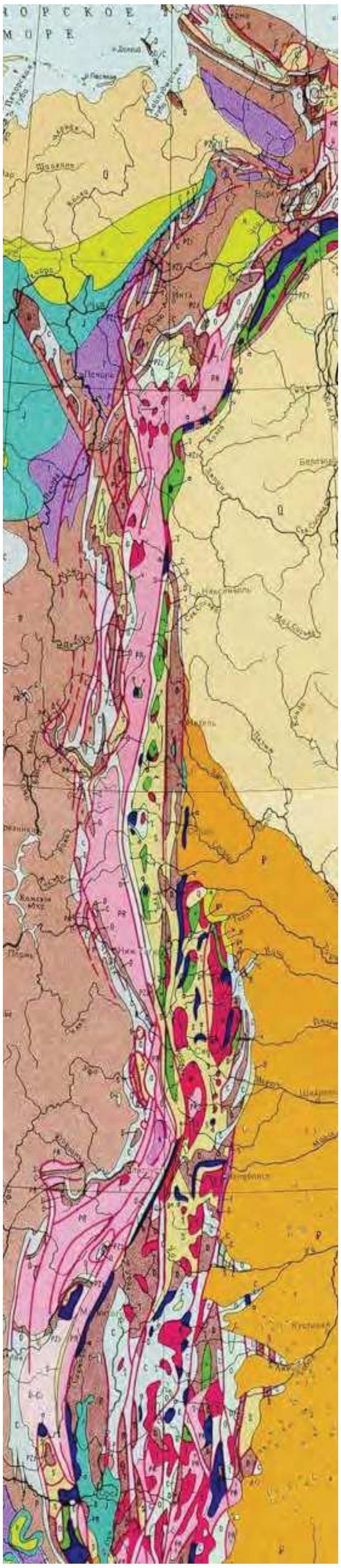

Vernadsky Institute of Geochemistry and Analytical Chemistry
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Magmatism of the Earth and related strategic metal deposits

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The mineral deposits of strategic metals are vulnerable to political and economic changes, and their availability is essential for high-technology, green energy, and other applications. The most of them are related to the deep-seated alkaline magmas.

This book offers a collection of papers presented at the 34th International Conference on Magmatism of the Earth and Related Strategic Metal Deposits held from August 4th to 9th 2017 in Miass, Russia. The conference articles are focused on understanding of the geological processes that produce high concentrations of critical metals in geological systems such as the transport of metals in the mantle and crust and enrichment processes, hydrothermal and metasomatic processes leading to the formation of such significant deposits. Papers in this book give a representative overview including mineralogy, geochemistry and origin of strategic metals deposits.

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The cover pictures are geological map of the Urals and «Ridges of Ural» of E.V. Nikolsky

Evgeny Vasilyevich Nikolsky (1917-1978) was a famous Russian artist who lived in Miass. The main theme of his artworks was Ural landscape. He had been making his paintings in different styles and techniques, but most of all he liked to paint with watercolours. In 1969 with this type of paint he had made an artwork "Ridges of Ural" which was painted in the mountains of Southern Ural. Nowadays, this artwork is being kept in local museum of Miass. This year we celebrate the centenary of the birth of this artist.

In terms of processes, there is no direct discriminator between the traditional concept of underplated material and lower crustal magmatic intrusions in the form of batholiths and sill-like features, and in the current review we consider both these phenomena as underplating. In this broad sense, underplating is observed in a variety of tectonic settings, including island arcs, wide extensional continental areas, rift zones, continental margins and palaeo-suture zones in Precambrian crust. We review the structural styles of magma underplating as observed by seismic imaging and discuss these first order observations in relation to the Moho.

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RARE METAL-RARE EARTH MINERALIZATION OF THE NORTHERN TIMAN (MALYJ KAMESHEK MASSIF)

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The alkaline magmatism revealed quite widely in Timan and Kanin Peninsula in the Late Precambrian. Monzonites are exposed in the northwestern part of the Kanin Peninsula (120x40m). In Northern Timan alkaline and nepheline syenites form massifs of the Bolshoy Rumyanichny, Krayny and Malyj Kameshek Capes. Here in the mouth of the Rumyanichnaya River a small exposure (150x120 m) of olivine-kersutite gabbro can be observed. In Middle Timan in the southeastern part of the Chetlassky Kamen a dyke series of alkaline picrites is observed; and in the South Sub-Timan, the syenites have been exposed by boreholes 1- and 4-Izkosgora at depth of 830 m.

