufaley middle massifs (PR_{1-2}); 11 – tectonic faults and nonconformities; 12 – main ore deposits and occurrences of Nb and REE associated with carbonatites (numbers in circles): 1 – Buldym (Nb and REE); 2, 3 – Vishnevogorsky (Nb) (2 – zone 125; 3 – zones 140 and 147); 4 – Spirikha (REE); 5 – Svetly (Nb); 6 – Kagansky (REE); 7 – Potanino (Nb); 8 – Uvildy (Nb); 9 – Baydashevo (Nb); 10 – Ishkul (Nb); 11 – Ilmensky, pit 97 (Nb and REE).

the complex – in the apical part of the Vishnevogorsky miaskite massif and in the 'saddle-like' miaskite deposit (Vishnevogorsky niobium deposit). They also occur in the root part of the massif – Purgino ore occurrence (see Fig. 1). Carbonatites make up stratal, dyke-like and vein-shaped bodies (up to 10 m in thickness and hundreds of meters long), forming an ore zone of 4 km in length and 30 m in width (ore zone 147, Vishnevogorsky niobium deposit). The richest ore zone of this deposit (zone 140) is associated with the northern miaskite satellite ('saddle-like deposit'), which occurs in the hinge of the Vishnevogorsky anticline, 50 m north of the Vishnevogorsky massif, and comprises a system of subparallel veins (carbonatites, albites and miaskitic pegmatoids). Carbonatites are also found in the fenite halo of the Vishnevogorsky intrusion (in the fenitised rocks of the Vishnevogorsky suite), forming stockworks and veins.

Early carbonatites (sövite I), which occur in the form of schliers and stratal bodies mainly in the root of the Vishnevogorsky intrusion, have a calcite composition and contain nepheline, feldspars, biotite, as well as accessory zircon, black-brown pyrochlore (hatchettolite), ilmenite, apatite, etc. Late carbonatites (sövite II) widely developed in the apical part of the Vishnevogorsky massif (often being confined to fold hinges) form coarse-grained leucocratic zones and veins in miaskites and early carbonatites, which are composed of calcite and large crystals (up to n cm) of fluorapatite, red and yellowish-brown pyrochlore, ilmenite, biotite, pyrrhotite and pyrite. In the exocontact fenite haloes of miaskite intrusions, late carbonatites are also represented by coarse-grained calcite veins and contain pyroxene (aegirine-augite), red-brown pyrochlore, apatite, ilmenite and titanite.

Numerous deposits and ore occurrences of pyrochlore-bearing carbonatites have been identified and explored in the Central Alkaline Belt (see Fig. 1). The largest of the deposits (Potanino niobium deposit) is located in the eastern contact of the Central Alkaline Belt, forming a linear, sometimes stockwork-like zone in miaskites and fenites (about 15 km long and up to 40 m thick). In addition, the following ore occurrences have already been identified in this area: Ishkul, Baydashevo, Uvildy and Svetloe Lake [Levin et al., 1997] (see Fig. 1).

GEOCHRONOLOGY OF THE ILMENY-VISHNEVOGORSKY COMPLEX

The first Rb-Sr and U-Pb isotope-geochronological data for rocks from the Ilmeny-Vishnevogorsky complex were reported in the 1970s–1980s. Miaskites from the Ilmeny-Vishnevogorsky complex yielded Rb-Sr whole-rock isochron ages of 446 ± 12 Ma (O_3) (Ilmenogorsky massif), 436 ± 31 Ma (S_1) and 478 ± 55 Ma (O_1) (Vishnevogorsky massif), which were interpreted as the age of miaskitic magma intrusion and crystallisation at the final stages of rifting in the lower – upper Ordovician (O_1–O_3) [Kononova et al., 1979; Kramm et al., 1983]. In addition, Rb-Sr mineral isochrons obtained for miaskites show an age of 245 ± 8 Ma, which corresponds to the age of metamorphism.

The U-Pb dating of zircons from the miaskites of the Ilmeny-Vishnevogorsky complex performed using isotopic dilution yielded Lower Silurian ages: 434 ± 15 Ma [Kramm et al., 1993] and 422 ± 10 Ma [Chernyshev et al., 1987]. A range of ages from the Lower Silurian to the Upper Devonian was obtained using in situ methods for dating zircons (SHRIMP and laser ablation). The age of zircons from the miaskite-pegmatites, miaskites and malignites of the Ilmenogorsky massif is estimated at 432 ± 3.7 Ma (S_1), 419 ± ± 7 Ma (S_2), 417 ± 7 Ma (S_2), 383 ± 14 Ma (D_3), respectively [Krasnobaev et al., 2010a, 2014], with zircons from the carbonatites of the Vishnevogorsky massif yielding 419 ± 20 Ma [Krasnobaev, et al., 2010b] and 417 ± 3 Ma (S_2) [Nedosekova et al., 2010, 2012, 2016].

In addition, the U-Pb isotope systems of zircons from the Ilmeny-Vishnevogorsky complex reveal subsequent metamorphic processes, accompanied by the loss of radiogenic Pb, dated at 261 ± 14 Ma [Chernyshev et al., 1987] and 279 ± 10 Ma (P) [Krasnobaev et al., 2010a]. A significant number of zircon grains from miaskites and miaskite-pegmatites U-Pb dated using in situ methods showed Permian ages: 269 ± 6 and 251 ± ± 6 Ma, respectively [Krasnobaev et al., 2014]; as well as Rb-Sr mineral isochrons obtained earlier [Kononova et al., 1979; Kramm et al., 1983].

The Sm-Nd mineral isochron for the carbonatites of the Vishnevogorsky massif, constructed using 5 analytical points (mineral fractions of calcite, biotite, apatite, pyrochlore and bulk sample), yielded a Lower Silurian age of 425 ± 44 Ma (S_1), thus showing the carbonatite magmatic stage in the functioning of the alkaline-carbonatite magmatic system [Nedosekova, Belyatskii, 2012]. In addition, a Sm-Nd mineral isochron obtained for the carbonatites from the saddle-like miaskite deposit shows an age of 388 ± 50 Ma (end of D_2) [Ivanov et al., 2010], probably reflecting the final stage in the formation of the Ilmeny-Vishnevogorsky miaskite-carbonatite complex.

Thus, the U-Pb, Rb-Sr and Sm-Nd geochronological data of alkaline rocks and carbonatites from the Ilmeny-Vishnevogorsky complex indicate multistage magma formation at the stage of Palaeozoic activation (≈440–390 Ma), as well as large-scale processes of alkaline metasomatism and pegmatite formation at the stage of Hercynian orogeny (≈350–250 Ma) and subsequent post-collision extension (≈250–240 Ma).

NB-ORE MINERALISATION

More than ten deposits and ore occurrences of niobium, zirconium and rare earths have been identified in the Ilmeny-Vishnevogorsky complex (see Fig. 1). The

Vishnevogorsky deposit – the first deposit in Russia where the industrial mining of Nb raw materials was carried out – is associated with pyrochlore-bearing carbonatites in the apical part of the Vishnevogorsky miaskite intrusion. The Potanino niobium deposit along with the Svetloe Lake, Baydashevo, Ishkul and Uvildy ore occurrences, which are also associated with carbonatites, have been explored in the Central Alkaline Belt [Levin et al., 1997; Zoloev et al., 2004].

