

Mineralogical and geochemical aspects of rare-earth elements behavior during metamorphism (on the example of the Upper Precambrian structural-material complexes of the Bashkir megaanticlinorium, South Urals)

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Abstract. The article provides new data on geochemistry and mineralogy of rare-earth elements (REE) in rocks of structural-material complexes of the Bashkir megaanticlinorium, which underwent metamorphic transformations of various nature: contact metamorphism (Suran section); syn- and postgenetic contact-dislocation metamorphism (Shatak complex) and hydrothermal metamorphism (Uluelga-Kudashmanovo zone). It has been established that when a magmatic melt is exposed to sediments, the latter are enriched with REEs with the formation of rare earth minerals (monazite, allanite, xenotime et al.). The study of the chemical composition of monazites and allanites showed that all variations of oxides in the composition of the former are due to isomorphous Ce-Ca-Th substitutions in the structure of minerals, but redistribution of these elements was an independent process characteristic of each structural-material complex. The study of allanites made it possible to establish the presence of isomorphism according to the Ca↔Ce, La, Nd principle, as well as the sharp difference between the characterized minerals in the amount of MgO, Fe* and MnO from analogues from other regions, which indicates the presence of a regional component in the chemical compositions of minerals altogether, geotectonic settings of mineralization formation. The temperature regimes of mineral-forming processes with metamorphic transformations of rocks calculated from chlorite and muscovite compositions (344-450°C – Suran section, 402-470°C – Shatak complex, 390-490°C – Uluelga-Kudashmanovo zone) indicate the possibility of stable coexistence of the association monazite-allanite. It was established that when a magmatic melt on the sedimentary substrate of the frame, the lanthanides enrich the exocontact rocks with the formation of newly formed REE-mineral associations. At the same time, the processes of formation of rare-earth mineralization are largely determined by the physicochemical parameters and thermobaric conditions of the accompanying and subsequent metamorphism.

Keywords: South Ural, Bashkir megaanticlinorium, structural-material complexes, Upper Precambrian, rare-earth elements, contact metamorphism, monazite, allanite

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Introduction

The genetic nature of the rare-earth mineralization of metamorphogenic type is the subject of lively discussion (Savko et al., 2010). There are at least two points of view on the rare-earth minerals (REE) behavior in the processes of metamorphism.

According to the first, the formation and decomposition of rare-earth phases during metamorphism occurs without

the participation of rock-forming aluminosilicates, which practically do not contain REE. Such phenomena are described in metapelites, where in detail the following is documented: the appearance of allanite during decomposition of detrital monazite under conditions of the green shale facies (Smith, Barero, 1990; Wing et al., 2003); a change in the paragenesis of florensite with monazite by the association of allanite with synchitis with high-pressure metamorphism (Janots et al., 2006); the replacement of allanite with monazite under the conditions of the epidote-amphibolite facies (Wing et al., 2003; Janots et al., 2009; Tomkins, Pattison, 2007, etc.). The formation of monazite during partial decomposition of REE-containing apatite in the rocks of the Bohemian

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array has also been established (Finger, Krenn, 2006). In addition, apatite and sphene monazite has been described in the Rogaland orthogneisses in southwestern Norway (Bingen et al., 1996).

The second point of view suggests that silicates, upon decomposition of which monazite is formed, can contain significant amounts of light REE and phosphorus (Lanzirotti, Hanson, 1996; Kohn, Malloy, 2004; Gibson et al., 2004). These ideas are based on a significant increase in the number of monazite with the advent of staurolite and data on high contents of light lanthanides and phosphorus in pomegranate, plagioclase, biotite, muscovite, and chlorite, while they were not found in staurolite (Kohn, Malloy, 2004). In addition, the growth of monazite and xenotime due to partial decomposition of pomegranate in metapelites has been described in the Canadian Cordilleras (Gibson et al., 2004) and in contact metamorphism in North Labrador (McFarlane et al., 2005).

Recently, we have obtained extensive new material on the geochemistry and mineralogy of REE in the Riphean deposits of the Bashkir meganticlinorium (South Urals), which allows us to characterize rare-earth

mineral formation in structural-material complexes that underwent metamorphic transformations of various nature using the example of a number of model objects: 1) "Suran section" where contact metamorphism is manifested in a "pure" form; 2) "Shatak complex" with syn- and post-genetic contact-dislocation metamorphism; 3) "Uluelga-Kudashmanovo zone", within which hydrothermal metamorphism is developed.

Geological and geochemical characteristics of objects

The Suran section is represented by carbonaceous shales, siltstones and carbonate rocks of the Lower Riphean Suranian Formation (Fig. 1), penetrated by igneous bodies of various thicknesses (from 1-2 m to 60 m).

Shales and silt shales consist of small (0.000n ... 0.00n cm) quartz grains, numerous elongated sericite flakes, feldspar tablets of close dimension and nest-like streaky chlorite secretions. The rocks are schistose with the formation of directive micro-textures, underlined by sericite flakes. Thin filamentous veins composed of sericite are observed. Carbon matter is relatively rare

