Mineralogical-geochemical features of contact zone rocks of the Shivey alkaline granite-quartz-syenite and Chadal gabbroic massifs (Eastern Tuva)

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Abstract. The Kaakhem (> 30,000 km²) is one of the major magmatic areal within the Altai-Sayan folded area (Eastern Tuva, Russia). Formations of the Kaakhemsky area were more than 250 million years with change of geotectonic conditions. The last stage is bound to intraplate magmatism (300 Ma ago). Massifs of bimodal association – gabbroic and alkaline granitoids particularly the Chadal gabbroic and the Shivey granite-quartz-syenite massifs were formed as a result of its activities within the Kaakhem magmatic areal. The object of the study are rocks breccia-like and drip-like structurs in the contact zone of the alkalai-granitoid Shivey and gabbroid Chadal massifs in the Kaakhem magmatic. Predecessors repeatedly noted that such structurs relationships have typical features of mingling: flexuous, scalloped contours of mafic bodies with orientation of protrusions towards granitoids; oval, rounded form of basal fragments; signs of plastic deformation in the basices and others. Geochemical analysis of rare and scattered elements contents in contact zone rocks showed strongly marked character of hybridization. Results of scanning electron microscope analysis and X-ray microanalysis let consider the probable sequence of mineralization in contact zone of massifs of bimodal association of gabbroic and alkaline granitoids of the Kaakhem magmatic areal. Relationship established between microtexture and geochemical inherity indicate the interaction of basic and granitic magmatic meits and it was formation of middle group rocks.

1. Introduction
The Kaakhem (> 30,000 km²) is one of the major magmatic areal within the Altai-Sayan folded area. Geochronological studies of rocks of the Kaakhem magmatic areal showed that its formation was a result of progression changes in the island-arc (562 Ma), accretionally-subductional (536 Ma), collisional (512 Ma), transform-shearing (480 - 385 Ma) [1] as well as intraplate (297 – 293 Ma) geodynamic situation [2]. Island-arc stage was accompanied by basalt-andesite-rhyolite volcanism. Accretionally-subductional magmatism begins with the formation of gabbroid massifs of high alkalinity with intraplate geochemical characteristics presenting the Altai-Sayan mantle hot spot (mantle plume). There are 3 manifestation stages of gabbroid magmatism and 6 of granitoid magmatism within 512 to 474 Ma. Predominant part of these granitoids is located in the west of the areal [3, 4, 5]. The next and the main stage of granite formation is post-collisional preceded by formation of gabbroids with intraplate marks after a break of 25 Ma in the interval of 455 – 445 Ma. Granitoids of this stage occupy hundreds of kilometers and form the major part of the Kaakhem areal. Granitoids' geochemical characteristics of this stage outline the features of the substrate composition from which granitic magmas were melted [1, 6, 7]. The last stage of granite formation is associated
with mantle plume (intraplate magmatism) which has existed ~ 300 Ma ago. Massifs of bimodal association – gabbroic and alkaline granitoids particularly the Chadal gabbroid and the Shivey alkaline granite-quartz-syenite massifs were formed as a result of its activities within the Kaakhem magmatic areal.

The object of the study are rocks breccia-like and drip-like structures in the contact zone of the Shivey and Chadal massifs (figure 1). Authors of the earlier research studies repeatedly noted that such texture relationships have typical features of mingling: meandering, scalloped, lobed margins of mafic bodies with orientation of protrusions towards granitoids; oval, rounded form of basic fragments; elements of plastic deformation in the basics (figure 2).

![Figure 1](image1.jpg)

**Figure 1.** Mingling ratios of the Shivey alkaline granite-quartz-syenite massif with the same-aged gabbroic of the Chadal Massif (photo by Khertek A K)

![Figure 2](image2.jpg)

**Figure 2.** Scalloped edges in the contact zone of the Shivey and Chadal massifs (photo by Khertek A K)

Fragments morphology of acidic composition inside the mafic has an isometric form or relatively large irregularly shaped domains with rounded boundaries. Such case is not typical because viscosity
of granitic magma is higher than the mafic one. Classic features of mingling include specific granite «veins» within basic bodies indicating impregnation of acid magma through contraction cracks separating the cooling basic body into fragments. All these features are usually treated as evidence of contact of two liquids with different viscosities, mechanical mixing with the simultaneous intrusion of basic and salic melts [8, 9].