The Nb-ore mineralisation of rare-metal deposits at the Ilmeny-Vishnevogorsky miaskite-carbonatite complex is represented by the minerals of the pyrochlore supergroup: pyrochlore proper, Uranpyrochlore (hatchettolite), betafite, as well as Ta-, REE- and Sr-bearing minerals of the pyrochlore group. Such minerals as ilmenorutile, columbite, fersmite, chevkinite-(Ce) are less common [Es'kova, Nazarenko, 1960; Es'kova et al., 1964; Efimov et al., 1985; Levin et al., 1997; Nedosekova, Pribavkin, 2015; Nedosekova et al., 2017]. The main ore minerals of the carbonatite deposits at the Ilmeny-Vishnevogorsky complex are those belonging to the pyrochlore group. Pyrochlore is present in various rocks – in miaskites and syenites, especially in their pegmatoid varieties, in miaskite-pegmatites, syenite-pegmatites, carbonatites and alkaline metasomatites (albitite, fenite, glimmerite, etc.). In the most significant amounts, pyrochlore is found in both early and late carbonatites (sövites I and II, respectively) of the Vishnevogorsky miaskite massif and the Central Alkaline Belt [Levin et al., 1997; Zoloev et al., 2004; Nedosekova, 2007; Nedosekova et al., 2009, 2017].

In miaskites and syenites, pyrochlore is represented by octahedral crystals of dark brown, sometimes orange colour (0.01–0.1 mm in size). In pegmatoid varieties, the size of pyrochlore increases up to 0.5 cm, whereas in pegmatites it comes up to several centimetres. The distribution of pyrochlore is uneven. In pegmatites and albitites, it forms streaky clusters and small disseminated particles, with crystal sizes ranging from 2–3 mm to several centimetres. In silicocarbonatites (melanocratic carbonate-silicate rocks) and in early carbonatites (sövite I), pyrochlore forms small grains of black and greenish-black colour (U-pyrochlore) (Fig. 2a). In late carbonatites (sövite II), pyrochlore forms octahedral and cubo-octahedral crystals (0.05–1.5 cm in size) of red-brown and yellow colour (Fig. 2b, c), containing relics of early (black) pyrochlore with traces of dissolution and transformation. The internal structure of pyrochlore crystals of late carbonatites is shown in Fig. 3a–f: relics of black U-(Ta)-bearing pyrochlore, surrounded by an intermediate zone of U-bearing hydrated pyrochlore, are sometimes preserved in the cores of crystals, whereas the peripheral part of the crystal is composed of light brown Sr-bearing pyrochlore (see Fig. 3e).

The Ilmeny-Vishnevogorsky complex has several minerals of the pyrochlore group, whose formation is associated with certain evolutionary stages in the functioning of the alkaline-carbonatite magmatic system, as well as the metamorphic transformations of the complex [Nedosekova et al., 2017]. According to the latest nomenclature of the pyrochlore group (pyrochlore supergroup) drawing on the predominant cation or anion in sites B = Nb, Ti, Ta; A = Ca, Na, REE, Y, Sr, Ba, Mn, Mg, U, Th; and Y = O, OH, F [Atencio et al., 2010], pyrochlores of the Ilmeny-Vishnevogorsky and Buldym complexes can be classified as U-(Ta)-bearing oxycalciopyrochlores (or uranium-pyrochlores, according to [Hogarth, 1977]) and fluorcalciopyrochlores (including Ta-, REE_{Ce}- and Sr-bearing varieties). U- and Sr-bearing varieties include kenopyrochlores having an A-site vacancy of over 50% relative to the A-site cations. The pyrochlore compositions are presented in ternary diagrams characterising the occupancy of sites A, B and Y (Fig. 4).

U-(Ta)-bearing oxycalciopyrochlores (15–24 wt % UO_2, 1–14 wt % Ta_2O_5) are found in early high-temperature carbonatites (sövite I) and silicocarbonatites of the Central Alkaline Belt (Potanino deposit, Uvildy ore occurrence) [Levin et al, 1997; Nedosekova et al.,

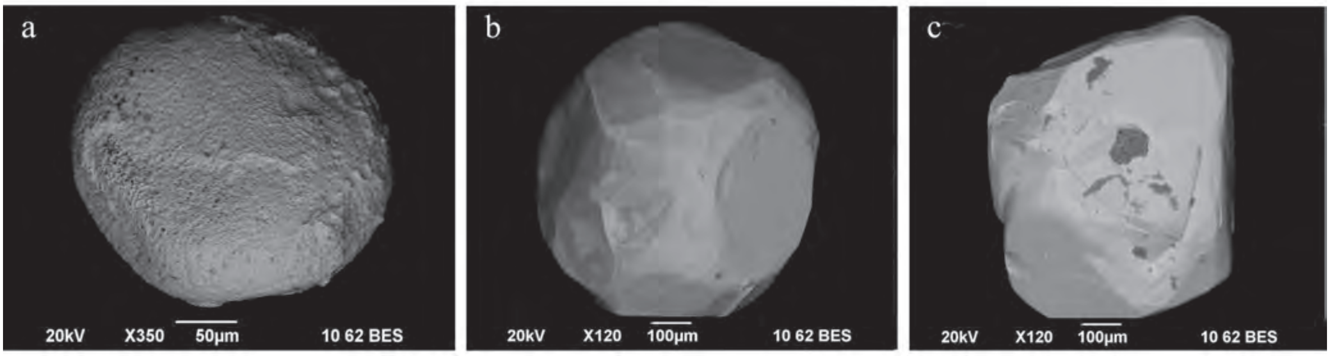

Fig. 2. Morphological features of pyrochlores from the Ilmeny-Vishnevogorsky complex: uranpyrochlore from early carbonatites, Uvildy Nb-occurrence (a); Sr-REE-bearing pyrochlores from late carbonatites, Vishnevogorsky Nb-deposit (b, c).

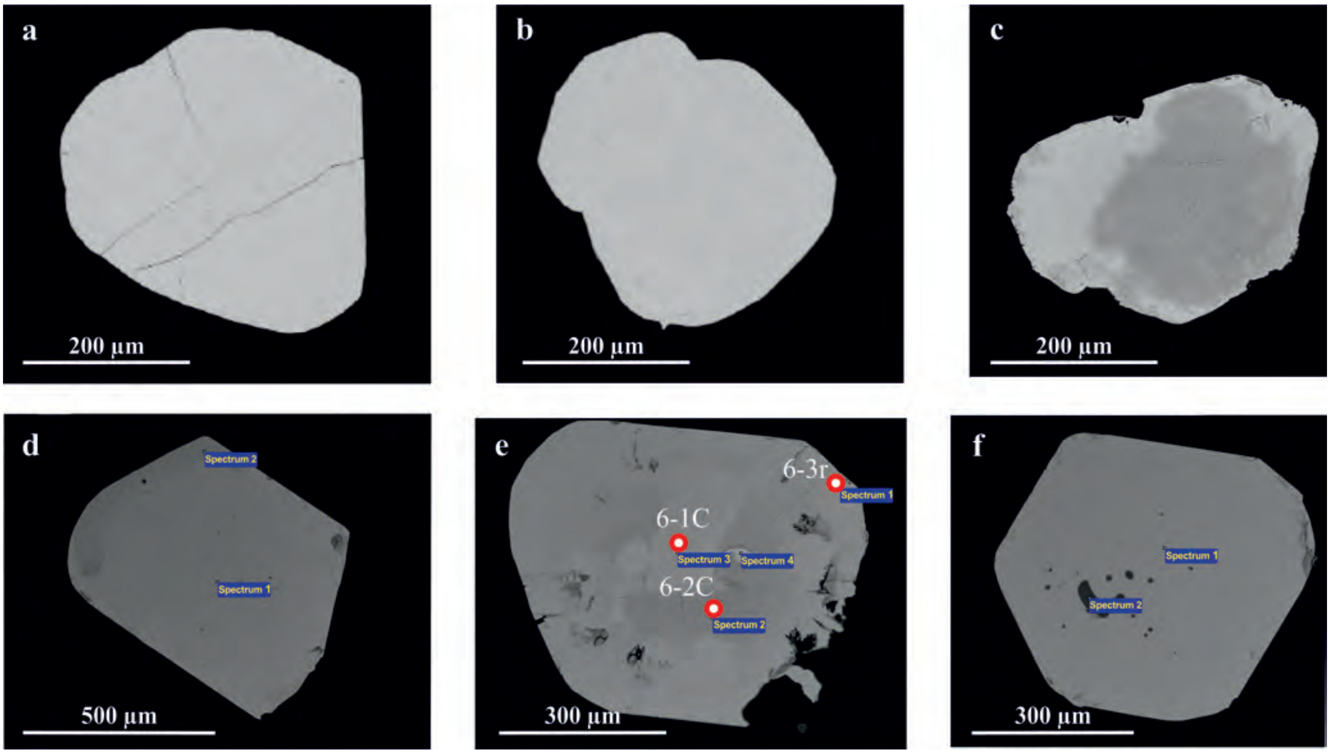

Fig. 3. Morphology and internal structure of pyrochlore crystals from the carbonatites of the Ilmeny-Vishnevogorsky complex (sample 331, sövite II, Vishnevogorsky deposit), BSE-image.

