New data on the substantial composition of Kalba rare metal deposits

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Abstract. Geotectonic position, features of the geological structure and rare metal specialization of the Kalba-Narym granitoid belt formed in the Hercynian cycle in the post-collision (orogenic) geodynamic situation are considered. A geological-genetic model for the formation of the leading type of rare-metal pegmatite deposits (Ta, Nb, Be, Li, etc.) is presented. They are spatially and genetically related mainly to the granitoids of the 1st phase of the Kalba complex, P1 (Bakennoye, Jubilee, Belaya Gora, etc.). The rhythmically pulsating orientation of the process of pegmatite formation with the introduction of ore-bearing fluids (H2O, F, B, Cl, Ta, Nb, Be, etc.) is emphasized from the intracamera focus of a semi-closed magmatic system. The preferred location of ore pegmatite veins in granitoids of moderate basicity occupying an intermediate position in the petrochemical composition between normal granites and granodiorites geochemically specialized in Li, Rb, Cs, Sn, Nb, Ta. The leading ore-controlling role of the latitudinal deep faults of the ancient site in the distribution of rare-metal ore fields and deposits (Ognevsk-Bakennoye, Asubulak, Belogorsk, etc.) is determined. There is a zonal structure of pegmatite veins, a gradual development of mineral complexes from the graphic and oligoclase-microcline (non-ore) to microcline-albite and color albite-spodumene (ore). The mineralization of pegmatite veins is determined by the degree of intensity of the manifestation in them of metasomatic processes (microclinization, albitization, greisenization, spodumenization, tourmalinization, etc.) and the identification of the main ore minerals (tantalite-columbite, cassiterite, spodumene and beryl). The diversity of the material composition of rare-metal pegmatites containing many unique minerals (cleavelandite, lepidolite, ambligonite, color tourmaline, spodumene, pollucite, etc.) is reflected, which brings them closer to the pegmatite deposits of foreign countries (Koktogai, Bernik Lake, etc.). New results of the investigation of the material composition of ore-bearing granites, pegmatites and typomorphic minerals using electron microscopy reflecting the distribution of rare-earth, rare-metal, chalcophile and other elements in them are presented. Indicators of rare metal ore formation are rock-forming minerals of granites (quartz, microcline, biotite, muscovite), ore and associated minerals (cleavelandite, lepidolite, cassiterite, etc.). The most informative minerals include mica (muscovite, gilbertite, lepidolite), colored tourmalines and beryls of different composition and color. Identified typomorphic minerals and geochemical elements-
indicators of rare metal pegmatite formation are considered as a leading search criterion in assessing the prospects of the territory of East Kazakhstan.

1. Introduction
At present, Kazakhstan faces the problem of recreating its own mineral and raw materials base of rare metals and, first of all, tantalum, niobium, beryllium, lithium, rare earth metals, which are widely used in the sphere of high technologies. Kalba-Narym tectonic zone is the main rare-metal-bearing structure in the territory of the Great Altai. Many deposits and ore occurrences of rare metals of various genetic types are concentrated there [1, 3]. Among them, there are deposits of rare metal pegmatites relating to the leading geological-industrial type, which in the past years were developed by Belogorsk ore mining and processing enterprise, but now they are suspended. The research works carried out in recent years show that the region's perspectives for rare metals have not been exhausted yet and it is possible to identify new rare metal occurrences not only on the surface and but also hidden at depth and buried under the cover of loose deposits. The actual task is to resume prognostic-metallogenic and geological explorations for rare metals in order to assess new promising areas and sites, as well as a more detailed study of known ore-bearing structures and objects. According to these facts, regional and local forecasting and search criteria have been developed, among which the most important are geological-petrological and mineralogical-geochemical factors and prerequisites [3, 7].