The rare metal – rare earth mineralization is associated with the rocks of the Malyj Kameshek syenite massif located in the central part of the Rumyanichnaya fault zone. The massif has an isometric shape with the area of about 2 km^2. Within the massif the syenites form two dike-like bodies about 100 m thick each, oriented northwestward and cutting the metamorphic shales of Upper Riphean Barmin series and metabasites. The contact with the shales, observed in the northeastern part of the massif, is clear, intrusive. In the exocontact zone with the syenites the shales are slightly hornfelsed. In the endocontact zone the syenites are represented by fine-grained, non-nepheline varieties. The primary intrusive contact between the basic and alkaline rocks is obscured by the processes of syenitization of metabasites and later processes of dislocation metamorphism and has the form of a gradual transition.

The intrusive syenites are represented by massive light gray or pink medium- and coarse-grained rocks containing nepheline in the most cases. The central part of the massif is composed of intensely syenithized metabasites transformed into apobasite syenites. These rocks have a more melanocratic appearance and are more fine-grained than the syenites. Depending on the degree of syenitization their color varies from dark gray to pink. The apobasitic syenites in the contact zone with the intrusive syenites are cut by thin (0.1-0.2 m) veins of syenite-aplites.

All magmatic formations of the Malyj Kameshek massif are cut by zones of mylonitization of the northwestern and sublatitudinal strikes. The sublatitudinal gneissic structure, observed in all varieties of syenites, is expressed by the orientation of finely flaked aggregates of biotite coinciding with the direction of the zones of intensive cleavage and mylonitization. The apobasitic syenites and syenitized metabasites of the central part of the massif, located within the sublatitudinal zone of intense dislocation metamorphism, suffered processes of silicification, carbonatization, muscovitization.

In the same part of the massif the main part of thin isometric albitite bodies is concentrated, which occur among the gneissic apobasite syenites and are confined to the intersections of cleavage and mylonitization zones. Separate bodies of albitites are observed in the north-eastern and north-western parts of the massif. The albitites are represented by massive fine-grained, mainly albite, red-pink and yellowish-white metasomatites on blastomylonites of apobasite syenites. The rocks have been drilled by a series of samples 172(1-4) and 174(1-4) in the central part of the massif and in the northwest part by samples 149(1-4).

Albitites are represented by massive, fine-grained rocks of red and beige color; the rock's color is conditioned by spreading fine-dispersed hematite and iron hydroxides on it. The basic matrix is represented by the association quartz + alkaline feldspar + albite, the microstructure is mainly lamellar. The microscopy reveals cataclase and mylonitization structures (Fig. 1). The rock composition: albite, alkaline feldspar (orthoclase), quartz; micas (biotite, muscovite) is rarely observed; the main accessory minerals are zircon, apatite, barite; secondary – ferrous chlorite. Rare metal - rare earth ore minerals are located in the intergranular space. Minerals were studied by microprobe analysis in epoxy-based thin sections (IEM RAS, Chernogolovka).

Our investigations found that the main bulk of the rocks is composed by albite with subordinate quartz and Kfs. All other mineral associations are located in the intercataclase space. We determined the presence of barium phases everywhere (Ba-containing Kfs and high-Ba rims in it, as well as a large amount of barite). Dark-color minerals are represented by micas: biotite and muscovite (possibly part of them with lithium). We found a wide development of various carbonate phases (calcite, dolomite, Fe-dolomite, manganese varieties). Fluorite is developed. Rare earth minerals are represented by phosphates (monazite, xenotime) and fluorine-rich carbonates (bastnesite, parisite, synchyzite and their high-potassium analogues). Rare metal minerals are represented by the smallest grains of pyrochlore and fergusonite, significantly Nb- and W-enriched rutiles. Titanium minerals are also represented by ilmenite and high-Mn ilmenite.