Analysis points correspond to those given in Table 1.

2009]. This type of pyrochlore is probably formed earlier than others (during the late magmatic stage of crystallisation), as evidenced by the relics of U-bearing pyrochlore in the later generations of Sr-bearing pyrochlore from late carbonatites (sövite II) [Levin et al., 1997] (see Fig. 3c, e).

Fluorcalciopyrochlores characterised by the maximal content of Nb_2O_5 (65–69 wt %), the most stoichiometric composition and the lowest content of microimpurities are widely developed in feldspar veins and in the late calcite carbonatites from the saddle-like miaskite deposit of the Vishnevogorsky massif. These pyrochlores comprise the main ore zones of the Vishnevogorsky deposit (ore zones 140 and 147). They are also found in the Potanino deposit.

Ta-bearing varieties of fluorcalciopyrochlore (1.5–5.0 wt % Ta_2O_5; 0–4.2 wt % UO_2) are found in nepheline pegmatites in the apical part of the Vishnevogorsky massif (ore zone 147), as well as in the carbonatites of the Potanino deposit. This pyrochlore is formed at the stage of pegmatite crystallisation.

Sr- and REE-bearing fluorcalciopyrochlores (3–6 wt % of $LREE_2O_3$, 1.5–4.5 wt % of SrO) are widespread in late carbonatites (sövite II) and in exocontact fenites of the Vishnevogorsky and Potanino deposits. These pyrochlore varieties form octahedral and cubo-octahedral crystals (see Figures 2 and 3d, f) exhibiting signs of metasomatic growth, as well as form rims around U-bearing relict (?) cores of pyrochlore (see Fig. 3c, e). It is likely that the formation of these pyrochlore varieties occurs at the final evolutionary stages (late carbonatite and syenite-pegmatite) of the complex and may also be associated with the metamorphic transformations at the collision stage.

METHODS OF ANALYSIS

The chemical composition of pyrochlores and aeschynites from the Ilmeny-Vishnevogorsky complex was studied at 60 nA and 20 kV using a CAMEBAX microprobe, with a probe beam size of 2 µm (analyst V.V. Sharygin, IGM SB RAS, Novosibirsk), as well as using a Cameca-100 microprobe (analyst D.V. Zamyatin, IGG UB RAS).

The U-Pb dating of high-uranium pyrochlore was carried out using LA-ICP MS (DUV-19). Pyrochlores having a uranium oxide content of less than 2.5% were dated through a method for the in situ U-Pb dating of individual pyrochlore crystals using a SHRIMP-II secondary-ion mass spectrometer, which was developed at the A.P. Karpinsky Russian Geological Research Institute (VSEGEI, St.Petersburg). A detailed description of the procedure is given in [Lepekhina et al., 2016]. The measurements of U-Th-Pb isotope ratios and element concentrations in pyrochlores, along with the standard calibration, were carried out using

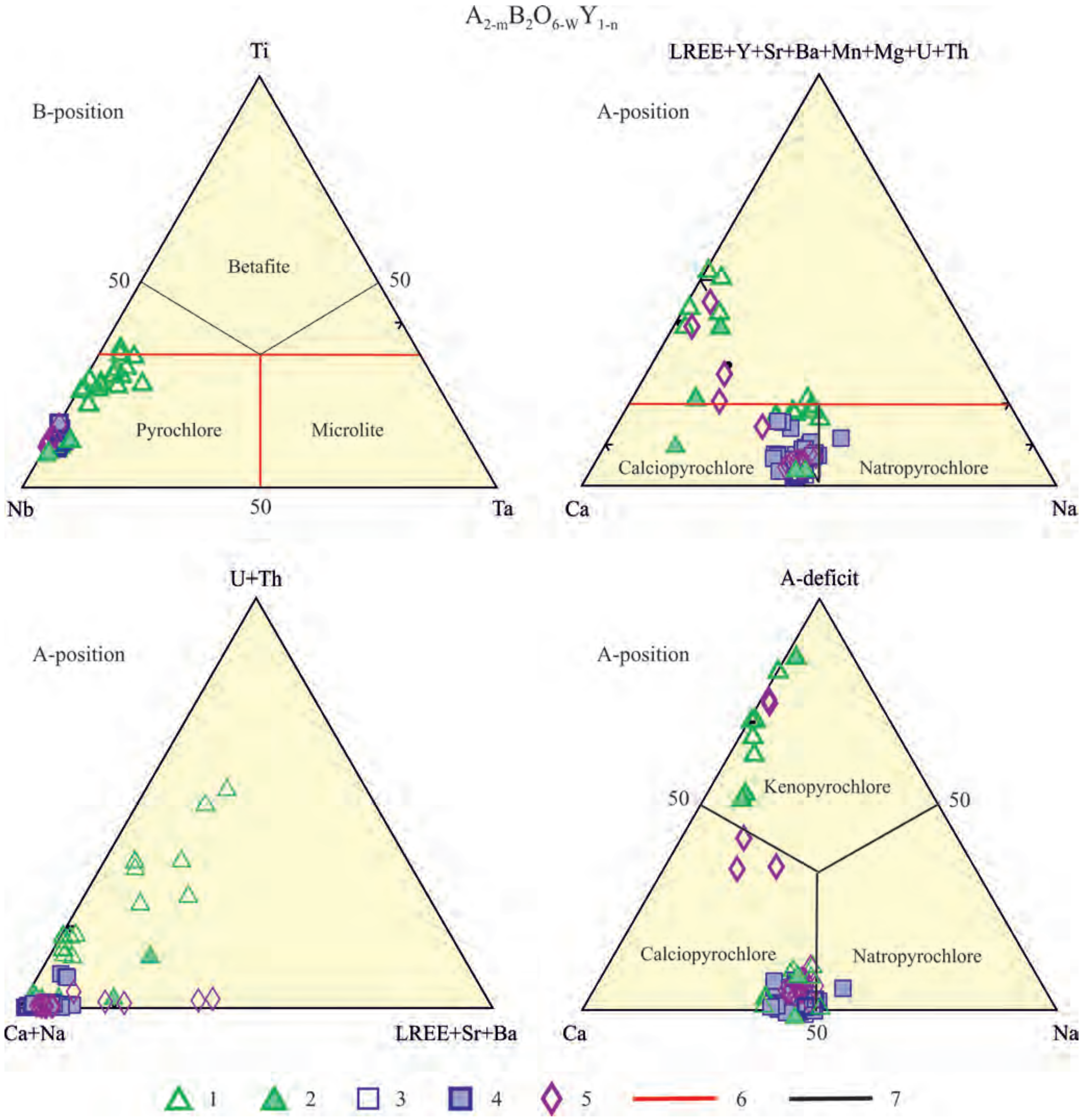

Fig. 4. Ternary composition diagrams showing the occupancy of sites B and A in the pyrochlore structure (p.f.u.).