2. Geological structure
According to the new geotectonic concepts, Kalba-Narym zone is characterized as analogenic block of the Earth crust (terrane), a fragment of the continental plate drifting in the paleo-Asiatic ocean and joined to the Great Altai in the stage of the Hercynian collision of C1. In the early stage of Hercynide (D2-C1), this was a large downfold made by carbon-carbonate-terrigenous formations (D2-C1) (Kystav-Kurchum, Takyr, Burabay and Dalankariy series). In the middle collision stage (C1-C3) molasse formation (Taubin series C2), hypabyssal minor-intrusions and gabbro-diabase dikes (Karabirjuk complex C2-3) and granodiorite-plagiogranites (Kunush complex C2-3) were limitedly appeared. The late post-collision (orogenic) stage was marked by vertical arched and blocky uplifts and a flash of intense granitoid magmatism of Permian time with the formation of a large Kalba-Narym granitoid belt of rare metal specialization (Kalbin Р1 and Monastyr Р2 complexes). In the final stage of the Hercynian cycle, the north - eastern belts of dikes of gabbro-diabase-granite-porphyritic formation were localized (Mirolyubov complex Р2-T1) [1].

According to the geological and geophysical data, Kalba-Narym zone is characterized by a sialic type of the Earth crust section with an increased depth of the meta-granitic layer up to 12 km and a reduced depth of the metabasalt up to 14-18 km with a metadoriorite layer thickness of 12-14 km. In geophysical fields, it is characterized by negative magnetic anomalies and a regional gravitational minimum, which is explained by the immersion of the surface of M (42-48 km) and K (18-26 km).

Kalba-Narym granitoid belt (KNB) is the main rare metal structure of the Altai accretion-collisional system and is considered in the structure of the Great Altai [2, 3]. It is located between West Kalbin and Irtysh tectonic zones and is limited by deep faults - Kalba-Narym (in the north-east) and Terektn (in the south-west). The considering ore-bearing structure is linearly extended in the north-west direction by more than 500 km at a width of 20-50 km. The structural-metallogenic model of KNB reflects the relationship of the ore-magmatic systems with the deep zones of the Earth crust and the upper mantle, and, consequently, the granite belt was formed as a result of the prolonged deep evolution of the lithosphere substance. The centers of magma formation originated, judging by the composition of the granite smelting, in the metagranite layer or on its boundary with the metadoriorite. Zones of transit heat-mass flows penetrated from the lower parts of the Earth crust and the upper mantle along the system of deep faults [3]. We also know the data of V.L. Khomichev that granites are the products of intra-chamber differentiation of the original “basic magma” (2010).
The ore-controlling role of latitudinal deep faults of ancient deposits and long-term activation is emphasized in the distribution of rare-metal pegmatite fields and deposits, especially at the nodes of their intersection with north-western, north-eastern or meridional disjuncts (Gremyachin-Kiin, Asubulak, Belogor, Mirolubov and others). Thus, Asubulak ore field is controlled by a latitudinal fault along which two ore-bearing strips of sublatitudinal strike can be traced: (1) Ungur (northern), including the ore objects of Carmen-Kuus, Akkesen, Ungursai, Plachgora and 2) Krasnokordon (southern), uniting the Yubileynoye industrial deposit of ore occurrences Krasny Cordon, Skalnoye and Budo in 1.5 km increments (Figure 1).

Figure 1. Scheme of the geological structure of the Asubulak ore field

The model of formation of rare metal pegmatite deposits is determined by their genetic connection with the granites of Kalba complex P1, and the spatial distribution of bodies mainly in medium-coarse-grained biotite granites of the I phase and their exocontacts [3, 6]. The processes of pegmatite
formation probably occurred in open or half-closed magmatic system with the rhythmically pulsating supply of ore-bearing distillates (H₂O, F, B, O, Ta, Nb, Be and others) from the intro- chambered center of granite massifs. The pulsating inflow of pegmatite-forming fluids determined the multi-rhythmic zonation of pegmatite veins, the phasic development of mineral complexes from graphical and oligoclase - microcline (barren) to microcline-albite and spodumene - containing (non-ferrous ore) with complex ores (Ta, Nb, Be, Li, Cs, Sn W).

3. Geological and petrological features
In the evolutionary range, granitoids of Kalba complex refer to the normal branch of differentiation and occupy an intermediate position between granodiorites and granites (Figure 2).