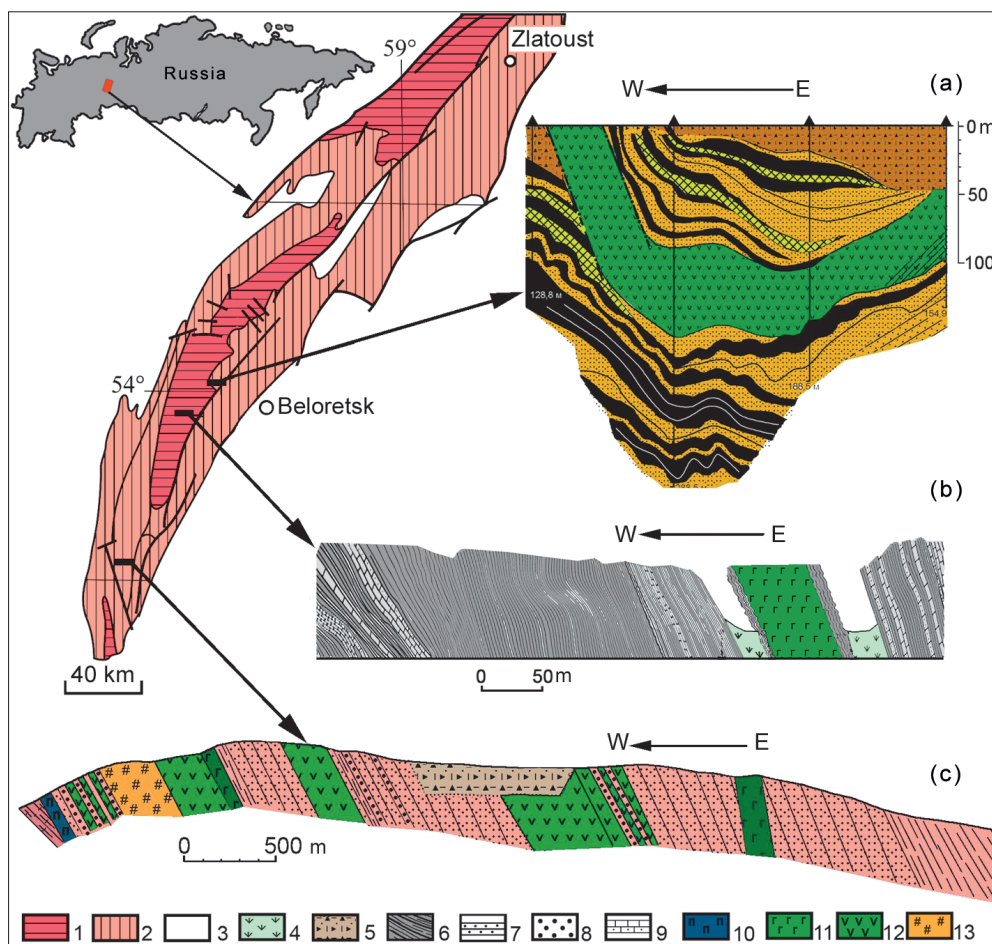


Fig. 1. Geological scheme of the western slope of the Southern Urals and the structure of the Uluelga-Kudashmanovo (a), Suran (b) and Shatak (c) sections. 1 – Lower Riphean deposits; 2 – Middle Riphean deposits; 3 – Upper Riphean-Paleozoic deposits; 4 – sodded areas; 5 – screes, weathering crust; 6 – clay shales; 7 – siltstones, shaly silts, sandstones; 8 – conglomerates; 9 – carbonate rocks with a variable amount of terrigenous component; 10 – picrites; 11 – gabbro, gabbro-dolerite; 12 – basalts; 13 – rhyolites.

in the form of thin veins or clots of irregular shape, unevenly scattered throughout the rock. Streakiness is expressed in the presence of dark and light-colored bands of variable thickness (from fractions of mm to 1-1.5 cm).

Carbonate rocks are represented by dark gray limestones, clayey limestones and fine crystalline dolomites.

The igneous rocks of the Suran section – coarse-grained metamorphosed gabbro of normal alkalinity, the primary minerals of which are plagioclase and clinopyroxene – have been preserved only in the form of relics. Clinopyroxene is amphibolized and chloritized, and plagioclase is albitized. The bodies of gabbroids have sub-consonant contacts with the host rocks, which suggests their occurrence in the form of multi-tier reservoir intrusions (sills) (Kovalev et al., 2017).

Exocontact rock is a fine-grained epidote-feldspar-sericite-quartz aggregate with nest-shaped chlorite secretions and irregular-shaped accumulations of tabular-prismatic amphibole crystals. Locally, along the veins, carbonatization develops – coarse-grained calcite or its heterogeneous aggregates and intergrowths.

The Shatak complex is a stratified volcanic-sedimentary association, which lies at the base of the Middle Riphean section of the Bashkir meganticlinorium (Fig. 1). Sedimentary rocks make up about 75% of its volume and are mainly represented by conglomerates and sandstones. Siltstones, shaly silts and shales are relatively rare. Conglomerates are developed at several stratigraphic levels. They are 70-80% composed of well-rounded fragments of quartzite sandstones and quartzites, less often of ferruginous quartzite-sandstones and microquartzites. Cement is a quartz sandy material and finely scaled sericite-chlorite mass. Sandstones are 80-90% composed of fragments of quartz with chlorite-sericite cement (Kovalev, Vysotsky, 2006).

The igneous rocks of the Shatak complex are represented by picrites, basalts and rhyolites. Picrites form a reservoir intrusion with a visible thickness of about 25-30 m, located on the border with the underlying sediments of the Yushinsky formation of the Lower Riphean. Metabasalt is green, greenish-gray, medium-fine-grained rock, which is characterized by microdoleritic, microphytic, apointersertic and porphyritic structure. They are composed of clinopyroxene, plagioclase, hornblende, titanomagnetite and magnetite. Secondary minerals are represented by amphibole of the actinolite-tremolite series, chlorite (pennin-clinochlor), epidote, sericite, titanite, leukoxen and hematite. Riolites are light gray rocks with a porphyry fluid and schlieren-taxite structure. The bulk is composed of a fine-grained quartz-feldspar aggregate. Acid plagioclase (andesine-oligoclase) is present in porphyry manifestations. Dark-colored minerals are represented by greenish-brown biotite and chlorite.

Apatite, allanite, monazite, titanite, epidote are found as accessory.

The Uluelga-Kudashmanovo zone is structurally confined to the Ishlinsky graben. It is located directly within the Yuryuzan-Zyuratkul regional fault, representing a narrow (100-250 m) strip of submeridional strike, traced at a distance of about 15 km (Fig. 1).

Metaterrigenous rocks of the zone are represented by sericite-quartz siltstones and carbonaceous shales of the Mashak Formation of the Middle Riphean (Parnachev et al., 1986). The rocks are characterized by a significant dislocation – crushing, corrugation, microbudding, rolling of quartz fragments with mosaic, cloud extinction, and the formation of plastic flow textures. Metasomatic recrystallization is expressed in the growth of quartz fragments and the enlargement of sericite with the formation of coarse-grained (up to 5 mm elongation) muscovite. Silica and carbonation are widely developed in rocks. The main difference between carbon-containing schists and siltstones is the lower dimension of quartz grains and the presence of carbonaceous matter, which forms layered-strip-like, cord-like and lumpy precipitates. In siltstones and shales, sulfide mineralization of the metamorphogenic type, represented by pyrite, pyrrhotite, sphalerite, chalcopyrite and galena, is widespread. The amount of sulfides on average is 0.1-0.5 wt. %, increasing in black shale horizons to 10-15 wt. %, where they form vein-disseminated mineralization (Kovalev et al., 2013).

The igneous rocks of this zone are intrusive bodies of gabbro-dolerite and effusives of the main composition. Albitite veins with a thickness of 15-20 cm, consisting of xenomorphic albite grains, coarse-grained (0.5-0.8 mm) muscovite, and a small amount of quartz and chlorite, were established in the upper part of the section. Intrusive rocks are largely metamorphosed. In the schist zones, they are transformed into carbonate-epidote (clinitoisite) -albit-quartz-chlorite schists and epidote-albite-quartz-amphibole rocks of massive texture. The metabasalts are composed of misoriented leaves of segregated plagioclase, clinopyroxene substituted by epidote and chlorite, and also products of volcanic glass devitrification. Together with the thin intercalations of lithocrystalline plastic tuff sandstones, they are schistose and are represented by epidote-quartz-chlorite formations.

Each of the structural-material complexes described is an independent unit, the mineralogical and geochemical analysis of which allows us to characterize the behavior of rare-earth elements in the process of its formation and transformation. As reference values for terrigenous rocks of the Suran section, REE contents in unchanged/“background”¹ rocks of the Suranian Formation of the lower Riphean of the Bashkir meganticlinorium are considered, for the sediments of the

Uluelga-Kudashmanovo zone, the content of lanthanides in clastic rocks of the Zigazino-Komarovskian Formation middle Riphean of the same structure are considered (Maslov et al., 2008).