1 – U-(Ta)-bearing oxycalciopyrochlores, 2 – Ta-bearing fluorcalciopyrochlores, 3 – fluorcalciopyrochlores, 4 – REE-Sr-bearing fluorcalciopyrochlores, 5 – Sr-REE-bearing fluorcalciopyrochlores, 6 – IMA classification for the pyrochlore group by [Hogarth, 1977], 7 – IMA classification for the pyrochlore group by [Atencio, 2010].

the SHRIMP-II ion microprobe at the Centre for Isotope Research (VSEGEI, St.Petersburg). Given that pyrochlore is significantly different from zircon in terms of crystallochemical features, at the stage preceding the analytical measurements of U-Pb ratios in pyrochlores from our collection, we experimentally selected the optimal regime and sequence for recording the ionic currents of elements taking mineral matrix composition and possible isobaric overlaps into account, as well as developed a scheme for measuring and calculating U-Pb ages. In situ dating of pyrochlore was accompanied by a detailed determination of the chemical composition of crystals at the micro-level.

Pyrochlore-331 (sövite II, Vishnevogorsky massif), which is characterised by relative areal geochemical homogeneity with an age of 230 ± 1.3 Ma and a U content of 1.500 ± 365 g/t, was used as an internal laboratory standard. Regular mass spectrometric analysis of pyrochlore-331 (over a period of 10 months) demonstrates acceptable for the standard dispersion of the obtained $^{206}Pb/^{238}U$ ratios when performing calibration according to the linear dependence of ln(Pb/U) on ln(UO/U). The measured $^{206}Pb/^{238}U$ ratios of pyrochlore were normalised against a value of 0.0363, which corresponds to 230 Ma (according to the model of [Stacey, Kramers, 1975]). With an average of 10–15 analyses per session, the error in measuring isotope ratios for a standard varies within 1–2% (2σ). The concentration of ^{238}U in the analysed pyrochlore samples was estimated relative to the average uranium content in pyrochlore-331 (≈1500 g/t). The correction of the measured Pb isotopic composition for non-radiogenic lead and the corresponding age was based on the Pb_c model composition and on the use of the Stacey–Kramers model [Stacey, Kramers, 1975], respectively. Errors associated with individual analyses (of ratios and ages) were calculated at the 1σ level, whereas the errors of calculated concordant ages are given in Figures 5–7 at the 2σ level. The processing of primary MS data along with the construction of concordia plots for the obtained isotope ratios was performed using the SQUID and ISOPLOT/EX programs [Ludwig, 2003].

U-Pb DATING OF MINERALS BELONGING TO THE PYROCHLORE GROUP (ILMENY-VISHNEVOGORSKY COMPLEX). RESULTS AND DISCUSSION

We studied the U-Th-Pb isotopic system of three chemically characterised pyrochlore samples from the Ilmeny-Vishnevogorsky complex belonging to different stages of ore formation: a) from early carbonatites (U-(Ta)-oxycalciopyrochlore, sample K-37-95, sövite I, Potanino deposit); b) from late carbonatites (Ta-bearing fluorcalciopyrochlore, sample K-43-62, sövite II, Potanino deposit); c) from late carbonatites (REE-Sr-bearing fluorcalciopyrochlore, sample 331, sövite II, Vishnevogorsky deposit). The representative analyses of the studied pyrochlore samples (characterising the core and rim of crystals) and their conversion to a crystal-chemical formula. are given in Table 1. The optical and backscattered-electron (BSE) images of pyrochlore varieties are shown in Figures 2 and 3.

As mentioned earlier, a sample of pyrochlore-331 from the Vishnevogorsky deposit was selected as an isotope-geochemical and geochronological standard. According to [Atencio et al., 2010], this pyrochlore is classified as Sr-REE-bearing (1.5–4.5 wt % SrO and 1.0–2.5 wt % LREE) fluorcalciopyrochlore. It occurs in late carbonatites (sövites II) – in biotite-calcite carbonatites with apatite, ilmenite, pyrrhotite, pyrite (apical part of the Vishnevogorsky miaskite massif). Pyrochlore forms large and small octahedral crystals and grains of brown, light brown (almost yellow) and red-brown colour.

The U-Pb isotopic analysis of this pyrochlore using in situ methods (SHRIMP-II, LA-ICP-MS), as well as isotope dilution employing chromatographic separation of elements and ID-TIMS revealed satisfactory repeatability of results. Thus, the dates of pyrochlore-331 grains obtained using two in-situ methods differ by no more than 0.5–1.0 Ma, with the uranium content varying within 30% (SHRIMP-II and LA-ICP-MS). The measured Pb isotopic composition of the internal standard for pyrochlore was corrected for the isotopic composition of the non-radiogenic component according to the lead composition in syngenetic calcite (Pb acceptor mineral characterised by a high Pb/U ratio), as well as the corresponding parameters of the model curve [Stacey, Kramers, 1975] for the evolution of Earth's Pb isotopic composition 230 Ma ago: $^{207}Pb/^{206}Pb = 0.851$, $^{208}Pb/^{206}Pb = 2.082$ and $^{206}Pb/^{204}Pb = 18.35$. Within the obtained error margins, the age and concentration characteristics of the pyrochlore grains in question are reproduced satisfactorily, thus the age and U content of pyrochlore-331 (230 ± 1.3 Ma and 1500 ± 365 g/t, respectively) were used for further U-Pb measurements of pyrochlore samples from the collection.

Using the age and concentration characteristics of pyrochlore-331, we measured the U-Pb ratios of the pyrochlore collection acquired from the rare-metal deposits of Ural carbonatite complexes relative to the U/Pb ratios of pyrochlore-331 grains, which were measured in the same session in the capacity of the calibration standard. Despite significant variations in the content of uranium (from 300 g/t to 1.9%), thorium (from 1400 g/t to 3%) and a high proportion of non-radiogenic lead (from 9 to 65% of ^{206}Pb), the U-Pb isotopic systems of the studied fluorcalciopyrochlores were practically closed and the age within the error margins was concordant. Relatively high contents of radiogenic lead ($^{206}Pb_{rad}$ = 14–300 g/t) account for the low error associated with individual measurements of isotopic ratios and results reproducibility, which expressed in terms of age leads to an error of concordant estimates at a level of 1–6 Ma. The results of U-Th-Pb isotope analysis for pyrochlores are presented in Table 2 and shown in Figures 5–7.

Uranpyrochlores formed in the early stages of carbonatite genesis in the sövites I of the Central Alkaline Belt (sample K-37-95, U-(Ta)-bearing oxycalciopyrochlore, Potanino deposit) are characterised by a slightly open U-Pb system and yield an age of 378.3 ± 4.9 Ma (see Fig. 5). The detected departure from the closed nature of the isotopic system of these pyrochlores reflects an increased degree of metamictisation of the crystal structure of the mineral due to the high content of radioactive U and Th, as well as the impact of late processes associated with the post-

Table 1. Chemical compositions (wt %) and formulae (p.f.u.) of the pyrochlore-group minerals from the Ilmeny-Vishnevogorsky carbonatite-miaskite complex, Urals