The first phase is characterized by an unbalanced composition of rocks (from normal granites to contaminated granites and granodiorites), accounting for about 70% of Kalba complex. It is represented mainly by medium-coarse-grained porphyritic biotite granites containing (%): plagioclase (No. 18-37) – 35-41, potassium feldspar – 15-20, quartz – 28-32, biotite up to 5-10, accessories - 0.5. Petrochemicals refer to the normal range of the sodium-potassium series ((Na₂O: K₂O = 0.78), low-plumazite (Ka = 0.69), moderate basicity (r = 0.34 kcal), and very high alumino-carbon. Accessory specialization - garnet-ilmenite-apatite, accessory minerals - zircon, monazite, sphene, tourmaline and others; minerals - indicators of mineralization - apatite, tourmaline, cassiterite, spodumene.

Geochemically, granites are enriched with Li, Rb, Cs, Sn, Nb, the content of Ta in them varies from 1.2 to 4.8 g/t. The increased content of rare elements (Ta, Nb, Be, Li, Sn) is found in rock-forming minerals with titan-inclusions, such as micas, as well as in accessory minerals - apatite, ilmenite, zircon and other minerals. The enrichment of granite melts with mineralizers - (extractors) of rare elements - B, F, C, Sn W has been revealed. In general, the geochemical type of granites is tin-tantalum (with lithium and beryllium) [3].
According to the results of mass spectrometry, the amount of rare-earth elements in granites of the first phase is 80.74 g/t. The enrichment of these granites with Nb, Sn and rare alkalis, especially Li (the ratio Cs: Rb: Li = 1: 1.6: 10), is established (Table 1).

**Table 1.** The content of rare elements in granites of the I phase of the Kalba complex (g / t)

| Sample № | Ta   | Nb  | Be  | Li   | Rb   | Cs  | Sn  | W  | Mo  |
|----------|------|-----|-----|------|------|-----|-----|----|-----|
| 0-21 (1) | 1.49 | 34.40 | 3.94 | 294.50 | 166.6 | 18.92 | 10.35 | 0.80 | 0.83 |
| 0-21 (2) | 1.75 | 14.84 | 2.29 | 289.60 | 150.1 | 21.98 | 11.91 | 0.46 | 0.43 |
| 0-21 (3) | 1.20 | 11.63 | 1.66 | 256.00 | 145.1 | 19.24 | 20.55 | 0.63 | 0.75 |
| 0-21 (4) | 0.89 | 12.74 | 3.31 | 107.50 | 164.4 | 40.87 | 18.74 | 0.66 | 0.53 |
| 0-21 (5) | 0.95 | 12.76 | 1.91 | 295.00 | 158.2 | 18.16 | 11.53 | 1.04 | 1.30 |
| Average value | 1.26 | 17.27 | 2.62 | 248.52 | 156.88 | 23.83 | 14.62 | 0.72 | 0.77 |

The calculated coefficients reflect a relatively uniform distribution of Rb and Li and a sharp increase in Rb/Cs ratio in later granitoids due to the increase in their potassium alkalinity (Figure 3). There is an increased tininess in regard to Ta and W, and the distribution of niobium and tantalum is uneven at a close ratio in granites of the I phase (1: 1) in all types of granitoids.

![Figure 3](image-url)

**Figure 3.** Diagram of distribution coefficients of the granitoid diagrams of granitoid Kalba and Zharma – Saur region

I-VII - intrusive complexes: I - kunush granodiorite - plagiogranite, P₁; II - IV kalba P₁ (II – porphyritic biotite granites of the first phase, III - biotite and IV - muskovite granites of the second phase); V - monastirske leucocratic P₂, VI - keregetas-espinsky alkaline granite P₂; VII - mirolyubov dyke P₂-T₁

Studies show that the original granite melts, according to the prevailing content of rare earths in the light group and enrichment with lithophilic rare elements, had a crustal origin. By this fact, they differ from the granitoids of the East Sayan zone of mantle-crustal origin enriched with heavy rare earths [2]. At the same time, we determined that the ore-bearing granites of Kalba, in addition to rare elements,
have high concentration of Zn, Pb, Cu and significant values of As, Sb, Ag, Au, Pt, Bi and other elements reflecting mixed sources of the ore matter, associated, probably, with fluid flows from different level areas of magmatism. That was reflected in the formation in pegmatites, except lepidolite, spodumene, tantalite-columbite, beryl and cassiterite, associated minerals (pyrite, galena, arsenopyrite, antimonite, gold and others).

