Petrography and Mineralogy of Granitoids of the Elikchan Massif (North-East of the Verkhoyansk-Kolyma Orogenic Region)

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Abstract. The article presents the results of a study of Elikchan granodiorite-granite massif with complex Sn-Au-Ag mineralization. It is shown that the massif localized in the zones of regional fault, where it was preceded and followed by subaerial volcanic outpourings. Considered typomorphic peculiarities of rock-forming, accessory, and restituir minerals of granitoids and petro- and geochemical features of the rocks. A polygenetic nature of the massif is documented, with the origination of parental melts of the amphibole-biotite granodiorites and granites from the lower and upper crustal protoliths, respectively, under the influence of deep heat and fluid fluxes rising from the metasomatized mantle to the magma-generation level. Geochemical specialization of granitoids on a wide range of ore elements characteristic of latite ore-magmatic systems has bee n established (Bi, As, Sb, Ag, Sn, W). It is shown that the crystallization of the granodiorites took place in conditions close to those of gold-bearing ore-magmatic systems, and the crystallization of granites in the conditions close to those rare-metal ore-magmatic systems, what obyasnyat preformationist associated mineralization. An important criterion for the potential ore content of specific magmatic formations and its possible implementation is the regime of volatile elements.

1. Introduction.
The Early Cretaceous granitoids are the most common magmatic rocks of the Verkhoyansk-Kolyma orogenic region. They form belts of large plutons that extend sub-conformably with a strike of the main folded structures along the border of the Kolyma-Omolen microcontinent and the Verkhoyansk margin of the Siberian continent – the Main and Northern one, and in the inner regions of the continental margin, they form chains of small massifs, that trace the zones of large faults, transverse or oriented at an angle to the direction of the main folded structures (Figure 1). The Northern belt splits into two branches, composed of arrays of different compositions. The granitoids composing the southern branch are similar to those of the Main belt. The massifs composing the north-northeast branch are localized in the zone of a regional
fault and are composed of granitoids close to the granitoids of the latite series, usually accompanied by complex (Au, Ag, Sn, W) mineralization [1]. One of these arrays is the Elikchan array considered in this paper. The aim of the research was to establish the conditions for generation and crystallization of its constituent rocks. The relevance of research is to determine the conditions that determine the ore productivity of magmatic systems and the polyformationality of accompanying mineralization.

Figure 1. Location diagram of the granitoids of the Verkhoyansk-Kolyma mesozoides, 1 – massifs of granitoids of longitudinal lines, 2 – transverse belts of granitoids, 3 – axes of folded structures, 4 – Elikchan massiv.

2. Research methods
The methodology included: study of the structure of massif in the field, sampling of all rocks included in their composition, study of petrographic thin sections, full silicate analysis (analysts D. A. Kulagin, G. N. Okhlopkova, S. E. Diakonova), quantitative spectral and atomic absorption analyses (N. N. Oleynikova, N. M. Tayurskaya, A. S. Vasilyeva, O. D. Zamiyskaya, Z. V. Khokhryakova); determination of compositions of rock-forming and accessory minerals, using Camebax-micro microanalyzer (S. P. Roev, L. A. Pavlova); Rb-Sr isotopia (A. I. Zaitsev). All these analyses were performed in the laboratory of physical and chemical analysis methods DPMGI SB RAS. In addition, the spectral laboratory of the Institute of Geochemistry SB RAS, under the guidance of O. V. Zarubina, conducted the determination of the content of trace elements (including rare earth elements) by the Inductively coupled plasma mass spectrometry. Calculations of P-T conditions of magma generation and crystallization are performed mainly by the GCDkit program, the program of calculations of compositions and parameters of crystallization of dark-colored minerals are indicated in the notes to the tables.