Element	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	Sample K37-95				Sample K43-62				Sample 331							
	Analysis points															
	2c	2r	8c	4r_alt	2	3	5	9	1-1c	1-2r	7-1c	7-2r	6-1c*	6-2c_alt*	6-3r*	8-1c
Nb_2O_5	38.72	39.58	45.60	50.42	63.83	61.66	62.03	63.44	65.58	60.23	66.59	65.64	60.33	52.08	59.26	66.98
Ta_2O_5	4.02	4.20	4.37	4.39	2.12	3.53	2.92	2.30	0.02	0.27	0	0.13	0.31	0.00	0.00	0.00
TiO_2	12.50	12.06	9.48	7.95	4.32	4.89	4.60	4.47	4.23	5.06	3.33	4.52	4.45	4.42	3.51	3.24
SiO_2	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.01	4.99	0.00	0.00	1.58	0.00	0.00	0.00
UO_2	22.11	21.00	16.43	12.44	0.08	1.80	0.83	0.00	0.16	0.57	0.19	0.21	3.72	3.72	0.85	0.2
ThO_2	0.78	0.80	0.59	1.11	2.05	1.59	1.97	2.26	0.56	0.78	0.63	0.61	0.3	0.53	0.59	0.46
Fe_2O_3	0.00	0.02	0.00	0.81	0.06	0.07	0.07	0.07	0.03	1.59	0.04	0	1.52	1.69	1.5	0.02
Y_2O_3	0.12	0.10	0.05	0.07	ND	ND	ND	ND	0.1	0.04	0.13	0.11	0.1	0	0.03	0.15
La_2O_3	0.31	0.41	0.44	0.61	0.32	0.22	0.59	0.14	0.51	1.49	0.22	0.54	0.37	0.7	1.08	0.68
Ce_2O_3	0.72	1.02	1.11	1.82	0.88	0.82	1.33	0.56	1.43	4.52	0.96	1.42	1.52	2.42	2.98	1.96
Nd_2O_3	0.94	0.95	0.95	0.94	0.38	0.26	0.37	0.12	ND	ND	ND	ND	ND	ND	ND	ND
MnO	0.00	0.00	0.00	0.02	ND	ND	ND	ND	0	0.74	0.00	0.00	0.21	0.42	0.5	0.04
MgO	0.03	0.01	0.01	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CaO	11.06	10.65	11.08	6.65	15.48	15.47	15.03	16.07	14.98	6.69	15.04	14.37	11.68	6.04	12.24	13.2
BaO	0.00	0.00	0.00	0.14	ND	ND	ND	ND	0	1.58	0.06	0	0.77	2.39	0.73	0
SrO	0.28	0.31	0.46	0.44	0.56	0.39	0.47	0.47	1.53	4.4	1.02	1.44	1.97	5.01	3.27	1.8
PbO	0.91	0.91	0.53	0.50	ND	ND	ND	ND	0.18	0.46	0.19	0.33	0.48	0.31	0.05	0.46
Na_2O	5.11	5.40	5.79	0.16	6.55	6.51	6.53	6.48	6.99	0.35	7.12	6.98	3.64	0.05	2.09	6.71
K_2O	0.01	0.01	0.01	0.57	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
F	1.44	1.51	1.38	1.65	5.25	4.74	4.86	5.21	4.58	0.50	4.29	4.43	2.76	0.24	2.13	4.21
Total	99.04	99.04	98.25	90.71	101.87	101.95	101.59	101.58	100.89	94.26	99.81	100.73	95.71	80.02	90.81	100.11
$O = F_2$	0.61	0.64	0.58	0.69	2.21	2.00	2.05	2.19	1.93	0.21	1.81	1.87	1.16	0.10	0.90	1.77
Total	98.44	98.41	97.67	90.02	99.67	99.95	99.55	99.39	99.0	94.0	98.0	98.9	94.55	79.92	89.9	98.3
The formulae are designed for two cations in site B (p.f.u.)																
B-position																
Nb	1.250	1.270	1.425	1.491	1.764	1.712	1.734	1.753	1.804	1.460	1.845	1.793	1.632	1.673	1.753	1.850
Ta	0.078	0.081	0.082	0.078	0.035	0.059	0.049	0.038	0.000	0.004	0.000	0.002	0.005	0.000	0.000	0.000
Ti	0.672	0.644	0.493	0.391	0.199	0.226	0.214	0.205	0.194	0.204	0.153	0.205	0.200	0.236	0.173	0.149
Fe^{3+}	0.000	0.004	0.000	0.040	0.003	0.003	0.003	0.003	0.001	0.064	0.002	0.000	0.068	0.090	0.074	0.001
Sum B	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
A-position																
Ca	0.847	0.810	0.820	0.466	1.014	1.018	0.996	1.052	0.977	0.268	0.987	0.930	0.749	0.460	0.858	0.864
Mn	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.384	0.000	0.000	0.011	0.025	0.028	0.002
Mg	0.003	0.001	0.001	0.002	0.000	0.000	0.000	0.000	ND	0.034	ND	ND	ND	ND	ND	ND
Ba	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.033	0.001	0.000	0.018	0.067	0.019	0.000
Sr	0.011	0.013	0.018	0.017	0.020	0.014	0.017	0.017	0.054	0.137	0.036	0.050	0.068	0.206	0.124	0.064
Pb	0.018	0.017	0.010	0.009	0.000	0.000	0.000	0.000	0.003	0.007	0.003	0.005	0.008	0.006	0.001	0.008
Na	0.708	0.743	0.776	0.020	0.776	0.775	0.783	0.768	0.825	0.036	0.846	0.817	0.422	0.007	0.265	0.795
K	0.001	0.001	0.001	0.048	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Y	0.004	0.004	0.002	0.002	0.000	0.000	0.000	0.000	0.003	0.001	0.004	0.004	0.003	0.000	0.001	0.005
LREE	0.051	0.061	0.063	0.080	0.035	0.029	0.052	0.018	0.043	0.118	0.027	0.043	0.0415	0.081	0.0975	0.059
U	0.351	0.332	0.253	0.181	0.001	0.025	0.011	0.000	0.002	0.007	0.003	0.003	0.050	0.059	0.012	0.003
Th	0.013	0.013	0.009	0.017	0.029	0.022	0.028	0.031	0.008	0.010	0.009	0.008	0.004	0.009	0.009	0.006
Sum A	2.007	1.996	1.953	0.847	1.875	1.883	1.887	1.886	1.915	0.767	1.916	1.861	1.374	0.920	1.414	1.806
F	0.325	0.339	0.302	0.341	1.015	0.921	0.950	1.007	0.881	0.085	0.831	0.846	0.522	0.054	0.441	0.813

Note. The chemical compositions of minerals belonging to the pyrochlore group were determined using: 1–8 – a CAMEBAX microprobe at the IGM SB RAS (Novosibirsk, analyst V.V. Sharygin); 9–16 – a Cameca-100 microprobe at the IGG, UB RAS (Ekaterinburg, analyst D.V. Zamyatin).

alt – altered; c – core of the crystal, r – rim of the crystal, ND – not detectable. *pyrochlore grain having early generation relics.

1, 2, 3 – U-(Ta)-bearing oxycalciopyrochlore; 4 – U-(Ta)-bearing hydropyrochlore (sample K-37-95, sövite I, Potanino deposit, Ilmeny-Vishnevogorsky complex); 5–8 – Ta-bearing fluorcalciopyrochlore (sample K-43-62, sövite II, Potanino deposit, Ilmeny-Vishnevogorsky complex); 9–16 – (sample 331, sövite II, Vishnevogorsky deposit, Ilmeny-Vishnevogorsky complex): 9, 11, 12, 16 – Sr-(REE)-bearing fluorcalciopyrochlore; 10 – Sr-(REE)-bearing kenopyrochlore; 13 – relics of U-bearing pyrochlore (grain core 6-1C, sample 331), 14 – U-bearing hydropyrochlore (middle zone of grain 6–2C, sample 331); 15 – Sr-(REE)-bearing fluorcalciopyrochlore (rim of grain 6-3r, sample 331) (see Fig. 3).