Contact zone of the Shivey and the Chadal massifs with mingling features occupy an area of about 12 km² according to geological observations. Granitoids generally save a leucocratic outlook in contact with gabbroic. Features of chemical mixing are widely occurred only in injection bodies intruding inside the basic associations directly in the contact of granitoids with basic where narrow zones with a width of 1–3 cm are occasionally noted where granitoids are enriched in femic minerals and in some cases they change their composition to a more basic one.

Gabbroic have clear reactionary effect indicators of granitic magma unlike granitoids. They are visually expressed in the abundance of bleaching spots and zones, often extending into the gabbroic bodies directly to the continuation of disappeared granitoid apophyses [9 - 12].

2. Object and methods of research
Composition of breccia-like and drop-shaped separate rocks was studied in contact zone of the Shivey and the Chadal massifs. Chemistry of minerals was studied by the electron microprobe analysis on a Tescan Vega II LMU scanning electron microscope with an Oxford INCA Energy 350 EDS system operated at an accelerating voltage of 20 kV, a beam current of 5 nA, a beam size of 1–2 μm and 120s count time. The operation conditions were the same for all minerals. The results were checked against natural minerals and synthetic phases used as standards (MAC 55 Standard Universal Block Layout+F/Cup, Micro-Analysis Consultants Ltd, UK) for calibration. The analyses were carried out at the National Research Tomsk State University (Tomsk). The concentrations of trace elements and REE were determined by ICP-MS on an Agilent 7500cx at the Tomsk University.

3. Petrography and mineralogy.
The Shivey massif has a complex structure and it is mainly composed of syenite-porphyry, leucocratic quartz syenite. The Chadal massif mainly consists of olivine gabbro, gabbro-norite, amphibole gabbro [13].

Petrography of contact zone rocks of the Shivey and the Chadal massifs differs from the petrography of the massifs rocks. Leucocratic rocks of contact zone are represented by biotite-hornblende syenite and quartz monzodiorite, mesocratic-quartz biotite-hornblende monzonite and subalkaline biotite-hornblende diorite.

Generalized data of petrographic analysis and scanning electron microscopy are given in table 1. Composition of rock-forming minerals of contact zone rocks corresponds to the rocks of the middle group of normal and subalkaline series: diorite-monzonite-syenite, the main part of studied rocks is both light and dark belonging to the monzonite series.

It is found that plagioclase is often more acidic than oligoclase-andesine typical for monzonites (№ 30-50) according to the studied chemical features of rock-forming minerals (table 2). There are zonation plagioclase individuals with a characteristic direct zonality (№ 56–35–15) with the marginal zone being insignificant and more similar to metasomatic one in rocks of monzonite series. Porphyry-like separations of orthoclase are corroded by acidic plagioclase (№ 19–20) in syenite. Plagioclase similar in composition is also found in the form of poikilitic inclusions in orthoclase. There is 9–12% of albite molecule in orthoclase content of studied rocks. The analyzed orthoclase individuals often contain 0.5–1 wt.% BaO. Orthoclase of quartz biotite-hornblende monzodiorite is mostly enriched by barium and there is no Ba at any quartz monzodiorite individuals according to energy-dispersive analysis (table 3).

Dark-colored minerals are represented by amphibole and biotite in the rocks. They form isometric aggregates which make rock slightly porphyry-shaped in subalkaline diorites.
Calcium amphiboles are established in the rocks of the contact between the Shivey and the Chadal massifs, the common chemical property of which is increased magnesia. They all correspond to magnesian hornblende. An inverse dependence of Si and Mg/(Mg+Fe$^{2+}$) content is observed in the structure of amphiboles (figure 3, table 4).