The REE contents normalized to the upper continental crust (Taylor, McLennan, 1985) in the exocontact rocks of the Suran section and unchanged/"background"¹ deposits of the Suranian formation, with the general trend similarity, differ quantitatively, which is clearly recorded in graphs (Fig. 2a) and in their average amounts – 165.9 ppm for the former and 118.4 ppm for the latter. The same trend is clearly visible in the

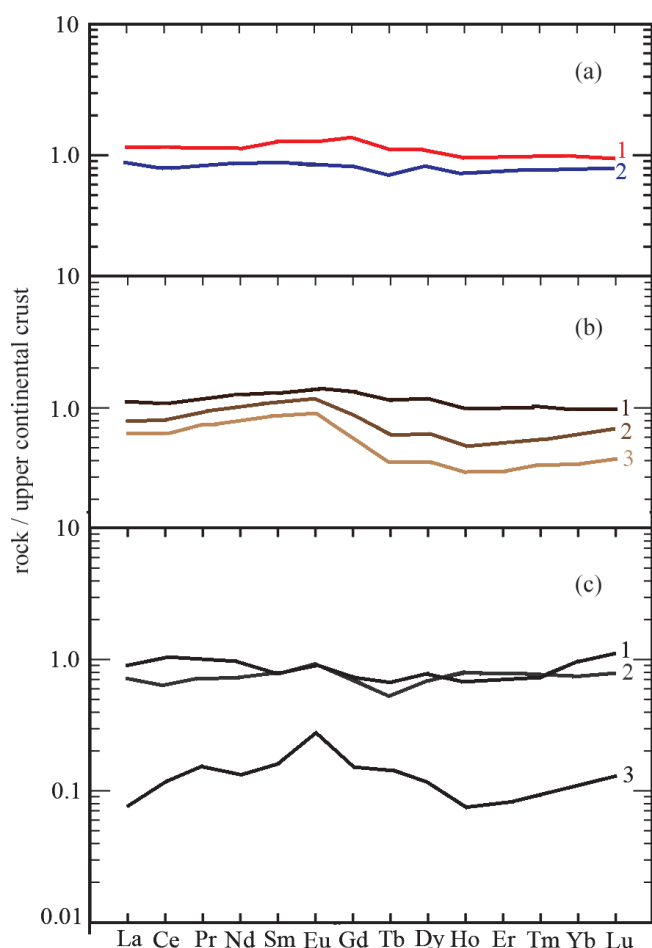


Fig. 2. Average REE contents normalized to the upper continental crust (Taylor, McLennan, 1985) in the rocks of the Suran section (a), the Shatak complex (b) and the Uluelga-Kudashmanovo zone (c). a: 1 – exocontact rocks ($n = 16$); 2 – unchanged deposits of the Suranian formation ($n = 11$); b: 1 – shales ($n = 21$); 2 – siltstones ($n = 5$); 3 – sandstones ($n = 8$); in: 1 – sulfidized carbonaceous shales ($n = 3$); 2 – unchanged deposits of the Zigazino-Komarovskian formation ($n = 11$); 3 – carbon-containing shales ($n = 8$). n is the number of analyzes.

¹Unchanged/"background" rocks here refer to as relatively slightly altered post-sedimentation (mainly isochemical) processes of sandstones, siltstones and clay shales of the lower and middle Riphean of the Bashkir meganticlinorium, which do not bear obvious signs of material remobilization, the impact of metamorphic-metasomatic processes or the introduction of ore components (Maslov, Kovalev, 2014).

Y – Ce diagram (Fig. 3a), where the amounts of Y and Ce in the exocontact rocks ($Ce_{av.} = 72.02$ ppm; $Y_{av.} = 22.26$ ppm) significantly exceed the contents of these elements in unaltered sediments of the Suran suite ($Ce_{av.} = 50.45$ ppm; $Y_{av.} = 9.8$ ppm).

A different picture in the distribution of REE is characteristic of terrigenous rocks of the Shatak complex. From the analysis of normalized contents (Fig. 2b) it follows that the amounts of REE directly depend on the lithological composition of the rocks (sandstones – $\sum REE_{av.} = 95.62$ ppm; siltstones – $\sum REE_{av.} = 123.22$ ppm; shales – $\sum REE_{av.} = 162.76$ ppm), which is most likely the result of the sorption abilities of the substance. Moreover, as can be seen from the Y – Ce diagram (Fig. 3b), the scatter in the contents of these elements in the shales is significant ($Ce = 16.2-157.0$ ppm; $Y = 3.81-61.4$ ppm), which may serve as an indirect sign REE redistribution in the process of metamorphic transformation of complex rocks.

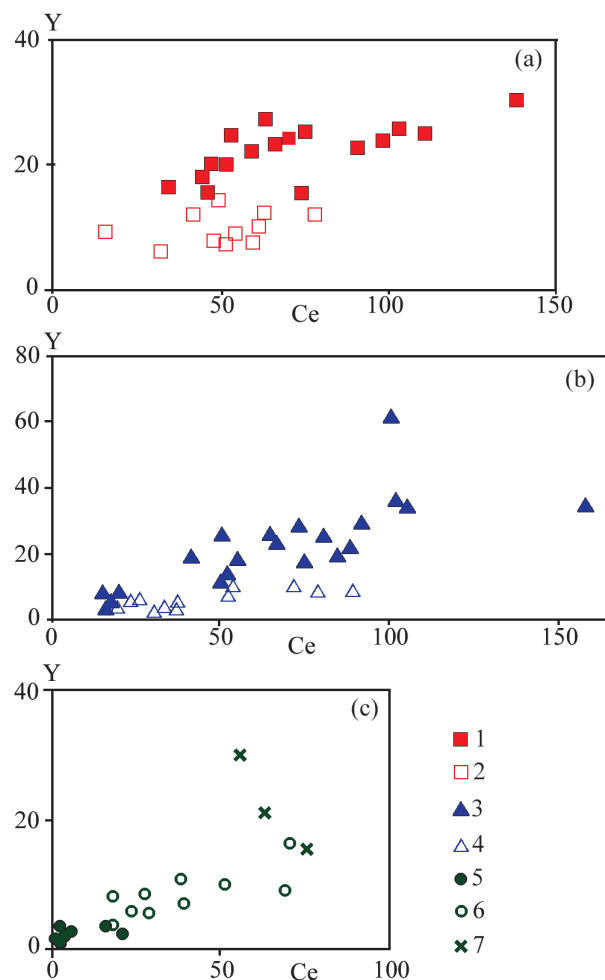


Fig. 3. Y – Ce diagrams for rocks of the Suran section (a), the Shatak complex (b) and the Uluelga-Kudashmanovo zone (c). 1 – exocontact rocks; 2 – unchanged / "background" deposits of the Suranian formation; 3 – shales; 4 – siltstones and sandstones not divided; 5 – carbon-containing shales; 6 – unchanged / "background" deposits of the Zigazino-Komarovskian formation; 7 – sulfidized carbonaceous shales.