Table 2. Composition and U-Th-Pb isotope system of the pyrochlore-group minerals from the Nb-deposits of Ilmeny-Vishnevogorsky carbonatite-miaskite complex (South Urals)

Sample No.	Host rock	Chemical type of pyrochlore according to [Atencio, 2010]	Composition of pyrochlore (main components, wt %)	Characteristics of the U-Th-Pb system of pyrochlore	U-Pb age of pyrochlore, Ma
Potanino Nb-deposit, Central Alkaline Belt, Ilmeny-Vishnevogorsky carbonatite-miaskite complex					
K37-95*	Sövite I	U-(Ta)-bearing oxycalciopyrochlore	Na_2O – 4.6 CaO – 9.1 Nb_2O_5 – 42.5 ($PbO + ThO_2 + UO_2$) – 20	[U]: 130000–240000 Th/U: 0.3–0.9	378.3 ± 4.9 n = 28
K43-62	Sövite II	Ta-bearing fluorcalciopyrochlore	Na_2O – 8.4 CaO – 14.6 Nb_2O_5 – 60.7 ($PbO + ThO_2 + UO_2$) – 2	[U]: 300–2800 Th/U: 8.6–92.0 $^{206}Pb_c$: 25–68%	216 ± 5.0 n = 15
Vishnevogorsky Nb-deposit, Ilmeny-Vishnevogorsky carbonatite-miaskite complex					
331	Sövite II	Sr-bearing fluorcalciopyrochlore	Na_2O – 8.5 CaO – 13.1 Nb_2O_5 – 65.1 ($PbO + ThO_2 + UO_2$) – 1	[U]: 620–4700 Th/U: 0.7–5.2 $^{206}Pb_c$: 9–39%	230 ± 1.5 n = 40

Note. The U-Pb dating of pyrochlore (less than 2.5 wt % UO_2) was performed through the method of ID-TIMS developed at VSEGEI (St. Petersburg) using a secondary-ion mass spectrometer SHRIMP-II. A detailed description of the technique is given in [Lepekhina et al., 2016].
*The U-Pb dating of U-bearing pyrochlore (more than 2.5 wt % UO_2) was performed using the method of laser ablation and ICP-MS.
n – number of analyses, [U] – concentration of U (g/t) calculated relative to the concentration of U (1500 g/t) in the in-house standard (pyrochlore-331); $^{206}Pb_c$ – relative proportion of non-radiogenic Pb. Detailed chemical composition is given in Table 1.

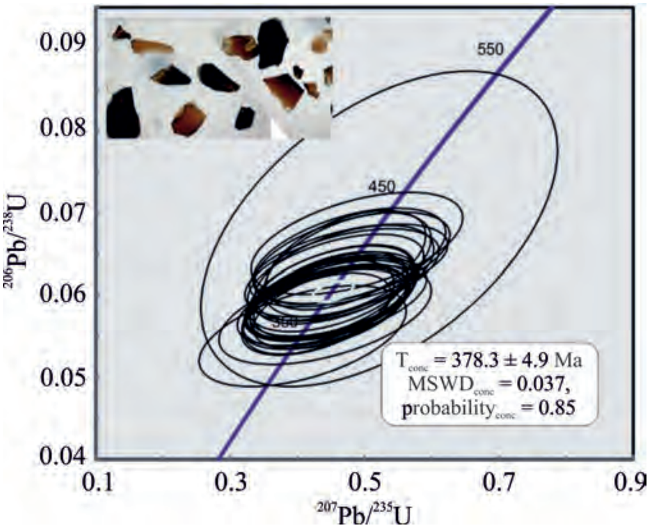

Fig. 5. U-Pb-diagram constructed according to LA-ICP-MS data for sample 37-95 of uranpyrochlore (only concordant analyses are given) from the carbonatites of the Potanino deposit (Ilmeny-Vishnevogorsky complex, South Urals)

The inserted picture shows the external forms of dated grains (incident light). Here and in figures 6 and 7, the error ellipses are at the 2σ level.

collision ore-metasomatic stage in the evolution of the complex 220–250 Ma ago.

As mentioned above, Sr-REE-bearing pyrochlore (sample 331, fluorcalciopyrochlore, sövite II, Vishnevogorsky deposit) yielded an age of 230 ± 1.5 Ma (see Fig. 6).

The youngest age (216 ± 5 Ma) was obtained for Ta-bearing fluorcalciopyrochlore from the late carbonatites of the Potanino deposit (sample K-43-62; see Table 2, Fig. 7).

Thus, the U-Pb system of the studied pyrochlore samples indicates the multistep formation of the Nb rare-metal mineralisation in the Ilmeny-Vishnevogorsky complex.

The earliest stage of ore formation (378 ± 4.9 Ma) – possibly associated with the primary crystallisation of the alkaline-carbonatite magmatic system – is determined from the U-Pb isotopic systems of the U-(Ta)-pyrochlores from the Potanino deposit [Krasnobaev et al., 2010a, 2014; Nedosekova et al., 2010, 2014; Ivanov et al., 2010; Nedosekova, 2012]. The U-Pb systems of zircons from the Ilmeny-Vishnevogorsky complex reveal a similar age cluster – 383 ± 14 Ma [Krasnobaev et al., 2010a]. The closest age of 388 + 50 Ma was yielded by the mineral Sm-Nd isochron obtained for the carbonatites of the richest ore zone of the Vishnevogorsky deposit (ore zone 140, saddle-like miaskite deposit) [Ivanov et al., 2010], which probably reflects the final stages in the functioning of alkaline-carbonatite magmatic system, as well as one of the main stages in the ore formation of the Vishnevogorsky niobium deposit. The following stages of ore formation are widely manifested at the Vishnevogorsky (230 ± 1.5 Ma) and later at the Potanino (217.2 ± 1.9 Ma) deposits. Mineral Rb-Sr isochrons obtained for miaskites show a close age of 245 ± 8 Ma (T_2), which corresponds to the stage

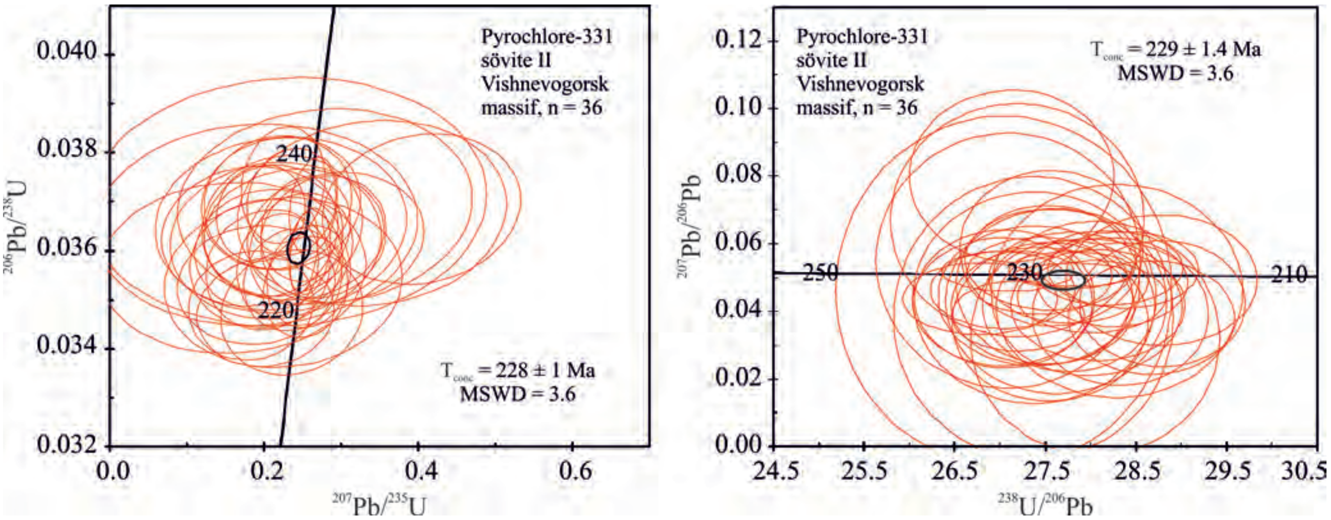

Fig. 6. U-Pb concordia diagram constructed according to SHRIMP-II data for pyrochlore (sample 331) from the late carbonatites of the Vishnevogorsky Nb-ore deposit (Ilmeny-Vishnevogorsky complex, South Urals).