**Table 1. Petrography the rocks of contact zone of the Shivey and Chadal massifs.**

| Rock type                | Leucocratic                                      | Mesocratic                                      | Quartz mononcite biotite-hornblende |
|--------------------------|--------------------------------------------------|------------------------------------------------|-------------------------------------|
|                          | Syenite biotite-hornblende                        | Quartz moncodiorite                             | Subalkaline diorite biotite-hornblende |
|                          | Quartz moncodiorite                               | Fine grained, monzonitic                        | Porphyroid matrix of fine grained    |
|                          | Medium and coarse grained, porphyroid             | Medium and coarse grained hypidiomorphic        | Porphyroid matrix of hypidiomorphic, monzonitic |
| Rock texture             | Fsp$^a$ 50-55 $%$; Pl$^b$ 30-70 $%$; Bt$^c$ 10-12 $%$; Am$^d$ 10-12 $%$; Q$^e$ $\leq$ 5 $%$ | Fsp 25 $%$; Pl$_{30-45}$ 50 $%$ (zoning of crystals); Bt 10-15 $%$; Am 10-15 $%$; Q $\leq$ 5 $%$ | Fsp 20 $%$; Pl$_{30-45}$ 50 $%$ (zoning of crystals); Bt 20 $%$; Am 20 $%$; Q $\leq$ 5 $%$ |
| Rock-forming minerals    | Mgt c V and Ti-Mgt - 1 $%$, Titanite < 1 $%$, Apatite < 1 $%$, Zircon (Hf) < 0,1 $%$. | Apatite (Sr, Cl) $\leq$ 1 $%$, Mgt and Ti-Mgt $\leq$ 1 $%$, Apatite < 1 $%$, Titanite $\geq$ 1 $%$, Zircon < 0,1 $%$, sulfides (pyrite, chalcopyrite). | Mgt and Ti-Mgt $\leq$ 5 $%$, Apatite $\geq$ 1 $%$, Titanite $\geq$ 1 $%$, Baryte, Sulfides (pyrite, sphalerite). |
| Secondary minerals       | Epidote Chlorite Group (Clinochlore)              | Apatite (Sr, Cl) $\leq$ 1 $%$, Mgt and Ti-Mgt $\leq$ 1 $%$, Apatite < 1 $%$, Titanite $\geq$ 1 $%$, Zircon < 0,1 $%$, sulfides (pyrite, chalcopyrite). | Mgt c Cr and Ti-Mgt $\leq$ 1 $%$, Apatite (c F) $\leq$ 1 $%$, Titanite $\geq$ 1 $%$, Zircon - s.g., Allanite - s.g., Monazite - s.g., Sulfides (pyrite, sphalerite). |
| Accessory minerals       | Mgt c V and Ti-Mgt - 1 $%$, Titanite < 1 $%$, Apatite < 1 $%$, Zircon (Hf) < 0,1 $%$. | Titanite $\geq$ 1 $%$, Mgt and Ti-Mgt $\leq$ 1 $%$, Apatite < 1 $%$, Titanite $\geq$ 1 $%$, Zircon < 0,1 $%$, sulfides (pyrite, chalcopyrite). | Titanite $\geq$ 1 $%$, Zircon - s.g., Allanite - s.g., Monazite - s.g., Sulfides (pyrite, sphalerite). |

$^a$ Fsp = orthoclase, Pl = plagioclases, Bt = biotite, Am = amphibole, Q = quartz.

$^b$ s.g. = simple grains.

More ferruginous varieties are essential for syenite amphiboles. Mg amount prevails over Fe in amphiboles of diorites and monzodiorites. Silica content in amphiboles from monzonites is higher than in individuals from syenite and diorites.