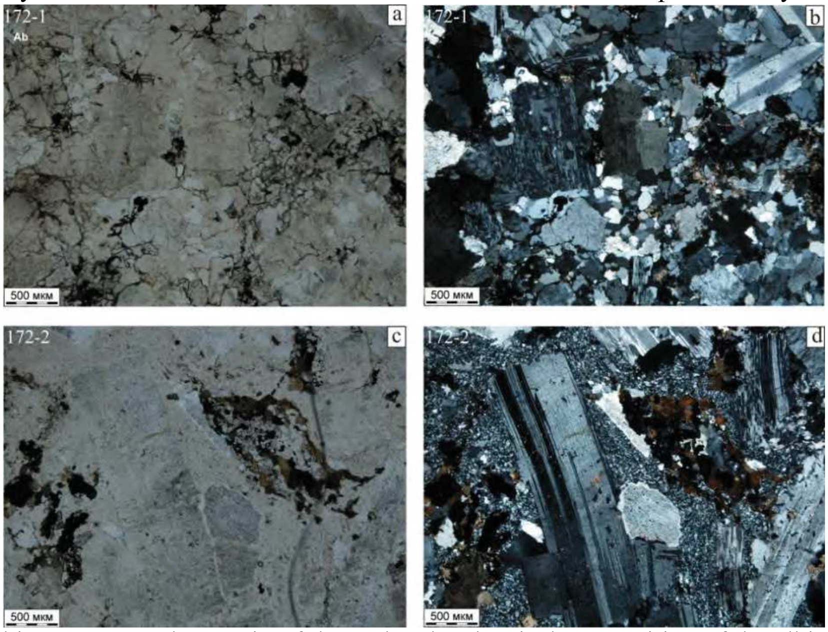

Fig. 1. Microstructures of ore-bearing albitites. Quartz-feldspar-albite aggregate with newly formed carbonates (a-b), large albite crystals in a mylonitized quartz-feldspar-albite matrix (c-d). a, c – without the analyzer.

Albite composes the matrix of the rocks, the chemical composition of the albite is without impurities. Potassium feldspar, in contrary, has an unusual chemical composition, barium enrichment is observed. Barium-potassium feldspar (barium orthoclase) forms spotted accumulations in the rocks associating them with carbonates and fluorite (Fig. 2, Fig. 3 a-c), the content of BaO in the main grains is 0-7 wt%, the content in the rims increases to 5-13 wt%.

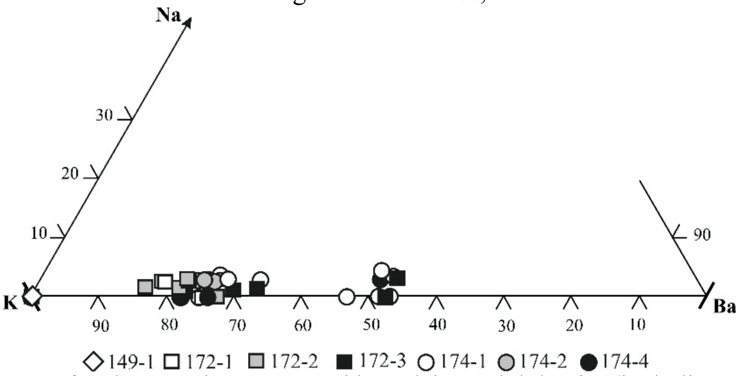

Fig. 2. K and Ba ratio in the orthoclase.

A group of carbonates is represented by calcite and dolomite (including Fe- and Mn-containing varieties), as well as fluorine-rich REE carbonates – bastnesite, synchisite and parizite (Fig. 3 d-e). Carbonates are noted in the intergranular space, aggregates 50-150 mkm in association with rutile, xenotime and thorium phases. The content of CaO in synchysite (wt.%) varies from 12 to 20, SrO 0-1.2, Y_2O_3 0-2, LREE oxides 20-42, MREE 6-24, HREE 0-0.7, thorium (ThO_2) 0-12. High-thorium synchisite-like phases is distinguished, in which the content of thorium (ThO_2) is from 14 to 34 wt%, CaO 10-20, SrO 0-1.2, Y_2O_3 0.2-1.4, the amount of rare earths drops noticeably LREE 10-27, MREE 3-5, HREE is absent. The content of CaO in parisite (wt.%) varies from 8 to 11, SrO 0-1, Y_2O_3 0-2.3, LREE 42-58, MREE 5-21, HREE 0-0.3, thorium is always present ThO_2 0-3. The quantity of rare earths in bastnesite (oxide wt.%) is LREE 52-64, MREE 6-10, HREE 0, SrO 0-0.3, Y_2O_3 0-0.8, thorium is also present – ThO_2 0-1.5. Distribution $LREE_{(La\text{-}Pr)}$–$MREE_{(Nd\text{-}Dy)}$–$HREE_{(Ho\text{-}Lu)}$ and Ca-Sr-Th in fluorine-rich REE carbonates is shown in Fig. 4-5.