The variations in REE contents caused by hydrothermal metamorphism processes are especially evident when analyzing the rocks of the Uluelga-Kudashmanovo zone. For example, sharply reduced REE amounts were found in carbon-containing shales, not only in comparison with uniform “background” rocks of the Zigazino-Komarovskian Formation, but also with average contents of these elements in the earth’s crust (Fig. 2c), and the trend itself has a complex configuration. At the same time, in sulfidized shales with a sulfide content of at least 50% of the sample volume, the amount of REE increases by almost 10 times (Σ REE in the carbon-containing shales – 16.67 ppm; Σ REE in the sulfidized shales – 137.43 ppm), which indicates the redistribution of rare earth elements in the process of metamorphogenic sulfide formation.

Research methods

The contents of rare-earth elements in 48 samples were obtained by inductively coupled plasma mass spectrometry (ICP-MS) at the Russian Geological Research Institute (VSEGEI) (St. Petersburg). The accuracy of REE measurements was (in ppm): La – 0.01; Ce – 0.01; Pr – 0.01; Nd – 0.01; Sm – 0.005; Eu – 0.005; Gd – 0.01; Tb – 0.005; Dy – 0.01; Ho – 0.005; Er – 0.01; Tm – 0.005; Yb – 0.01; Lu – 0.005.

The study of REE minerals was carried out on a REMM-202M scanning electron microscope with a Z-5 X-ray energy dispersive spectrometer (SiLi detector, resolution 140 eV), secondary (SE) and reflected

(COOMPO) detectors of electrons at the Institute of Mineralogy of the Ural Branch of the RAS (Miass). For quantitative analysis, pure metal standards and/or synthetic and natural mineral standards were used.

Rare earth mineralization

REE minerals are found in the rocks of all studied structural-material complexes. They are represented by monazite, xenotime, calcium cyanoanilite, allanite, yttrium-containing epidote, cerianite, REE-containing thorite and a significant amount of unidentified REE and Th-REE compounds of complex composition (Kovalev et al., 2017).

Monazite is the most abundant mineral. Almost complete absence of faceted crystals is a characteristic feature of all studied monazites (Fig. 4). The mineral is found in the form of xenomorphic grains forming clusters of irregular shape, sometimes in the form of elongated columnar discharge (Fig. 4a, b). It was found both in metaterrigenous and apomagmatic rocks in the Uluelga-Kudashmanovo zone. In terms of chemical composition, all monazites are cerium species ($Ce_{av.} \geq La_2O_3 + Pr_2O_3 + Nd_2O_3 + Sm_2O_{3av.}$). Separate crystals contain Sm_2O_3 , Gd_2O_3 , ThO_2 , UO_2 , FeO and SiO_2 , and the content of silicon oxide in unidentified phases rises to 49.89-54.67 wt. %. In the monazite of the Shatak complex, the REE contents are subject to significant fluctuations. In particular, monazite with 20.42 wt. % Nd_2O_3 and 12.32 wt. % Sm_2O_3 . In addition, all the studied minerals belong to Th-containing varieties of monazite

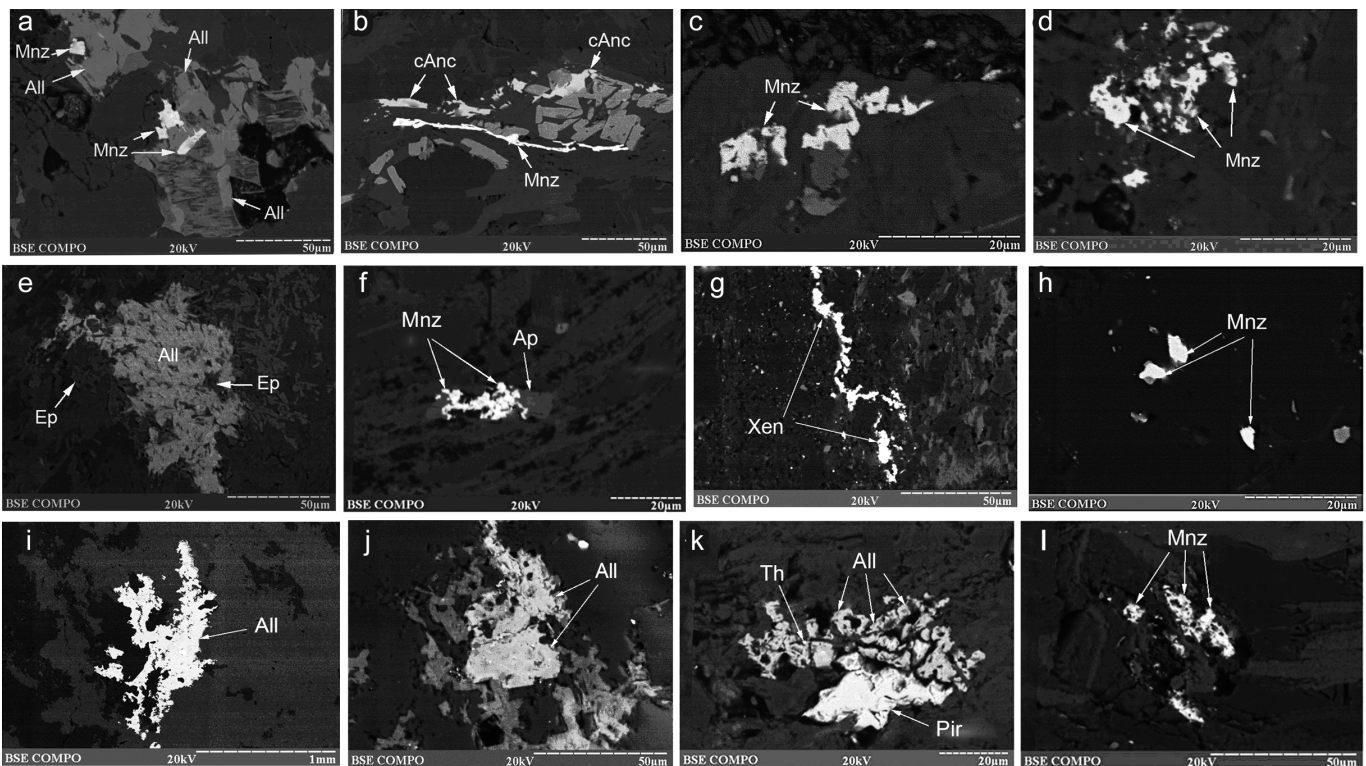


Fig. 4. Microphotographs of rare-earth minerals from the rocks of the Suran section (a – f), the Shatak complex (g – j) and the Uluelga-Kudashmanovo zone (k – l). Mnz – monazite; cAnc – calcioankilite; Xen – xenotime; All – allanite; Ep – epidote; Th – thorite; Pir – pyrrhotite; Ap – apatite.

with Ce_2O_3 contents varying over a wide range (from 13.35 to 35.71 wt.%).

Xenotime in the rocks of the Suran section and the Uluelga-Kudashmanovo zone is found in the form of independent xenomorphic secretions or in paragenetic intergrowths with monazite and associations with rutile and muscovite. It contains SiO_2 , FeO , ThO_2 , and UO_2 . In the rocks of the Shatak complex, xenotime was found in the form of chain-streaky segregations composed of intergrowths of faceted crystals or xenomorphic precipitates, as well as rims on zircon crystals. Xenotime “microbranches” are located in conglomerate cement and have a complex branching and discontinuous shape (Fig. 4g). In the chemical composition of xenotime, in addition to the characteristic impurity Gd, Dy, Tb, Ho, Yb, Nd and Sm are established. In addition, U-Th-containing differences are also found.