Biotite is present at rocks in varying amounts and it is a typical biotite because annite and phlogopite component contents are $\sim$ 50–50% (figure 4, table 4). Biotite is low-titaniunm (Ti=TiO$_2$/(TiO$_2$+FeO$^+$+MgO+MnO) of 0.10 units from all the presented species of contact zone rocks. More ferruginous biotite is characteristic for syenites, magnesium biotite are characteristic for monzodiorites.
Ti and Fe oxides (ilmenite, magnetite), calcium phosphate (apatite), silicates (titanite, zircon) are present at accessory minerals. Ilmenite and magnetite are present at all contact rocks of the Chadal and the Shivey massifs. Magnetite has 2 generations. Vanadium is present (V₂O₅ 0.3–0.5 wt.% in magnetite of the second late generation in the form of an impurity, chromium (Cr₂O₃ from 0.4–2.0 wt.%) is fixed in diorite individuals. Ilmenite is TiO₂/FeO* from 0.9 to 1.3 according to type-chemical criteria, the presence of manganese impurities (1.4–4.75 and 8.8–15 wt.%) corresponds to individuals from granitoids and alkaline rocks. A significant amount of pyrophanic molecule (MnTiO₃) is characteristic of individuals from quartz monzodiorites and quartz amphibole-biotite monzonites. The exsolution texture is occurred in ilmenite from monzodiorite and diorite, there are lamellas of magnetite (I) subparallel extended, less often they are of irregular shape in ilmenite matrix.

Titanite is present at all the described rocks and can form both hypidiomorphic secretions and can be a substitution product of ilmenite or can form fouling border around ilmenite. Titanite of late generations is often enriched with iron, it may be due to the smallest presence of iron oxide (magnetite) proper in titanite matrix.

**Table 2.** Representative major-element compositions of plagioclases from the rocks of contact zone of the Shivey and Chadal massifs.

| Rock | 1 (zoned mineral) | 1 (5) | 2 (5) | 3 (7) | 4 (5) | 5 (6) |
|------|------------------|-------|-------|-------|-------|-------|
| SiO₂ | 54.62            | 60.22 | 67.29 | 64.81 | 63.68 | 64.06 |
| TiO₂ |                  |       |       |       |       |       |
| Al₂O₃| 28.66            | 25.66 | 21.07 | 22.82 | 22.42 | 22.42 |
| MgO  |                  |       |       |       |       |       |
| MnO  |                  |       |       |       |       |       |
| Fe₂O₅|                  |       |       |       |       |       |
| CaO  | 11.79            | 7.49  | 3.01  | 4.21  | 3.98  | 3.98  |
| Na₂O | 4.96             | 7.51  | 9.31  | 9.33  | 9.12  | 9.51  |
| K₂O  | 0.21             | 0.31  | 0.75  | 0.20  | 0.36  | 0.40  |
| BaO  |                  |       |       |       |       |       |
| Total| 100.23           | 101.46| 101.41| 101.35| 99.62 | 100.58| 101.08| 99.99 |
| Si,  apfu| 2.46 | 2.65 | 2.94 | 2.84 | 2.83 | 2.815 | 2.74 | 2.77 |
| Ti   |                  |       |       |       |       |       |       |
| Al   | 1.52             | 1.33  | 1.08  | 1.17  | 1.17  | 1.16  | 1.26  | 1.23 |
| Mg   |                  |       |       |       |       |       |       |
| Mn   |                  |       |       |       |       |       |       |
| Fe   |                  |       |       |       |       |       |       |
| Ca   | 0.57             | 0.35  | 0.14  | 0.20  | 0.19  | 0.19  | 0.29  | 0.25 |
| Na   | 0.43             | 0.64  | 0.79  | 0.79  | 0.79  | 0.81  | 0.70  | 0.72 |
| K    | 0.01             | 0.02  | 0.04  | 0.01  | 0.02  | 0.02  | 0.02  | 0.01 |
| Ba   |                  |       |       |       |       |       |
| Ca (An) | 56.13 | 34.95 | 14.54 | 19.71 | 19.03 | 18.40 | 28.26 | 25.45 |
| Na (Ab) | 42.68 | 63.35 | 81.18 | 79.23 | 73.92 | 79.42 | 70.18 | 73.38 |
| (Ort) | 1.19             | 1.70  | 4.29  | 1.07  | 2.06  | 2.19  | 1.56  | 1.18 |