Zircon-thorite phases. Zircon is observed as both separate, almost non-thorium phases (small idiomorphic, occasionally zonal crystals and rounded shell individuals), and high-thorium varieties in the joints with thorite and its derivatives, often with xenotime border (Fig. 3f). Fergusonite and pyrochlore were observed in single small aggregates.

Despite a high content of minerals of light rare earths (carbonates), there is a lot of xenotime in the rocks.

Xenotime forms individual grains and crystals, up to 50-70 mkm, developed everywhere, the content of Y_2O_3 is 26-43 wt%. Dy and Gd high enrichment is observed in the rims (up to 9 wt.% of Dy_2O_3 and 14 wt.% Gd_2O_3). The observed Y, Ce, Ca, Nb, Ta, Ti microphases are estimated by eschinite-euxenite.

Rutiles and ilmenites form aggregates in association with carbonates (Fig. 3 g-h), niobium content in Nb-rutile reaches 15 wt% of Nb_2O_5, tungsten in W-rutile up to 5 wt% of WO_3, manganese content in Mn-ilmenite reaches 25 wt% MnO.

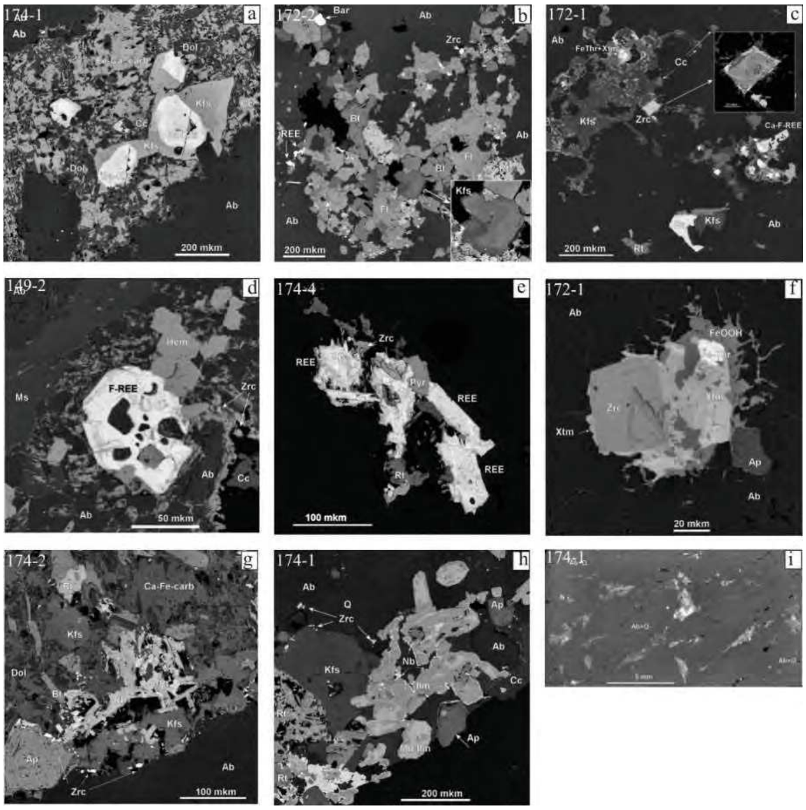

Fig. 3. Ore accessory minerals. Distribution in rocks grains of high-barium Kfs (a-c), aggregates of fluorine-rich REE carbonates (d-e), zircon and xenotime joint in albite matrix (f), Nb-rutile and apatite in carbonate-feldspar aggregate (g), Mn-rich ilmenite (h), the distribution of ore minerals in the intercataclase space in the albitites (i).