3. Research results
3.1. Geological structure of the territory
The Elikchan massif occupies a large part of the similarly-named ore-magmatic field. It intrudes the Jurassic terrigenous strata and volcanic rocks of diverse composition. In the Late Jurassic period, small stocks and dikes of gabbro and diabases were formed. In the Berriasian-Barremian period was preceded by subaerial outflows of lavas of variegated composition with parameters of volcanic rocks of active continental margins [2]. A volcanic-plutonic association of mainly acidic flow units and granitoid was formed in the Aptian. K-Ar isotopic age of andesites – 140±5 Ma, rhyodacites –127 Ma, rhyolites – 120 Ma. Rb-Sr isochronous age of granodiorites of the Elikchan massif – 134±2 Ma, biotite granites – 122±1.4 Ma, pegmatite– 116±2 Ma. At the end of the Aptian, felsic volcanic covers and fractured bodies and small rods of alkaline feldspar granite and rhyolite porphyry were formed in
a post-collisional uplift environment, and in the Albian, there were outpourings of volcanic rocks and the introduction of dikes of trachyandesites and trachybasalts (Figure 2).

Figure 2. Geologic map of the Elikchan and Istekh ore fields [3]
1 – Quaternary deposits (Q); 2-4 – Cretaceous system: 2 – upper series: volcanic formations of the medium middle composition; 3 – upper series: rhyolites, their tufts and tufflavas (K2); 4 – lower series: dacites, andesidacites, andesites and their tufts, tuffstones and tuff siltstones K2; 5-7 – Jurassic system: 5 – upper series: polymictic sandstones, siltstones and claystones (J3); 6 – middle series: polymictic sandstones, siltstones and claystones (J2); 7 – lower series: calcareous sandstones, claystones and siltstones; 8-9 – Late Cretaceous dikes: 8 – trachyandesites, and trachydolerites (βµ K2); 9 – rhyolite porphyry (λπ K2); 10 – dikes of aplite and pegmatites (iK1) and stocks of leucogranites (ιγ K1); 11 – granites (γ K1); 12 – granite porphyry (γπ K1); 13 – granodiorites (γδ K1); 14 – dikes of quartz diorites (qδ K1); 15 – Late Jurassic dikes of gabbro – diabases (νβ J3) and stocks and small bodies of gabbro (ν J3); 16 – stratigraphic and intrusive contacts; 17 – tectonic contact and faults; 18–21 – ore occurrences: 18 – gold; 19 – tin; 20 – tungsten; 21 – tin deposits. The massifs of granitoids: E – Elikchan, NE – North Elikchan massif, UE – Upper Elikchan massif.

3.2. Petrography and mineralogy of magmatic rocks
Elikchan massif is composed of amphibole-biotite granodiorites and granites and biotite granites. The early magmatic mineral association of granodiorites and amphibole-biotite granites is represented by an andesine labradorite and high-calcium magnesioaugite. Plagioclase contains semi-dissolved restite cores of both the more basic (62–67% an) and more acidic (26–29% an) composition and their clusters, which suggests a heterogeneous composition of magmogeneration substrates. Generally, the plagioclase is characterized by multi-layered rhythmic zoning. Each rhythm has a direct zoning and ends with the dissolution of its peripheral zone, along which borders there are numerous gas-liquid micro-inclusions, as well as micro-inclusions of apatite and light mica, that is, the end of the straight-zonal rhythm coincides with the beginning of the melt distillation. The zone following the dissolution is more basic and less structurally ordered: № 43, su 0.7 // № 50, su 0.5–0.48, su 0.3–0.46, su 0.6–0.44, su 0.7–0.37, su 0.9–0.22 su, 1 // № 42, su 0.6–0.38, su 0.8 // № 44, su 0.6–0.40, su 0.9–0.26 su, 1 – № 4, su 0.9 // borders of rhythms, su degree of structural order). In other words, there is a combination of back-progressive zoning, which is formed during magma
intrusion, with direct regressive zoning of the formation chamber. This structure of plagioclases indicates a multi-stage magma intrusion, with repeated stops in intermediate chambers, where crystallization involved dissolution and loss of the fluid phase. K-feldspar of granodiorites is a high and intermediate orthoclase (2VNp = 48–62°, degree of triclinicity 0.4–0.7).

Clinopyroxene corresponds to pyroxenes of continental basites of mafic index ratios (f = 22.4%) and TiO$_2$ contents (0.7%) [4]. Estimated temperature of its formation 930°C. In addition, in the samples of granodiorites, corroded grains of subcalcic magnesioaugite (f = 31.7, TiO$_2$ = 0.33) with estimated temperature of crystallization 1260°C are found (calculations for [5]). It is also similar in composition to the clinopyroxenes of basites and hyperbasites, and we have referred it to restite.