1 Composite grain.
2 Numerals in panel stand for: 1 = quartz monzodiorite; 2 = syenite biotite-hornblende; 4 = quartz monconite biotite-hornblende; 5 = quartz monconidiorite biotite-hornblende.
3 Numerals in braces show number of analyses.
4 (–) is below detection limit.
5 Atoms per formula units (apfu) are based on 8 oxygens
6 An = anorthite minale (molecule), Ab = albite, Ort = orthoclase.
Table 3. Representative major-element compositions of orthoclase from the rocks of contact zone of the Shivey and Chadal massifs.

| Rock                              | Leucocratic |               | Mesocratic |               |
|-----------------------------------|-------------|---------------|------------|---------------|
|                                   | 1 (6)       | 2 (6)         | 4 (5)      | 5 (6)         |
| SiO$_2$, wt.%                     | 65.84       | 64.79         | 64.45      | 64.67         |
| TiO$_2$                           | -           | -             | -          | -             |
| Al$_2$O$_3$                       | 18.32       | 18.33         | 18.245     | 18.3          |
| MgO                               | -           | -             | -          | -             |
| MnO                               | -           | -             | -          | -             |
| FeO                               | -           | -             | -          | 0.25          |
| CaO                               | -           | -             | -          | -             |
| Na$_2$O                           | 1.21        | 1.21          | 1.29       | 0.98          |
| K$_2$O                            | 15.57       | 15.31         | 15.46      | 15.70         |
| BaO                               | -           | 0.39          | 0.48       | 0.70          |
| Total                             | 100.93      | 100.00        | 99.94      | 100.58        |
| Si, apfu$^d$                      | 3.00        | 2.99          | 2.975      | 2.98          |
| Ti                                | -           | -             | -          | -             |
| Al                                | 0.98        | 1             | 0.99       | 0.99          |
| Mg                                | -           | -             | -          | -             |
| Mn                                | -           | -             | -          | -             |
| Fe                                | -           | -             | -          | 0.01          |
| Ca                                | -           | -             | -          | -             |
| Na                                | 0.11        | 0.11          | 0.12       | 0.09          |
| K                                 | 0.91        | 0.90          | 0.91       | 0.92          |
| Ba                                | -           | 0.01          | 0.01       | 0.01          |
| Ca (An)$^e$                       | -           | -             | -          | -             |
| Na (Ab)$^f$                       | 10.5        | 10.56         | 11.11      | 8.52          |
| K (Ort)$^g$                       | 89.5        | 88.75         | 88.06      | 90.25         |
| Ba (Cel)$^g$                      | 0.00        | 0.69          | 0.83       | 1.23          |

$^a$ Numerals in panel stand for: 1 = quartz moncodiorite; 2 = syenite biotite-hornblende; 4 = quartz monconite biotite-hornblende; 5 = quartz moncodiorite biotite-hornblende.

$^b$ Numerals in braces show number of analyses.

$^c$ (-) is below detection limit.

$^d$ Atoms per formula units (apfu) are based on 8 oxygens.

$^e$ An = anorthite minale (molecule), Ab = albite, Ort = orthoclase, Cel = celsian.

Apatite is presented by fluoroapatite. It has idiomorphic outlines. Apatite can be poikilitic inclusion in zircon, potassium feldspar, magnetite, ilmenite (at syenite). The apatite in the form of the finest individuals is found in all rock-forming minerals (except quartz) and also take places between parallel thin amphiboles crystals in the quartz monzodiorite.

Zircon forms classical two-pointed crystals. Its chemical composition is close to theoretical one. There is Hf (average value is up to 1.5 wt.% HfO$_2$) in the form of an impurity element.