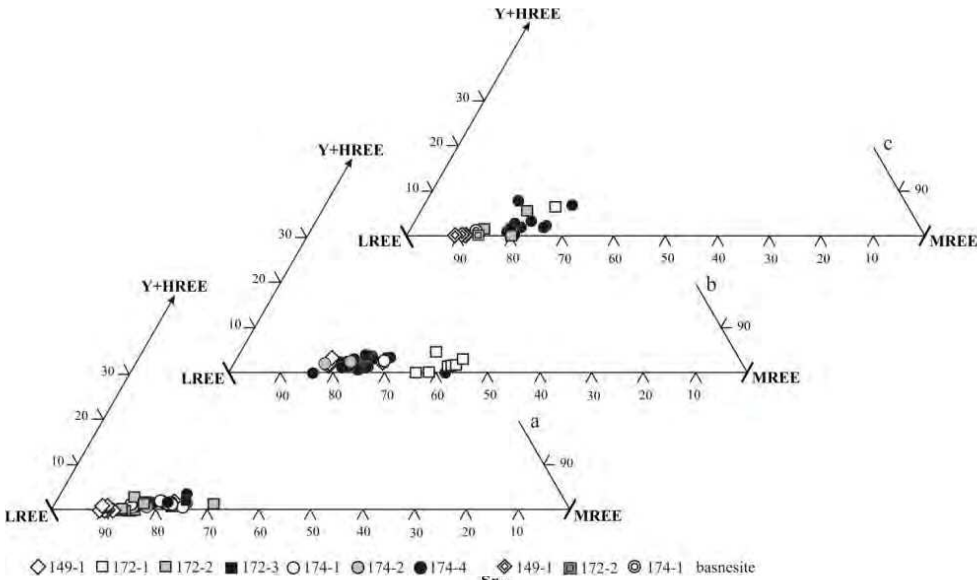

Fig. 4. Ratio of $LREE_{(La-Pr)}$–$MREE_{(Nd-Dy)}$–$HREE_{(Ho-Lu)}$ in fluorine-rich rare earth carbonates. A – parisite, b – synchisite, c – Th-synchitisite and bastnesite.

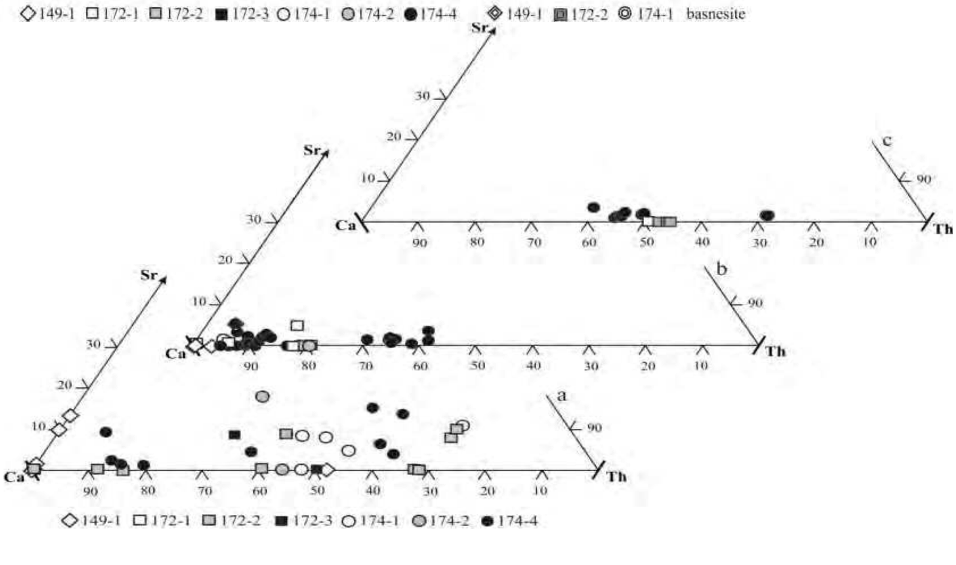

Fig. 5. Ratio of Ca-Sr-Th in fluorine-rare earth carbonates (for a-c see fig. 4).