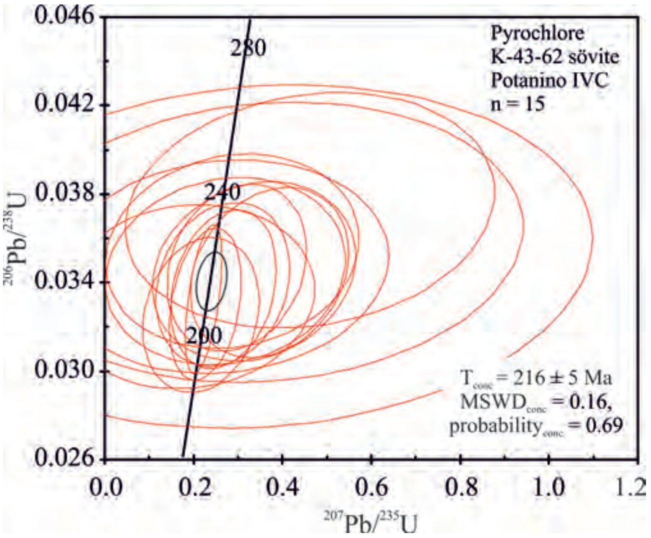

Fig. 7. U-Pb concordia diagram constructed according to SHRIMP-II data for pyrochlore (sample К-43-62) from the carbonatites of the Potanino deposit, Ilmeny-Vishnevogorsky complex.

of metamorphic transformations in the Ilmeny-Vishnevogorsky complex [Kononova et al., 1979; Kramm et al., 1983]. Ages associated with the stage of late-collision metamorphism [Puchkov, 2010] are also yielded by the U-Pb isotopic systems of zircons from the miaskites – 269 ± 6, 279 ± 10 Ma [Krasnobaev et al., 2010a, 2014] – and zircons from the carbonatites of the Ilmeny-Vishnevogorsky complex – 279 ± 10 Ma [Krasnobaev et al., 2010b], 280 ± 8 (Nedosekova et al., 2014). A considerable number of zircons from miaskite-pegmatites yield an age of 251 ± 6 Ma, which confirms that the formation of pegmatites and rare-metal ores in the pegmatites of the Ilmeny-Vishnevogorsky complex is associated with the late-collision and post-collision stages in the development of the Ural Orogen.

Thus, the formation of niobium ores occurred both at the final stage in the functioning of the alkaline-carbonatite magmatic system (≈380–390 Ma ago) and at the post-collision stage (≈230–250 Ma ago) in the formation of Ural carbonatite complexes. The late stages of ore formation at the Ilmeny-Vishnevogorsky complex are probably associated with the remobilisation and redeposition of alkaline-carbonatite and rare-metal substances. The formation of pyrochlore from the HFSE-enriched fluid is associated with large-scale processes of alkaline metasomatism and pegmatite formation; it concluded the transformation of rocks from carbonatite complexes at the late-collision and post-collision stages in the formation of the Ural Orogen (≈280–220 Ma).

CONCLUSION

Studies have revealed that the U-Pb isotopic system of pyrochlore (even in the case of high-uranium varieties of the mineral) can be quite successfully used for dating rare-metal mineralisation, at least in situ version. Moreover, the mineralogical and paragenetic analysis of pyrochlore, which accompanies and precedes U-Pb analytical work, provides the opportunity to adjust the versions of the applied analytical method (laser ablation, secondary-ion microprobe) and interpret obtained geochronological data correctly. Clearly, the rare-metal niobium mineralisation of the Ilmeny-Vishnevogorsky complex was formed over a relatively long time interval (from 380 to 220 Ma), with its development accompanying various formation and transformation stages of magmatic complexes. In addition, the ore potential of mineralisation evolved over time as well. While high-uranium varieties of pyrochlore, the main ore mineral, were predominantly formed in the early stages, REE-Sr-bearing high-Nb varieties are mainly associated with the late stages of metasomatic recrystallisation.

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REFERENCES

Atencio D., Andrade M.B., Christy, Giere R., Kartashov P.M. (2010) The pyrochlore supergroup of minerals: nomenclature. *Canad. Miner*., **48**, 673-698.

Bagdasarov Yu.A. (2014) On some conditions of formation of carbonatites of the linear fissure type. *Litosfera*, (4), 113-119. (In Russian)

Braccialli L., Parrish R.R., Horstwood M.S.A., Condon D.J., Najman Y. (2013) U-Pb LA-(MC)-ICP-MS dating of rutile: New reference materials and applications to sedimentary provenance. *Chem. Geol*., **347**, 82-101.

Chernyshev I.V., Kononova V.A., Kramm U., Grauetrt B. (1987) Isotope geochronology of alkaline rocks of the Urals in the light of zircon uranium-lead data. *Geokhimiya*, (3), 323-338. (In Russian)

Deng X.-D., Li J.-W., Zhao X.-F., Hu H., Selbyc D., Souza Z.S (2013) U-Pb isotope and trace element analysis of columbite-(Mn) and zircon by laser ablation ICP-MS: implications for geochronology of pegmatite and associated ore deposits. *Chem. Geol*., **344**, 1-11.

Efimov A.F., Es'kova E.M., Lebedeva S.I., Levin V.Ya. (1985) Typochemistry of accessory pyrochlore in rocks of the alkaline complex of the Urals. *Geokhimiya*, (2), 202-208.

Es'kova E.M., Nazarenko I.I. (1960) Pyrochlor of Cherry Mountains, its paragenetic associations and features of the chemical composition. *Voprosy geologii, geokhimii i genezisa mestorozhdenii redkikh elementov* [Questions of geology, geochemistry and genesis of deposits of rare elements]. Proc. IMGRE, **4**, 33-50. (In Russian)

Es'kova E.M., Zhabin A., Mukhitdinov G. (1964) *Mineralogiya i geokhimiya redkikh elementov Vishnevykh gor* [Mineralogy and geochemistry of rare elements of the Cherry Mountains]. Moscow, Nauka Publ., 319 p. (In Russian)

Hogarth D.D. (1977) Classification and nomenclature of the pyrochlore group. *Amer. Mineral*., **62**, 403-410.

Ivanov K.S. (2011) About the nature of Ural carbonatites. *Litosfera*, (1), 20-33. (In Russian)

Ivanov K.S., Valizer P.M., Erokhin Yu.V., Pogromskaya O.E. i dr. (2010) On the genesis of carbonatites of the fold belts (on the example of the Urals). *Dokl. Akad. Nauk*, **435**(2), 218-222. (In Russian)

Kononova V.A., Dontsova E.I., Kuznetsova L.D. (1979) The isotopic composition of oxygen and strontium of the Ilmen-Vishnevogorsky alkaline complex and the genesis of miaskites. *Geokhimiya*, (12), 1784-1795. (In Russian)

Kramm U., Blaxland A.B., Kononova V.A., Grauert B. (1983) Origin of the Ilmenogorsk-Vishnevogorsk nepheline syenites, Urals, USSR, and their time of emplasement during the history of the Ural fold belt: a Rb-Sr study. *J. Geol*., **91**, 427-435.