### Table 1. Compositions of the pyroxenes, amphiboles and biotites of granitoids of Elikchan massif

| Oxydes, % | O2129 | O196/12 | O196/11 | K11/1 | K27/11 | K165 |
|----------|------|--------|--------|-------|--------|------|
| SiO$_2$  | 50.85 | 52.27  | 51.07  | 47.45 | 37.08  | 36.17 |
| TiO$_2$  | 0.70  | 0.33   | 0.5    | 0.79  | 4.93   | 4.62 |
| Al$_2$O$_3$ | 2.54 | 2.98  | 5.32  | 8.60  | 13.23  | 13.48 |
| Cr$_2$O$_3$ | 0.05 | 0.02   | 0.02  | 0.04  | 0.01   | 0.01 |
| Fe$_2$O$_3$ | 5.02 | 0     | 3.49  | 4.88  | 1.22   | 1.58 |
| FeO     | 3.76  | 13.45  | 9.80  | 10.69 | 16.91  | 16.39 |
| MnO     | 0.30  | 0.48   | 0.55  | 0.71  | 0.28   | 0.06 |
| MgO     | 16.14 | 16.27  | 15.18 | 12.47 | 12.55  | 12.76 |
| CaO     | 20.90 | 11.75  | 10.75 | 11.28 | 0.08   | 0.00 |
| Na$_2$O | 0.25  | 0.84   | 1.14  | 1.53  | 0.06   | 0.14 |
| K$_2$O  | 0.01  | 0.24   | 0.13  | 0.13  | 0.91   | 0.98 |
| Cl      | 0.04  | 0.04   | 0.04  | 0.12  | 0.07   | 0.11 |
| F       | 0.15  | 0.09   | 0.53  | 0.10  | 0.19   | 0.25 |
| H$_2$O* | 1.81  | 1.97   | 3.96  | 3.91  | 2.06   | 1.29 |
| Total   | 100.73 | 98.74  | 100.26 | 100.79 | 100.20 | 99.66 |
| f       | 22.4  | 31.7   | 32.7  | 40.5   | 44.6   | 43.9 |
| P, kbar | 930   | 1260   | 740   | 812    | 761    | 752 |
| log fO$_2$ | -133 | -133  | -117  | -11.5  | -15.1  | -11.5 |
| log fH$_2$O | 3.3  | 3.3   | 3.3   | 3.3   | 3.3    | 3.3 |
| log fHF  | -0.6  | -0.6  | -0.2  | -0.2  | -0.2   | -0.2 |
| log fHCl | 4.3   | 4.3   | 4.3   | 4.3   | 4.3    | 4.3 |
| H$_2$O*,% | 5.3   | 3.5   | 29.3  | 3.0   | 5      | 8    |

Notes. O212/9, O19/11, O196/11 and K11/1 – granodiorites; K27/11 – amphibole-biotite granite, K16/5 – biotite granite. Determination of temperatures: T [7]; pressure P - [8]; log f O$_2$ - [9]; log f H$_2$O, log f HCl, log f HF by [10]

Amphibole replacing clinopyroxene, is represented by magnesian hornblende (f = 26.3–40.5%). It crystallized with high and moderate oxygen activity, T = 820–740°C, and the water content in the melt 5.3–2.9% (calculations for [6]). Single relics of Fe-tschermakite were observed in schlieren clusters of hornblende. It is comparable to amphibolites (f = 84.7%, Al$_2$O$_3$ = 13.05).
Biotite is predominantly magnesian (Table 1). It begins to crystallize somewhat later than the large amphibole grains. According to the composition, it corresponds mainly to the biotite of cow-mantle magma derivatives (Figure 3a), and is comparable in low aluminous to biotites of magmatic rocks of increased alkalinity. Biotite was formed in the environment close to the amphibole, water content in the melt 3.5–5% (Figure 3b). The relatively high activity of oxygen and high activity of chlorine and water during biotite crystallization are similar to those of gold-bearing ore-magmatic systems [11]. In the accessory fraction, titanomagnetite, magnetite, sphene, orthite, ilmenite, Cl-apatite, zircon. Accessory magnetite contains 0.3–0.5% Cr₂O₃. The pyrope minal content (19–24%) in the accessory garnet corresponds to the lower-crust of magmogeneration [12]; ZrO₂/HfO₂ ratio in the accessory zircon reaches gabbro values – 79–80.