Thus, in albitites the main ore mineralization is shown in the form of grains (fluorine)carbonates of REE in the intergranular spaces (Fig. 3i). In association with carbonates – high-barium feldspar, xenotime (including HREE-enriched), a wide range of titanium minerals (rutile, Nb- and W-rutile, ilmenite, Mn-ilmenite), zircons (low- and high-thorium) and thorites, as well as undiagnosed mixed phases (Zr-Th -Si+Y-P), phases with niobium and uranium, in single structures monazite, pyrochlore, fergusonite were found. The rocks show an unusually high content of thorium, there is a large number of undiagnosed thorium phases (REE carbonates, phosphorus and ferro-thorites, etc.). Rare sulfides are represented by micrograins of pyrite, galenite, molybdenite. The role of barium mineralization in the form of high-barium feldspars and abundant barite is high. The albitites are saturated with hematite and iron hydroxides. The main REE minerals are fluorine-rich REE carbonates (TR wt.%): bastnesite (61-72), synchisite (34-58), Th-synchitisite (13-33), parisite (53-72).

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MINERALS OF THE PYROCHLORE SUPERGROUP FROM METASOMATIC ASSOCIATIONS OF MINERALS OF CHALCOPHILE ELEMENTS IN THE PELAGONIAN MASSIF, MACEDONIA

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Metamorphic rocks, which form exocontact aureoles around metha-rhyolitic bodies among early Paleozoic metamorphic complex near Nežilovo village in Pelagonian massif (Macedonia), are characterize by anomalous high concentrations of chalcophile elements, first of all As, Sb, Zn, Pb, Cu (Jančev, Chukanov, 2008; Chukanov et al., 2015; Jančev et al., 2016). Unlike the majority of endogenous associations of minerals of these elements, Nežilovo metasomatites practically don't contain sulfides and sulfosalts. Arsenic concentrates here mainly in tilasite, which in some areas is the main mineral of the rock, as well as in accessory apatite-group minerals. Zinc enters into rock-forming silicates (pyroxenes, amphiboles, micas, talc), which contain several % of ZnO, and in spinel-group minerals (mainly gahnite and franklinite), with are important accessories and in some cases rock-forming minerals. Different secondary and accessories minerals of metasomatites (including rinmanite, various members of epidote, pyrochlore, högbomite and hollandite supergroups, plumboferrite and crichtonite groups) are the main concentrators of Pb and Sb. These parageneses show unusual conditions of mineral formation are characterized by a wide diversity. Postmagmatic fluids, connected with meta-rhyolites are considered as a possible source of some specific chalcophile and rare elements (Pb, Zn, Sb, As, Cu, Ba, *REE* etc.) in the contact-metasomatic rocks (Jančev, Bermanec, 1998).

In this work we study isomorphism and compositional variations of pyrochlore-supergroup minerals (PSM) from metasomatites of the ore body No. 9 located in dolomitic marbles, as well as their relationships with associated minerals as indicators of local geochemical situations. Metasomatic bodies and dolomitic marbles are crossed by tilasite-baryte veinlets with variable quantities of silicates, quartz, calcite and dolomite, in which PSM play the main role among accessories. These minerals have a varying composition and complex zoning. Other secondary and accessory minerals of this association are K-feldspar, albite, Zn-containing minerals (clinopyroxene, magnesioriebekite, ferribarroysite, phlogopite, talk, members of the högbomite supergroup), braunite, hematite, zircon, Zn spinels, almeidaite, Pb-containing members of the epidote supergroup, minerals of the rutil-tripuhyite series, As-bearing fluorapatite, gasparite-(La).

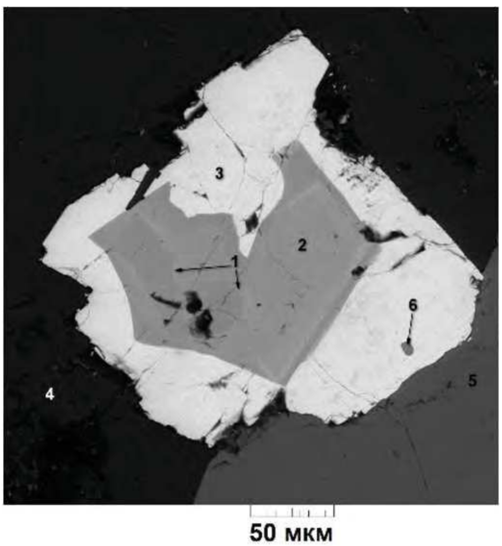

Fig. 1. Zoned crystal of PSM: hydroxycalcioroméite (1), fluorcalcioroméite (2), hydroxyplumboroméite (3). Associated minerals are: albite (4), tilasite (5), zircon (6). Sample 9999B. BSE image.