Kramm U., Chernyshev I.V., Grauert B., Kononova V.A., Breker V. (1993) Typology and U-Pb systematics of zircons: the study of zircons in the nepheline syenites of the Ilmen mountains, the Urals. *Petrologiya*, **1**(5), 536-549. (In Russian)

Krasnobaev A.A., Rusin A.I., Busharina S.V., Lepekhina E.N., Medvedeva E.V. (2010a) Zirconology of amphibole miaskites of the Ilmenogorsk massif (South Urals). *Dokl. Akad. Nauk*, **430**(2), 227-231. (In Russian)

Krasnobaev A.A., Rusin A.I., Valizer P.M., Busharina S.V. (2010b) Zirconology of calcite carbonatites of the Vishnevogorsky Massif (Southern Urals). *Dokl. Akad. Nauk*, **431**(3), 1-4. (In Russian)

Krasnobaev A.A., Valizer P.M., Anfilogov V.N., Nemov A.B., Busharina S.V. (2014) Zirconology of pegmatites of the Ilmensky mountains. *Dokl. Akad. Nauk*, **457**(4), 455. (In Russian)

Lepekhina E.N., Antonov A.V., Belyatskii B.V., Rodionov N.V., Berezhnaya N.G., Shevchenko S.S., Sergeev S.A. (2014) Features of U-Pb pyrochlore dating from the alkaline-ultrabasic polyphase massif Kovdor (North. Karelia): isotope-geochemical characteristics of the evolution of the composition of pyrochlore group minerals. *Region. geologiya i metallogeniya*, (67), 86-94. (In Russian)

Levin V.Ya., Ronenson B.M., Samkov V.S., Levina I.A., Sergeev N.I., Kiselev A.P. (1997) *Shchelochno-karbonatitovye kompleksy Urala* [Alkali-carbonatite complexes of the Urals]. Ekaterinburg, Uralgeolkom Publ., 274 p. (In Russian)

Ludwig K.R. (2003) User's manual for Isoplot/Ex. Version 2.49. A geochronological toolkit for Microsoft Excel. Berkeley Geochronology Center, Berkeley, CA, USA. Spec. Publ., **1a**, 75 p.

Lumpkin G.R., Ewing R.C. (1995) Geochemical alteration of pyrochlore group minerals: pyrochlore subgroup. *Amer. Mineralog*., **80**, 732-743.

Millonig L.J., Gerdes A., Groat L.A. (2012) U-Th-Pb geochronology of meta-carbonatites and meta-alkaline rocks in the southern Canadian Cordillera: a geodynamic perspective. *Lithos*, **152**, 202-217.

Millonig L.J., Gerdes A., Groat L.A. (2013) The effect of amphibolite facies metamorphism on the U-Th-Pb geochronology of accessory minerals from meta-carbonatites and associated meta-alkaline rocks. *Chem. Geol*., **353**, 199-209. doi: 10.1016/j.chemgeo.2012.10.039

Mitchell R.H. (2005) Carbonatites and carbonatites and carbonatites. *Canad. Mineral*., 43, 2049-2068.

Nedosekova I.L. (2007) New data on carbonatites of the Ilmeny-Vishnevogorsk complex (the Southern Urals, Russia). *Geol. Rud. Mestorozhd*., **49**(2), 146-164. (In Russian)

Nedosekova I.L. (2012) Age and sources of the Ilmeny-Vishnevogorsk alkaline complex (the Southern Urals): geochemical and Rb-Sr, Sm-Nd, U-Pb and Lu-Hf isotopic data. *Litosfera*, (5), 77-95. (In Russian)

Nedosekova I.L., Belousova E.A., Sharygin V.V. (2010) Sources of the substance of the Ilmeny-Vishnevogorsk alkaline complex according to Lu-Hf isotopic data in zircons. *Dokl. Akad. Nauk*, **435**(2), 234-239. (In Russian)

Nedosekova I.L., Belousova E.A., Sharygin V.V., Belyatsky B.V., Baynova T.B. (2013) Origin and evolution of the Il'meny-Vishnevogorsk carbonatites (Urals, Russia): insights from trace-elements compositions, Rb-Sr, Sm-

Nd, U-Pb and Lu-Hf isotope data. *Mineral. Petrol.*, **107**, 101-123.

Nedosekova I.L., Belousova E.A., Belyatskii B.V. (2014) U-Pb age and Lu-Hf isotopic systems of zircons of the Ilmeny-Vishnevogorsk alkaline carbonatite complex, Southern Urals. *Litosfera*, (5), 19-32. (In Russian)

Nedosekova I.L., Belyatskii B.V. (2012) Age and sources of the substance of the Ilmeny-Vishnevogorsk alkaline complex (the Southern Ural): Rb-Sr, Sm-Nd, U-Pb and Lu-Hf isotope data. *Dokl. Akad. Nauk*, **446(**1), 71-76. (In Russian)

Nedosekova I.L., Belyatskii B.V., Belousova E.A. (2016) Rare elements and isotopic composition of hafnium as indicators of the genesis of zircon during the evolution of the alkali-carbonatite magmatic system (Ilmeny-Vishnevogorsk complex, Urals, Russia).*Geol. Geofiz.*, **57**(6), 1135-1154. (In Russian)

Nedosekova I.L., Vladykin N.V., Pribavkin S.V., Bayanova T.B. (2009) Ilmeny-Vishnevogorsk miaskite-carbonatite complex: origin, ore content, sources of matter (Urals, Russia). *Geol. Rud. Mestorozhd.*, **51**(2), 157-181. (In Russian)

Nedosekova I.L., Zamyatin D.A., Udoratina O.V. (2017) Ore specialization of carbonatite complexes of the Urals and Timan. *Litosfera*, **17**(2), 60-77. (In Russian)

Nedosekova I.L., Pribavkin S.V. (2015) Ore niobium mineralization of rare-metal deposits and ore occurrences of Ilmeny–Vishnevogorsk alkaline carbonatite complex (Southern Urals). *Ezhegodnik-2014. Tr. IGG UrO RAN*, **162**, 175-183. (In Russian)

Pöml P., Menneken M., Stephan T., Niedermeier D.D.R., Geisler T., Putnis A. (2007) Mechanism of hydrothermal alteration of natural self-irradiated and synthetic crystalline titanite-based pyrochlore. *Geochim. Cosmochim. Acta*, 71, 3311-3322.

Puchkov V.N. (2010) *Geologiya Urala i Priural'ya (aktual'nye voprosy stratigrafii, tektoniki, geodinamiki i metallogenii)* [Geology of the Urals and Urals (Current problems of stratigraphy, tectonics, geodynamics and metallogeny)]. Ufa, DizainPoligrafServis Publ., 280 p. (In Russian)

Rass I.T., Abramov S.S., Utenkov U.V. (2006) The role of fluids in the petrogenesis of carbonatites and alkaline rocks: geochemical indicators. *Geokhimiya*, (7), 692-711. (In Russian)

Rusin A.I., Valizer P.M., Krasnobaev A.A., Baneva N.N., Medvedeva E.V., Dubinina E.V. (2012) Nature of garnet-anorthite-clinopyroxene-amphibole rocks of the Ilmenogorsk complex (South Ural). *Litosfera*, (1), 91-109. (In Russian)

Stacey J.S., Kramers J.D. (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth Planet. Sci. Lett.*, **26**, 207-221.

Wetzel F., Schmitt A.K., Kronz A., Worner G. (2010) In situ ^{238}U-^{230}Th disequilibrium dating of pyrochlore at submillennial precision. *Amer. Mineral.*, **95**, 1353-1356.

Zoloev K.K., Levin V.Ya., Mormil' S.I., Shardakova G.Yu. (2004) *Minerageniya i mestorozhdeniya redkikh metallov, molibdena, vol'frama Urala* [Minerageny and deposits of rare metals, molybdenum, tungsten of the Urals]. Ekaterinburg, 336 p. (In Russian)