**Figure 3.** The parameters of biotite composition in Elikchan massif
1 – granodiorites, 2 – granites
a) Ratios F/OH and Mg/Fe in biotites. Fields of biotite compositions [13] – biotite of derived melts: I – formed by contamination and assimilation of sub-sea meta sediments; II – mantle; III – cow-mantle; IV –mantle-crustal; V – crustal anatectic
b) P–T-diagram of the granite-water system for independent P_total and P_H₂O [14]

Plagioclase of biotite granites is nonzonal or with indistinct direct zoning. Its composition varies from oligoclase-andesine to oligoclase-albite (32–12 % an). K-feldspar of biotite granites–intermediate and low cryptoperthitic microcline, usually significantly albitized. Biotite is highly ferruginous. The water content in the melt is 8%. According to the composition parameters, biotite corresponds to biotites of crustal granites of the ilmenite series. The accessory fraction of granites contains: magnetite, orthite, manganese ilmenite, F-OH-apatite, spinel and hercynite. During greisenization, muscovite aggregates are developed in association with single spessartine-almandine grains (20% spess), arsenopyrite nests, and later tourmaline grains with cassiterite.

3.3. Petro-and geochemical features of granitoids
Chemical composition of the rocks of the Elikchan massiv varies from quartz diorites to alkaline granites (Table 2, Figure 4a). rocks are metaaluminous or very slightly supersaturated with alumina, and their composition parameters correspond to the granitoids of the continental arcs of the active margins of the continents (Figure 4b, 4c). Granodiorites and granites are characterized by asymmetric trends of the distribution of chondrite normalized contents of rare earth elements, with a rapid typical for rare metal systems, are close to clarks [15].
Table 2. Chemical composition of the granitoids of Ekitchkan massif

| Rocks          | Oxides, % | Granodiorites | Granites |
|----------------|-----------|---------------|----------|
|                |           | Oxides, %     |          |
|                | 207/3     | 10/2          | 12/1     |
| SiO₂           | 62.86     | 63.76         | 63.84    |
| TiO₂           | 0.68      | 0.62          | 0.59     |
| Al₂O₃          | 15.26     | 15.16         | 15.43    |
| Fe₂O₃          | 1.41      | 1.17          | 0.62     |
| FeO            | 3.28      | 3.98          | 4.20     |
| MnO            | 0.09      | 0.07          | 0.06     |
| MgO            | 2.98      | 2.74          | 2.52     |
| CaO            | 4.00      | 3.99          | 3.78     |
| Na₂O           | 3.28      | 3.04          | 3.00     |
| K₂O            | 4.56      | 3.96          | 3.99     |
| P₂O₅           | 0.22      | 0.21          | 0.22     |
| CO₂            | 0.55      | 0.10          | 0.22     |
| F              | 0.12      | 0.09          | 0.08     |
| Li₂O           | 0.005     | 0.014         | 0.015    |
| Rb₂O           | 0.0203    | 0.014         | 0.014    |
| S              | 0.02      | 0.10          | 0.10     |
| Total          | 99.96     | 100.12        | 99.77    |
| Fe/Fe+Mg       | 61.1      | 65.3          | 65.7     |
| T°C            | 1044      | 1036          | 1029     |