4. Features of mineral composition

Pegmatites are divided into three types: 1) oligoclase - microcline (barren), 2) microcline - block with beryl and columbite (slightly ore-bearing) and 3) albite with several mineral complexes (ore). In the ore veins, taking into account the works of A.I. Ginzburg, E.P. Pushko, O.D. Gavrilenko and our data, the following mineral associations or complexes are distinguished: microcline, albite - microcline, albite, quartz-albite-muscovite, spodumene - cleavelandite - quartz, lechidolite-pollucite - cleavelandite (non-ferrous).

Mineral and chemical composition of ores are very diverse. The main useful components are Ta, Sn, Li, Rb, Cs. The main vein and ore minerals are albite, microcline, quartz, muscovite, spodumene, beryl, tantallite-columbite, pollucite and cassiterite. Accessory minerals are apatite, tourmaline, garnet, gilbertite, muscovite, oncosin, cookeite, eucryptite, arsenopyrite, pyrite, calcite, mangan tantalite, montebrasite, amblygonite, petalite, molybenite and others. Minerals that are rare in occurrence - sphene, epidote, biotite, chlorite, graphite, pyroxene, hornblende, struverite, ixiolite, bertrandite, ampanagabeite, cyrtolite, pyrochlore, wolframite, scheelrite, monazite, titano-ferrite, etc.

A great contribution to the study of the mineralogical composition of Kalba pegmatites was made by A.I. Ginzburg, V.D. Nikitin, S.G. Shavlo, N.A. Solodov, V.I. Kuznetsov, Yu.A. Sadovskiy, V.A. Filippov, and others. Pegmatites are characterized by a wide variety of minerals and contain more than 80 minerals in terms of their material composition and structural features. The main rock-forming minerals (%): albite, quartz, microcline and muscovite; accessory minerals are apatite, tourmaline, garnet, gilbertite, fluorite, calcite, and others. A unique complex of minerals of several generations (albite, cleavelandite, lepidolite, pollucite, spodumene, petalite, ambloginote, polychrome tourmaline, beryl, tantallite-columbite, cassiterite, and others) was found in a number of ore fields and deposits. The main ore minerals are tantalite-columbite, cassiterite, spodumene and beryl [1, 3].

New researches of the material composition of pegmatites were carried out by authors using electron microscopy in order to study typomorphic minerals and geochemical elements - indicators of rare metal pegmatite formation. On a number of typical deposits (Bakennoye, Yubileynoye, Medvedka, Tochka, and others) specimen and samples were taken from the inclosing granites, metasomatic formations and pegmatite veins. Analytical studies were carried out mainly in EKSTU “IRGETAS” laboratory on the ICP-MS mass spectrometer with inductively coupled plasma, which determines 73 elements with high sensitivity, and on the scanning electron microscope JSM-6390 LV. X-ray structural spectrometer SRV-1M was used to determine the composition of ore minerals. Isotope studies were carried out at the Institute of Geology and Mineralogy of SB RAS (Novosibirsk).

Mineralogical search criteria are determined by the degree of intensity of metasomatic processes in pegmatite veins (microclinization, albitization, greysening, and others) and identification of typomorphic minerals (microcline, albite, cleavelandite, muscovite, lepidolite, tourmaline, spodumene, and others). The conducted researches established that the leading minerals-indicators of rare metal ore formation are specular stones of different composition and colour, which are characterized by high concentration of Li, F and rare elements. Thus, for quartz- microcline – albite pegmatites of Yubileynoye deposit, bladed clear muscovites of high fluorinity (F> 1-1.5%) enriched with Ta, Nb, Be, Sn and rare alkalis are typical (Table 2).
Table 2. Content of elements in muscovites from rare metal pegmatites of the Jubilee deposit (g / t)