Calcioankilite, first discovered in 2016 in terrigenous rocks of Russia (Kovalev, Kovalev, 2017), was established in exocontact rocks of the intrusive body of gabbro of the Suran section in association with monazite, muscovite, chlorite, albite, and titanite (Fig. 4b). It is represented by intergrowths of elongated prisms or xenomorphic secretions. By chemical composition, it belongs to the cerium variety of calcioankylite ($0.98-0.99$ f.k. Ca, $(La + Pr)/(Ce + Nd) = 0.36$).

Allanite occurs in the form of intergrowths of tabular crystals (Fig. 4a), and also forms granular aggregates up to $200 \mu m$ in size (Fig. 4 e,i,j) often in association with epidote, thorite, and iron sulfides (Fig. 4k). By chemical composition, all the discovered minerals belong to the cerium ($Ce_2O_3 \geq La_2O_3 + Pr_2O_3 + Nd_2O_3$). Ferruginous allanites ($FeO - 10.49-10.64$ wt.%) with a low content of MgO ($0-0.21$ wt.%) and MnO ($0-0.08$ wt.%) are found in the Uluelga-Kudashmanovo zone; in the Shatak complex zonal ones are found (in wt.%: La – edge 3.03, center – 1.33; Ce – 6.67 and 4.62; Nd – 2.55 and 2.03; $Al_2O_3 - 20.18$ and 22.98 ; $SiO_2 - 37.34$ and 39.37 ; $CaO - 15.07$ and 17.45 , respectively). In addition, relatively large (up to 1 mm in elongation) xenomorphic allanite precipitates of nonstoichiometric composition ($(Ca_{0.71} Ce_{0.22} La_{0.07} Pr_{0.05} Nd_{0.11})_{1.16} (Al_{0.31} Fe_{0.50} Mg_{0.03})_{0.84} (Si_{1.98} Al_{1.02})_3 O_8$; $(Ca_{0.67} Ce_{0.26} La_{0.07} Pr_{0.04} Nd_{0.11})_{1.15} (Al_{0.33} Fe_{0.50} Mg_{0.02})_{0.85} (Si_{1.98} Al_{1.02})_3 O_8$; $(Ca_{1.76} Ce_{0.17} La_{0.07} Nd_{0.07} Pr_{0.04})_{2.11} (Al_{2.07} Fe_{0.78} Mg_{0.04})_{2.89} (Si_{3.54} Al_{0.46})_4 O_{14}$), in which the total amount of REE (at $Ce > Nd > La > Pr$) varies from 20.48 wt. % to 33.37 wt. % were found in the upper part of the Shatak complex in the horizon of interbedded sandstones and shales. Compounds close in ($(Ca_{1.31} La_{0.18} Ce_{0.42} Nd_{0.08} Pr_{0.06})_{2.05} (Al_{2.03} Fe_{0.81} Mg_{0.10} Mn_{0.01})_{2.95} (Si_{3.70} Al_{0.30})_4 O_{14}$ and $(Ca_{0.55} Ce_{0.21} La_{0.10} Pr_{0.03} Nd_{0.06})_{0.95} (Al_{0.63} Fe_{0.33} Mg_{0.03} Mn_{0.01} Ti_{0.05})_{1.05} (Si_{2.65} Al_{0.35})_3 O_8$) with a total REE content – 20.01 wt. % and 18.51 wt. %, respectively, were found in conglomerates from the base of the complex.

There is a Y-containing epidote in association with allanite (Fig. 4f) in the rocks of the Suran section, in the form of prismatic crystals, their intergrowths, and xenomorphic precipitates of $300-400 \mu m$ in size. The presence of yttrium in its chemical composition suggests that the mineral is part of the isomorphous series epidote – allanite.

A comparative analysis of the chemical composition of minerals described above makes it possible to characterize the features of mineral formation in various structural-material complexes. In Fig. 5, the $CaO - ThO_2$ diagram for monazites is presented, from which it can be seen that all minerals are quite clearly grouped into three fields. The first one characterizes monazites from rocks of the Uluelga-Kudashmanovo zone, which are characterized by the presence of ruthenium-free varieties and the maximum amounts of calcium in the composition of minerals. Monazites from exocontact rocks of the Suran section (field II) differ in significant variations in CaO contents with relatively small changes

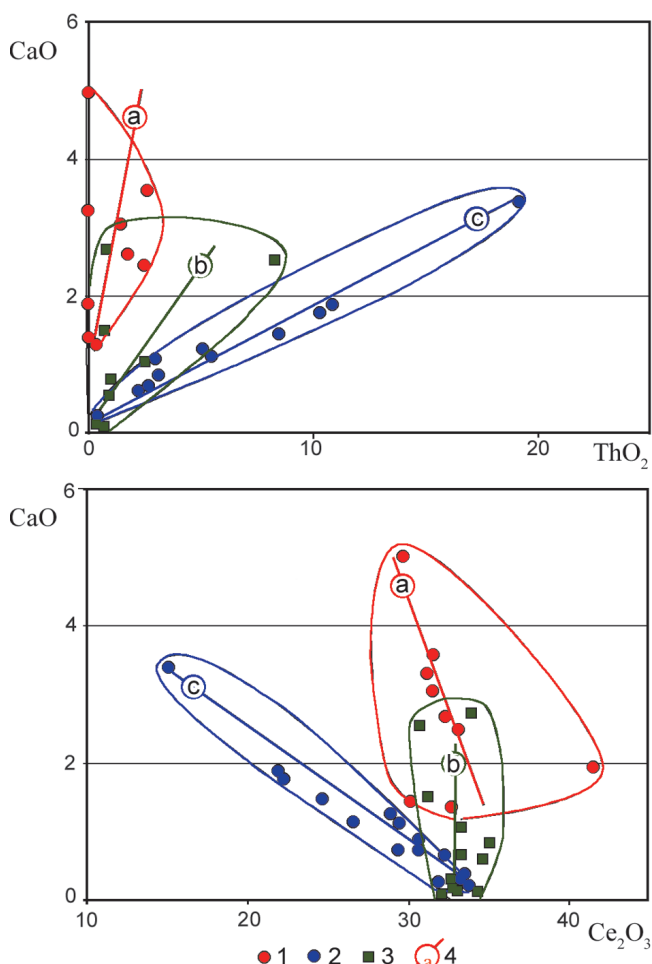


Fig. 5. Diagrams of $CaO - ThO_2$ and $CaO - Ce_2O_3$ for monazites from the Upper Precambrian structural-material complexes of the Bashkir megaanticlinorium. 1 – Suran section; 2 – Shatak complex; 3 – Uluelga-Kudashmanovo zone; 4 – trends in the content of components (a – Suran section; b – Uluelga-Kudashmanovo zone; c – Shatak complex).

in the amounts of thorium. The minerals of the third group (Shatak complex) have a well-defined direct relationship between the contents of CaO and ThO₂ with an approximation coefficient of 0.96 and the presence of varieties with a maximum amount of ThO₂. Between the minerals of the first and second groups, common features of changes in the contents of oxides are visible. They are characterized by the presence of two “local trends” (the first is a sharp increase in the amount of calcium and the second is a direct relationship between the contents of CaO and ThO₂). This is most likely due to a certain similarity of contact and hydrothermal metamorphism and, possibly, to the presence of two generations of monazites, one of which was formed from REE of the fluid phase, and the second during metamorphic recrystallization of a phosphate-containing sedimentary substrate.