| Elements, ppm | B         | 14 | 38 | 24 | 20 | 30 | 26 | 30 | 50 | 26 | 32 | 34 | 20 | 70 |
|---------------|-----------|----|----|----|----|----|----|----|----|----|----|----|----|----|
|                | Sn        | 6  | 4  | 10 | 5  | 7  | 6  | 8  | 10 | 5  | 11 | 11 | 10 | 5  |
|                | W         | 5  | 15 | 11 | 5  | 5  | 5  | 5  | 17 | 10 | 5  | 6  | 7  |    |
|                | Mo        | 7  | 10 | 10 | 6  | 5  | 2  | 10 | 6  | 5  | 3  | 7  | 1.5| 10 |
|                | As        | 31 | 30 | 30 | 32 | 43 | 68 | 30 | 53 | 48 | 23 | 27 | 31 | 70 |
|                | Bi        | 5  | 0.3| 0.3| 10 | 0.5| 1  | 1  | 0.2| 0.4| 1  | 10 | 3  |    |
|                | Sb        | 3  | 10 | 48 | 2  | 5  | 3.8| 4  | 4.8| 5.2| 12 | 7  | 10 | 5  |
|                | Pb        | 18 | 8  | 24 | 33 | 58 | 52 | 20 | 37 | 20 | 15 | 18 | 10 | 10 |
|                | Ag        | 2  | 0.15| 0.1| 0.15| 0.2| 10 | 0.1| 0.15| 0.15| 0.1| 0.5| 0.15|    |
|                | Au        | 0.01| 0.1| 0.2| 10 | 0.006| 2 | 0.001| 0.02| 0.001| 0.02| 0.001| 0.001|    |
|                | Ba        | 1300| 1400|1000 |1030|1200 |1300 |1400 |940 |1500 |770 |960 |910 |1252|
|                | Sr        | 1200 |920 |530 |830 |530 |1100 |880 |620 |560 |180 |260 |260 |884 |
|                | Co        | 14  | 5  | 15 | 2  | 9  | 13 | 3  | 5  | 3  | 5.8 | 5.7| 12.5|    |
|                | Ni        | 31  | 30 | 30 | 35 | 15 | 24 | 22 | 30 | 24 | 6.2 | 16 | 13 | 29 |
|                | V         | 120 | 100|100 |120 |100 |120 |85 |100 |49 |21  |38 |44 |50  |    |
|                | La        | 43  | 39 | 50 |52  |    |    |    |    |    |    |    |    |    |
|                | Yb        | 1.7 | 2.2| 2.46|2.82|    |    |    |    |    |    |    |    |    |

Notes: The analyzes were performed at IGABM SB RAS – analysts of D. A. Kulagina, G. N. Okhlopkova, S. E. Diakonova. H₂O not included in the amount. Melt temperature by [16].
Figure 4. Parameters of the chemical composition of the rocks of Elikchan massif
1 – granodiorites and 2 – granites
a) SiO$_2$ – Na$_2$O + K$_2$O ratios in granitoids. Diagram fields [17]: I – gabbro; II – gabbro-diorites; III – diorites, IV – granodiorites, V – granites; VI – subalkaline gabbro; VII–VIII – monzonites; IX–X – syenites; XI – alkaline granites;

b) Aluminousit and geodynamic position of granitoids. Diagram fields [18], granitoids: IAG – of island-arcs, CAG-of continental arcs, CCG – of continental collision, POG – of postorogenic, CEUG – of continental epeirogenic uplift, RRG – of riftogenic.

c) Sr – Rb/Sr ratios in granitoids. Trends of differentiation of typical series [19]: I – tholeitic series of island arcs, II – calcareous-alkaline series of island arcs, III – calcareous-alkaline series of active margins, IV – series of rift zones of continents; I, S, A – petrotypes of granitoids.

The high activity of chlorine, the main extragent of Au, during the crystallization of granodiorites was favorable for the decrease from LREE to HREE and a very slight minimum of Eu, and are also close to those of magmatic formations of the active margins of continents (Figure 5).

The granodiorite melt was generated as a result of selective melting of amphibolites [20]: Al/(Mg+Fe) mol. = 0.2–0.4, Ca/(Mg+Fe)mol. = 0.5–0.8). In accordance with this, the melt temperature is determined as 1040–1060°C at a pressure of 1.2–1.4 GPA (calculation for [21]). Granite melt is formed at a higher level – as a result of selective melting of the dacite-rhyolite horizons of the crust: (Al/(Mg+Fe) = 1.8–3, Ca/(Mg+Fe) = (0.6–0.9) at a temperature of 880–920°C.

At the J. Maeda diagram (Figure 6) the points of granodiorite and granite compositions indicate counter trends, which allows us to speak about the independent development of their magmatic hearths and confirms the assumption about the polygyny of massif.