| №  | Sample № | Ta  | Nb  | Be  | Li  | Rb  | Cs  | Sn  | W   | Mo  |
|----|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1  | 5953-6   | 27.87 | 3996 | 5645 | 4869 | 894 | 502.2 | 4.35 | 0.06 |
| 2  | 4953     | 28.47 | 70.64 | 3996 | 4787 | 513.2 | 567.6 | 4.44 | 0.13 |
| 3  | 5980-6   | 23.98 | 218.8 | 38.28 | 5465 | 4849 | 639.4 | 557.8 | 6.59 |
| 4  | 4987-r   | 31.44 | 23.02 | 2190 | 4016 | 261.5 | 574.7 | 8.91 | 0.84 |
| 5  | 4984-r   | 39    | 214.7 | 29.28 | 9478 | 4849 | 639.4 | 557.8 | 6.59 |
| 6  | 2234-1   | 121.14 | 147.37 | 23.14 | 4564 | 4114 | 547.6 | 323.4 | 21.69 |
| 7  | 2235-3   | 63.47 | 156.81 | 20.73 | 3299 | 1144.9 | 218.8 | 320.6 | 18.34 |
| 8  | 4215-a   | 153.1 | 185.1 | 22.14 | 413.9 | 1144.9 | 218.8 | 320.6 | 18.34 |
| 9  | 2212-1   | 121.6 | 301.1 | 28.17 | 2844 | 3226 | 448.6 | 348.2 | 15.62 |
| 10 | 2212-3   | 1795 | 406.1 | 32.6 | 2408 | 1144.9 | 218.8 | 320.6 | 18.34 |
| 11 | 4973-r   | 67.39 | 692  | 35.89 | 1010 | 1555 | 99.75 | 216.44 | 25.92 |

Note. The results of mass spectrometric analysis (ICP-MS). Analyst S.N. Polezhaev

Flaky muscovites of green colour, with higher Ta contents (up to 233 g / t) and Nb (up to 380 g / t), are characteristic of quartz-albite-muscovite (greysen) complex. For quartz-cleavelandite-spodumene (non-ferrous) complex, coarse-flaky lepidolites reflecting rich complex ores (Ta, Nb, Li, Cs, Sn) are enriched with Li (up to 16240) and Rb (up to 1718 g / t) (Table 3, Figure 4).

Table 3. Content of rare elements in mica (g / t).

| №  | Characteristic of rock | Ta  | Nb  | Be  | Li  | Rb  | Cs  | Sn  | W     | Mo  |
|----|------------------------|-----|-----|-----|-----|-----|-----|-----|-------|-----|
| 1  | Lepidolite             | 10.34 | 50.94 | 4.74 | 16240 | 1718 | 263.0 | 81.46 | 11.69 | 12.52 |
| 2  | Gilberite              | 18.52 | 24.1 | 6.4 | 3835 | 5210 | 3328 | 148.5 | 1.93 | 0.55 |
| 3  | Muskovite              | 224.76 | 283.47 | 35.46 | 3837.54 | 3848.54 | 513.26 | 448.87 | 11.69 | 3.90 |
|    | Average                | 84.54 | 119.5 | 15.5 | 7970.8 | 3592.2 | 1368 | 226.3 | 7.33 | 5.66 |

Note. The coefficients are calculated from the results of ICP-MS (g / t). Analyst S. N. Polezhaev

Figure 4. Microinclusion of minerals in muscovite of pegmatite deposits
The cryptocrystalline muscovite (zilbertite) differences of Carmen-Kuus ore occurrences are characterized by anomalous values of Cs (3328) with Li (3835) and Rb (5210 g/t). Microinclusions of tantalite, cassiterite, fluorapatite and other minerals were fixed in muscovites on the SEM image (Figure 4).