A similar picture of the distribution of monazites by genetic groups is also clearly visible on the CaO-Ce₂O₃ diagram (Fig. 5), from the analysis of which it follows that the relationships between the indicated oxides in each group are characterized by aspecificity: for monazites from the Suran section, there is a significant spread in cerium content and a weakly manifested inverse relationship between CaO and Ce₂O₃; minerals from the rocks of the Uluelga-Kudashmanovo zone differ in significant variations in CaO amounts with small changes in Ce₂O₃; monazites from rocks of the Shatak complex are characterized by a clearly manifested inverse relationship between calcium and cerium with

an approximation coefficient of 0.94.

In general, all the oxide variations in Fig. 5 are due to isomorphous substitutions of Ce-Ca-Th in the structure of monazite. The fundamental conclusion follows from the above description of minerals and analysis of diagrams, that the redistribution of these elements was realized in an independent process characteristic of each structural-material complex.

In addition to monazite, allanite is a mineral characteristic of the rocks of all the described complexes. For a comparative analysis of the chemical composition of allanites, we used data on minerals from the Paleoproterozoic carbon schists of the Tim-Yastrebovsky paleorift (Voronezh crystalline array) (Savko et al., 2010) and to allanites from the metamorphic schists of the Puyva Formation of the Subpolar Urals (Kovalchuk, 2015). The results are plotted on the MgO-Fe*, MnO-Fe*, Al₂O₃-CaO, Ce₂O₃-CaO, Nd₂O₃-CaO, La₂O₃-CaO diagrams (Fig. 6).

From the consideration of these diagrams it follows that, firstly, allanites from structural-material complexes of the Urals and carbonaceous schists of the Tim-Yastrebovsky paleorift sharply differ in the amount of MgO, Fe* and MnO, forming local disjoint fields, which indicates the presence of a “regional component” in the chemical compositions of minerals, most likely due to geotectonic conditions of mineralization formation. Secondly, between the contents of Al₂O₃ and CaO in allanites from all structural-material complexes, a direct relationship is established; in this case, the maximum

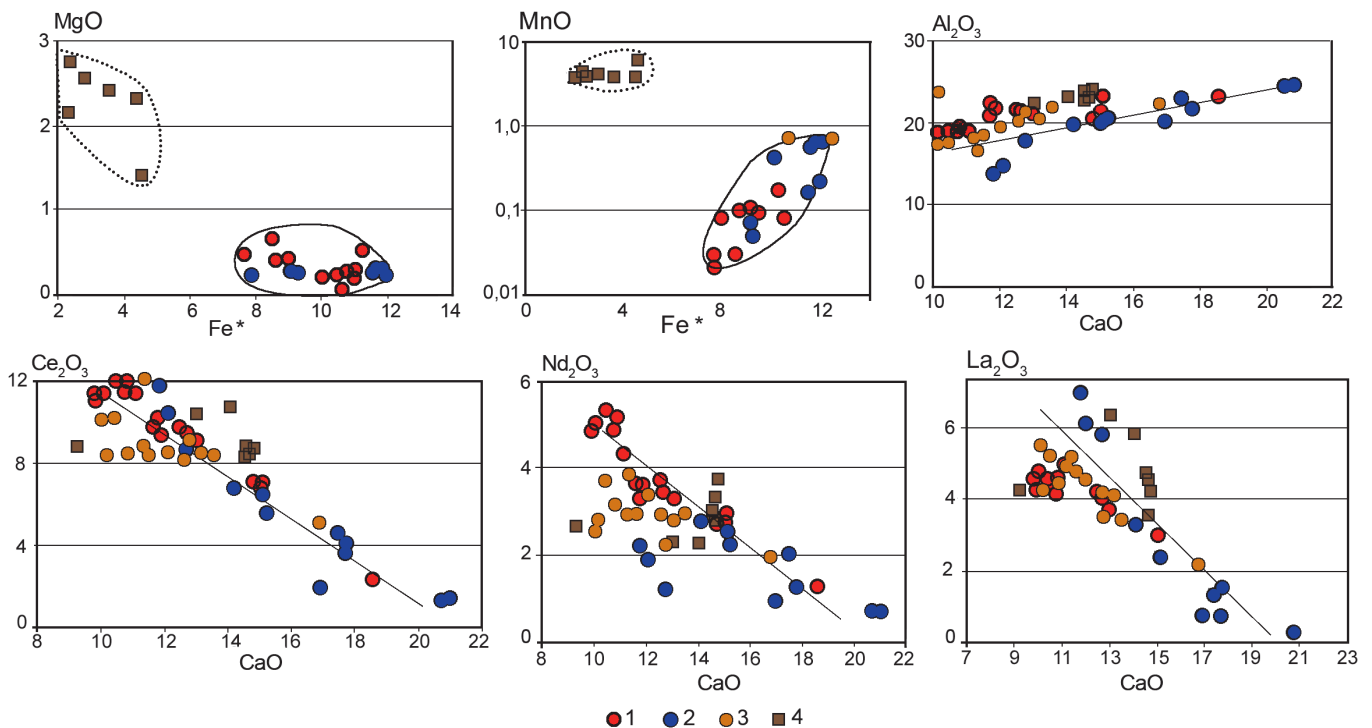


Fig. 6. Diagrams of element contents (wt.%) in the allanites of the Suran section and the Uluelga-Kudashmanovo zone (1), the Shatak complex (2), the metamorphic schists of the Puyva Formation of the Subpolar Urals (3, according to Kovalchuk, 2015) and the Tim-Yastrebov structure of the Voronezh crystalline array (4, according to Savko et al., 2010). Fe* – total iron in the form of FeO.

dispersion of the quantities of both components is characteristic of minerals from the complexes described in this work. Thirdly, all allanites of the Ural region are characterized by an inverse relationship between the calcium content on the one hand and REE on the other, indicating a wide isomorphism according to the $\text{Ca} \leftrightarrow \text{Ce, La, Nd}$ principle, which, as shown above, is also characteristic of monazites; at the same time, this dependence is absent in allanites from carbon schists of the Tim-Yastrebovsky paleorift (a change in the amount of calcium occurs at almost constant contents of Ce, Nd, and La).

Thermobaric metamorphism parameters

The chemical compositions of chlorites were used to evaluate the thermal parameters of metamorphism of the characterized complexes. The temperatures of their formation were calculated by the formula $T = -61,9229 + 321,9772 \times \text{Al}^{\text{IV}}$ (Kranidiotis, MacLean, 1987).