Geochemical specialization of granitoids is mostly expressed, in chalcophile elements – Sb, Bi, Ag, As, as well as in W and B, i.e. on elements that are especially characteristic of latite magma derivatives, as well as increased Ba, Ni, Co contents and La/Yb values (18–20) [1]. The main role of the volatiles here belongs to B, while the contents of F, Li, and Rb, generation of gold-ore occurrences. At the same time, melt stops in intermediate chambers during the intrusion, which involved partial distillation of the melt, did not contribute to the formation of a thick ore-bearing fluid flow. Accordingly, only small Au-Ag ore occurrences are identified within this massif and its exocontact aureoles.

Biotite granites are characterized by slightly higher Li, B, and Sn contents in comparison with granodiorites, and they were crystallized under reducing conditions with slightly higher fluorine activity than granodiorites. This brings them closer to rare metal systems. However, the melt reached the saturation stage only at the late stage of the crystallization of granites of the Istekh massif, but even then the water pressure in the system remained below the total (Figure 3b). As a result, only disseminated mineralization is associated with granites which is mainly of mineralogical interest.
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Figure 5. Chondrite-normalized [22] distribution of rare earth elements in magmatic rocks
1 – granodiorite, 2 – amphibole-biotite granite, 3 - biotite granite, 4 – leucogranite;

In the post-magmatic stage, along the fault zones and zones of increased fracturing, both granitoids and trachydolerites were propylitized, with the supply of Pb, Sb, As, Ag, Au, which concentrations increase up to 100 times. Concentrations of Sn, Mo, and B also increase slightly. Occurrences of Au low-sulfide ore formation are confined to this site.

4. Discussion of results
The Elikchan massif is localized in the zones of regional tension faults that functioned at least throughout the entire Cretaceous. Granitoids of massif are similar in most composition parameters to granitoids of the latite series, which genesis is usually related to the processes of syntexis or fluid interaction of crustal and mantle magmas [1]. Granodiorites record restite clinopyroxene, corresponding to that of basites and ultrabasites; tschermakite typical for amphibolites and eclogites; clusters of restite oligoclase and high calculated temperatures of the parental melts, this fact indicates a heterogeneous structure of magmad-forming substrates and the beginning of melting when they are affected by the main melt. This interaction also explains the low values in the 87Sr/86Sr granodiorites (0.7057). Granite melts are formed at higher crust horizons, have purely crustal values of 87Sr/86Sr (0.7110–0.7112) and are similar in chemical composition to S-type granites. Consequently, the studied granitoid massifs are polygenetic.

Crystallization of granodiorites under conditions of high activity of oxygen, water and chlorine, favorable for the generation of gold mineralization [11]. High significance correlation of gold with trace elements of the iron group Co, Ni, V, Cr (correlation coefficient $r = 0.46–0.99$), on one hand, and significant – with borum ($r = 0.47$), on the other, indicate a polygenic source of Au, and simultaneous high significance correlation of Au with Ag, Bi, Pb, Cu ($r = 0.48–0.77$) provided the complexity of the deposit [24]. For the Elikchan massif, during the formation of which there was a multi-stage magma intrusion with stops in intermediate chambers, where crystallization was accompanied by separation and discharge of the fluid phase, the early magmatic flow of solutions was dispersed, and as a result, only small Au-Ag manifestations were generated. Biotite granites were crystallized in conditions similar to those of rare metal systems. However, water pressure in the systems even at the end of crystallization remained lower than the total one, so despite the well-defined geochemical specialization of granites in Sn, W, Mo, Ag, only impregnated cassiterite, wolframite, molybdenum are associated with them.
5. Conclusions
The Elikchan massif is a polygenic polyformational magmatic formation. The typomorphism of minerals of the early magmatic association and restites in granodiorites, the proximity of rocks to granitoids of the latite series indicate the presence of basic rocks in the magma-forming substrate and allow us to assume the origin of granodiorite magma under the influence of heat and substance of deep magmas and partial mixing or impregnation with the latter of the formed melt. Biotite granites correspond to crustal formations in terms of composition parameters. The massif involves complex polygenetic and polyformational mineralization, which is one of the necessary criteria for high ore productivity of territories. However, the formation conditions of the massif were unfavorable for the generation of large-scale deposits.

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