![Figure 5. Diagram of distribution rare element in mica (g / t)](image)

Informative minerals also include tourmalines of different composition and colour, among which the schorl with low values of rare elements reflect simple pegmatites, and polychrome tourmalines with anomalous contents of rare alkalies indicate ore mineral complexes (Table 4).

| Minerals              | Ta  | Nb  | Be  | Li  | Rb  | Cs   | Sn   | W   | Mo  |
|-----------------------|-----|-----|-----|-----|-----|------|------|-----|-----|
| Tourmaline (polychrome)| 37.2| 97.1| 2.66| 2986| 605.6| 135400| 19.26| 1.86| 1.73|
| Rubellite (pink)      | 43.7| 128.9| 5  | 226.2| 14.9 | 61.57 | 1.26 | 2.48|
| Sherl (Black)         | 7.6 | 22.6| 2   | 135.4| 6.7  | 22.1  | 4.87 | 0.82| 1.93|

Note. The results of mass spectrometric analysis. Analyst S. N. Polezhaev

In order to compare significant differences in beryl composition from different deposits are given (Table 5). Beryls from block microcline pegmatites are poor in Ta and Nb. Aquamarines of the
Delbegei massif are enriched with Ta and Nb, they contain more Sn with a low content of rare alkalis. Emeralds are characterized by low contents of rare elements and an anomalous value of Cr (636.4 g / t). The contents of Ta, Nb, Mo are higher for blue beryl, and white beryl with anomalous values of Li, Cs, Ta, Nb reflects rare metal pegmatites of Koktogay deposit (China).

**Table 5. Content of rare elements in beryl (g / t)**

|    | Ta  | Nb  | Be  | Li  | Rb  | Cs  | Sn  | W   | Mo  | Cr  |
|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1  | 1.73| 3.79| 3577| 294.77| 60.35| 320.2| 14.76| 2.52| 1.34| 25.44|
| 2  | 1232| 8080| 15380| 108.2| 28.11| 57.77| 45.86| 4.77| 0.28| 122.20|
| 3  | 169.2| 109.4| 15780| 50.04| 17.5| 48.89| 45.86| 10.32| 2.30| 636.40|
| 4  | 0.4| 9.5| 30210| 42.66| 7.7| 35.09| 3.19| 1.9| 33.63| 68.78|
| 5  | 54.69| 27.2| 10390| 240.8| 29.5| 177.7| 2.26| 1.56| 495.3| 44.32|
| 6  | 284| 96.95| 12060| 6782| 205.2| 15220| 2.31| 1.9| 33.63| 68.78|

Note: 1 - beryl greenish-gray from block microcline pegmatites of Kalba, 2 - aquamarine from greisens of Delbegetey massif, 3 - aquamarine from quartz vein of Delbegetey massif, 4 - emerald, 5 - beryl blue, ore field of Koktogay, 6 - beryl white, ore Kotogay field (China).

5. **Conclusion**

The main regularities of the distribution of rare metal-bearing granitoid belts, which were formed in the post-collisional (orogenic) geodynamic environment (P_1-T_1), are determined in tectonic structures with the sialitic type of the Earth crust section. In Kalba-Narym belt, the leading deposits of rare-metal pegmatites are genetically related to granites of the 1st phase of Kalba complex (P_1). The ore-controlling role of latitudinal deep faults in the location of pegmatite ore fields and deposits is emphasized. The geological-genetic model of pegmatite formation reflects the gradual development of mineral complexes from the graphite and oligoclase- microcline (barren) to spodumene-containing one (non-ferrous) with rich complex ores (Ta, Nb, Be, Li, Cs, Sn). Mineralogical factors for the estimation of rare metal pegmatites are determined by the intensity degree of the metasomatic processes occurrences (microclinization, albitization, greysening, spodumenization, silicification) in them, the indicators of which can be typomorphic minerals (cleavelandite, muscovite, lepidolite, spodumene, colour tourmalines, pollucite, and others) similar for industrial pegmatite deposits of foreign countries (Koktogay, Bernik Lake, King Mountain, and others) [4, 5, 8, 9].

The leading role in ore formation is attached to albitization process, which is the initiator of all subsequent metasomatic transformations of pegmatite veins. Albitization is also associated with the formation of rare-earth mineralization in alkaline granites of Upper Espe deposit and rare metal mineralization in albitites at Vasylykovskoye gold-bearing deposit. The processes of albitization are also widely shown in other rare metal objects (Karacus, Alakha, Novo-Akhmirov, and others) [7]. The identification of micro- and fine-dispersed inclusions of rare and rare-earth minerals and geochemical elements (Au, Ag, Pt, Ir, U) in ores is of scientific importance, these results are recommended to take into account in the practice of geological explorations.

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