In accordance with the classification (Drits, Kossovskaya, 1991), chlorites from exocontact rocks of the Suran section fall into the fields of Fe-Mg chlorites of clastogenic formations and Fe-Mg and Mg-Fe chlorites of the main igneous rocks, and the temperature range of their formation is 212-344 °C (Fig. 7) with a relatively small fluctuation in the iron content (0.4-0.5). The confluence of the figurative points of the studied chlorites to the indicated fields and small variations in the iron content indicate their formation from the fluid phase under the influence of magmatic melt on the rocks of the frame. The formation temperatures of chlorites from apomagmatic rocks of the Uluelga-Kudashmanovo zone are in the range of 171-377 °C, and from metaterigenous ones – 148-410 °C. At the same time, it is clearly seen that chlorites from para- and orthoporods significantly differ in iron content (Fig. 7). This is due to the fact that Mg-chlorites of the ortho-rocks are the result of the replacement of clinopyroxenes, and Fe-chlorites were formed during the hydrothermal process, covering both igneous and terrigenous rocks, which is confirmed by the confinement of all points of the composition of the studied minerals to the field of Fe-Mg-chlorites of clastogenic formations on the geocrystallochemical classification diagram of V.A. Drits and A.G. Kossovskaya (1991).

The subdivision of minerals into two groups – “high-magnesian” and “low-magnesian”, is also characteristic of chlorites of the Shatak complex (Fig. 7). The temperature range for the formation of the first ones is ~ 308-350 °C; of the latter ~ 318-402 °C. According to the classification of V.A. Drits and A.G. Kossovskaya (1991) chlorites of the Shatak complex correspond to Fe-Mg-chlorites of clastogenic formations and Fe-Mg- and Mg-Fe-chlorites of the main igneous rocks, which

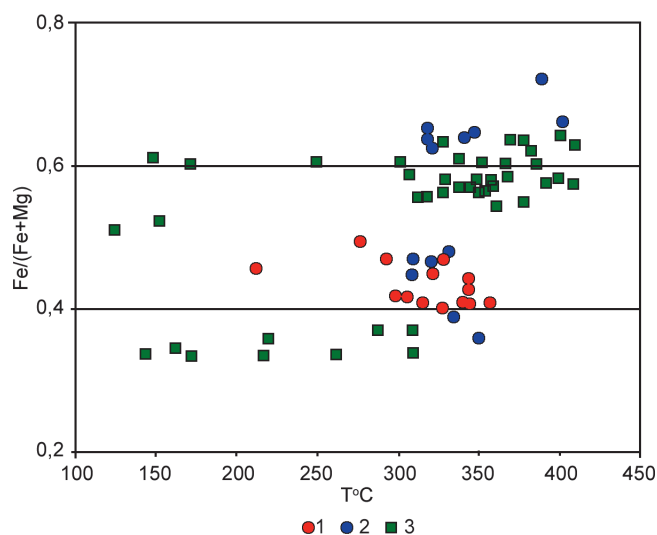


Fig. 7. $\text{Fe}/(\text{Fe}+\text{Mg})-T^{\circ}\text{C}$ diagram for chlorites from rocks of various Upper Precambrian structural-material complexes of the Bashkir meganticlinorium. 1 – Suran section; 2 – Shatak complex; 3 – Uluelga-Kudashmanovo zone.

indicates the formation of minerals in a single process of transformation of the complex rocks.

In addition to chlorites, in order to determine the thermobaric conditions for the metamorphism of the described complexes, we analyzed the compositions of light mica. The thermobaric parameters of their formation are shown in Fig. 8a, the analysis of which shows that the maximum temperature corresponded to ~ 450 °C, and the pressure was ~ 6-7 kbar. In this case, a rather well-pronounced tendency to a decrease in temperature with increasing pressure is observed. Thus, variations in the P-T parameters indicate the existence of two stages of metamorphism in the Suran section. The first stage (max T, min P) is an exocontact metamorphism; the second stage (min T, max P) is stress pressure with regional metamorphism.

In the rocks of the Uluelga-Kudashmanovo zone, muscovite is present both in the form of small-scaled varieties (sericite), which are part of the cement of shales and silt shales, and in the form of relatively large-sheeted crystals and their aggregates, which are found in terrigenous and apomagmatic rocks. Interpretation of the position of points in the $\text{Si} - \text{Na}/\text{Na} + \text{K}$ diagram (Fig. 8c) indicates that light mica in the apomagmatic rocks of the indicated zone formed in the intervals: pressure ~ 2.0-9.8 kbar; temperature – 390-450 °C. In this case, the minimum temperatures do not coincide with the minimum pressure, which indicates the predominance of stress load during metamorphism. For terrigenous rocks, the scatter of temperature and pressure values is close to those characteristic of apomagmatic formations ($T = \sim 390-490^{\circ}\text{C}$, $P = \sim 2.5-9.9$ kbar). As well as for apomagmatic rocks, the maximum and minimum temperatures and pressures established for terrigenous formations do not correlate between themselves.

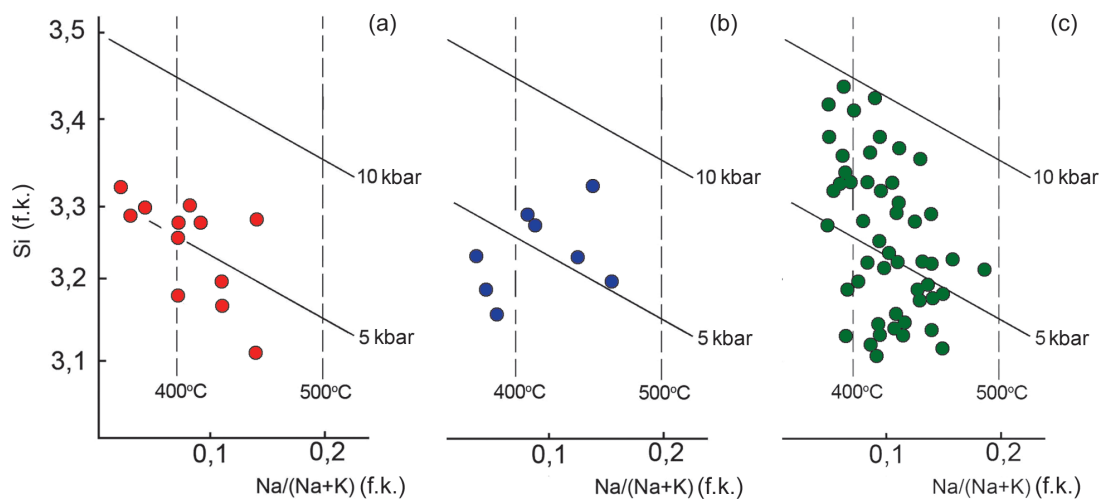


Fig. 8. Si (f.k.)–Na/(Na+K) (f.k.) diagrams for light mica from terrigenous complexes of the Bashkir meganticlinorium (a – Suran section; b – Shatak complex; c – Utuelga-Kudashmanovo zone). Pressure isogradic line (Chopin, 1981; Massonne, Schreyer, 1989); temperature isogradic line (Dobretsov et al., 1974; Krogh, Raheim, 1978).

In terrigenous rocks of the Shatak complex, newly formed muscovite is found in coarse clastic sediments of the Kuzelginsky sub-formation in association with a chloritoid and epidote. An assessment of the thermobaric parameters of its formation (Fig. 8b) showed that the maximum temperature and pressure corresponded to: $T = \sim 470\text{ }^{\circ}\text{C}$, $P = \sim 8\text{ kbar}$, and the minimum were: $T = \sim 380\text{ }^{\circ}\text{C}$, $P = \sim 3\text{ kbar}$.

Discussion of results and conclusions

The question of the matter sources during the formation of rare-earth mineralization, as noted above, remains the subject of heated debate. The general sequence of the change of REE index minerals with progressive metamorphism of metapelites is described as follows: detrital monazite \rightarrow metamorphic allanite \rightarrow metamorphic monazite \rightarrow apatite (Smith, Barero, 1990; Wing et al., 2003; Finger, Krenn, 2007; Janots et al., 2009; Savko et al., 2010, etc.). At the same time, estimates of the thermobaric parameters of these substitutions, as well as the mechanisms of mineral reactions in the above studies vary significantly.

On the example of materials from the Suran section, it was shown that rare-earth mineralization is formed during exocontact metamorphism, where igneous rocks are the source of REE. Moreover, mineral associations include both monazite and allanite, although cases where monazite and allanite are found in the same paragenesis are quite rare (Savko et al., 2010, and others). Based on the established fact of the formation of rare-earth mineralization as a result of exocontact metamorphism, we can consider the genetic conditions for the formation of REE mineralization in other structural-material complexes described in this work.

Due to the fact that igneous rocks are one of the sources of REE, and metamorphism is the main process of rare-earth mineralization formation, it is logical

to link these processes with the geodynamic regimes of the territory's development at certain time stages. The igneous rocks of the Surans section belong to the Middle Riphean (Larionov et al., 2006), the first third of which was characterized by the manifestation of plume processes (Puchkov, Kovalev, 2013, Puchkov, 2013, Ernst, 2014), accompanied by active riftogenesis and wide spread of magmatism within the Bashkir megaanticlinorium in all its manifestations (dikes and sills, dike swarms and belts, volcanic-plutonic associations and intrusive stratified arrays).

The introduction of magmatic melts in the upper horizons of the crust with fluid development of sedimentary substrate in such geodynamic settings led to the formation of exocontact and fluid-magmatic types of rare-earth mineralization, differing in the scale of local manifestation of magmatism (in the case of single bodies, an exocontact type is formed (Suran section); in the case of plutonic association the fluid-magmatic type is formed (Shatak complex). The fact that rare-earth mineralization in the rocks of the named complexes was formed in a single process is evidenced by a well-defined inverse relationship between the CaO content and the sum of REE in the monazites and allanites of each complex with approximation coefficients of 0.975 and 0.967 respectively (Fig. 9a, b).

The thermal conditions for the reaction of allanite \leftrightarrow monazite have not been precisely established to date. Most authors believe that allanite replaces monazite in the range of 400–450 $^{\circ}\text{C}$ and remains stable up to the amphibolite facies. Monazite reappears in the temperature range 450–530 $^{\circ}\text{C}$ (Smith, Barero, 1990; Wing et al., 2003; Janots et al., 2006 and others). In addition, it was found that the decomposition temperature of allanite with the formation of monazite can vary depending on the contents of CaO and Al_2O_3 in the rocks (Wing et al., 2003). It is important for our

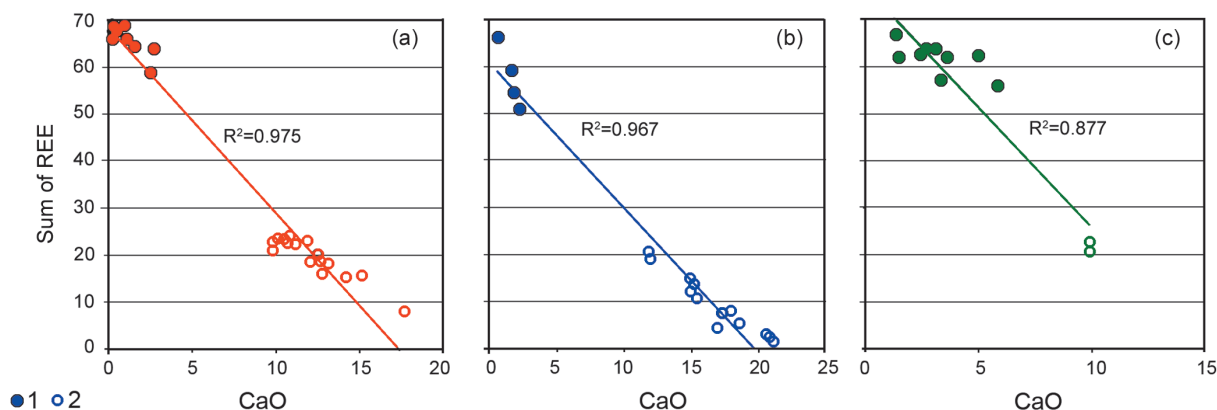


Fig. 9. The diagrams sum of REE – CaO for monazites (1) and allanites (2) from rocks of the Suran section (a), the Shatak complex (b) and the Uluelga-Kudashmanovo zone (c).

studies that the calculated temperature regime of mineral formation (344-450 °C – Suran section, 402-470 °C – Shatak complex) is close to the coexistence temperatures of both phases.

The main mechanism for the formation of rare-earth minerals in the rocks of the Uluelga-Kudashmanovo zone was a hydrothermal type metamorphism, which manifested itself in this zone ~ 600 Ma ago (Kovalev et al., 2013). According to modern geodynamic constructions, in the Vendian, the territory of the region developed in a compression mode (Puchkov, 2000), and the physicochemical conditions of mineral formation were determined by the functioning of local multidimensional fluid-hydrothermal systems, which were formed when rifting magmatism was replaced by processes of water crustal palingenesis and regional metamorphism. A specific feature of the mineral-forming processes of this stage was the redistribution of REE during metamorphic sulfide formation (Fig. 2), as well as significant variations in the CaO content in the monazite composition (Fig. 5) with the previously established isomorphic substitution of thorium for calcium in the mineral structure and the appearance of thorium-free high-calcium monazite and native thorium minerals (Kovalev et al., 2017). Moreover, the maximum temperature of metamorphism of 390-490 °C, as well as in the structural-material complexes described above, suggests the coexistence of both monazite and allanite. In this situation, the possibility of the monazite formation due to the decomposition of allanite cannot be ruled out, although this has not been found in a direct study of mineralization.

Thus, the behavior of REEs in the Late Precambrian structural-material complexes of various compositions and genetic nature of the Bashkir megaanticlinorium is determined by the effect of magmatic melt of the main composition on the sedimentary substrate of the frame, in which lanthanides enrich exocontact rocks. It leads to the appearance of newly formed REE-mineral associations. The formation of rare-earth mineralization

are largely controlled by physicochemical parameters and thermobaric conditions of concomitant and subsequent metamorphism.

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