There are minerals of rare earths (monazite, allanite) and Zr (baddeleyite) in association with listed mineral species.
Table 4. Representative major-element compositions of amphibole and of mica from the rocks of contact zone of the Shivay and Chadal massifs.

| Mineral | Amphibole | Mica |
|---------|-----------|------|
|         | Leucocratic | Mesocratic | Leucocratic | Mesocratic |
| Rock    | 1 (6) | 2 (6) | 3 (8) | 4 (6) | 5 (4) | 1 (5) | 2 (2) | 3 (4) | 4 (6) | 5 (7) |
| SiO₂, wt. % | 49.18 | 45.95 | 49.87 | 49.49 | 46.29 | 37.76 | 36.7 | 37.25 | 37.16 | 37.18 |
| TiO₂    | 1.25 | 1.20 | 1.11 | 1.13 | 1.44 | 3.97 | 3.96 | 4.27 | 3.30 | 3.64 |
| Al₂O₃   | 6.02 | 6.41 | 5.40 | 5.68 | 7.22 | 13.73 | 13.82 | 13.79 | 14.2 | 13.87 |
| MgO     | 14.9 | 11.00 | 14.34 | 12.69 | 11.65 | 13.09 | 11.25 | 12.56 | 12.53 | 12.22 |
| MnO     | 0.85 | 0.73 | 0.33 | 0.62 | 0.43 | 0.77 | 0.40 | - | 0.37 | 0.03 |
| FeO₈    | 13.5 | 18.27 | 14.49 | 15.96 | 17.53 | 18.67 | 21.4 | 19.39 | 20.6 | 20.21 |
| CaO     | 11.69 | 12.06 | 12.26 | 12.10 | 12.16 | - | 0.16 | 0.07 | - | - |
| Na₂O    | 1.28 | 1.22 | 0.89 | 1.18 | 1.23 | - | - | - | - | - |
| K₂O     | 0.51 | 0.74 | 0.49 | 0.61 | 0.75 | 9.33 | 8.73 | 9.25 | 8.61 | 9.53 |
| Cl      | - | 0.02 | - | 0.03 | - | 0.06 | - | - | - | - |
| P₂O₅    | - | 0.47 | - | - | - | - | 0.11 | - | - | - |
| Total   | 99.16 | 98.04 | 99.15 | 99.47 | 98.66 | 97.36 | 96.23 | 96.65 | 96.92 | 96.67 |
| Si, apfu d | 6.99 | 6.86 | 7.13 | 7.16 | 6.81 | 2.85 | 2.83 | 2.85 | 2.81 | 2.85 |
| Ti      | 0.13 | 0.13 | 0.12 | 0.12 | 0.16 | 0.23 | 0.23 | 0.24 | 0.19 | 0.21 |
| Al      | 1.00 | 1.13 | 0.91 | 0.97 | 1.26 | 1.22 | 1.25 | 1.24 | 1.26 | 1.25 |
| Mg      | 3.18 | 2.46 | 3.08 | 2.75 | 2.57 | 1.48 | 1.30 | 1.44 | 1.42 | 1.4 |
| Mn      | 0.10 | 0.09 | 0.04 | 0.07 | 0.05 | 0.05 | 0.03 | - | 0.02 | - |
| Fe      | 1.60 | 2.28 | 1.73 | 1.93 | 2.16 | 1.18 | 1.37 | 1.24 | 1.30 | 1.29 |
| Ca      | 1.78 | 1.93 | 1.88 | 1.87 | 1.92 | - | 0.01 | 0.01 | - | - |
| Na      | 0.35 | 0.36 | 0.25 | 0.33 | 0.35 | - | - | - | - | - |
| K       | 0.09 | 0.14 | 0.09 | 0.11 | 0.14 | 0.9 | 0.86 | 0.9 | 0.83 | 0.93 |
| Cl      | - | 0.01 | - | 0.01 | - | 0.01 | - | - | - | - |
| P       | - | 0.06 | - | - | - | - | - | - | - | - |
| O       | - | - | - | - | - | 0.27 | 0.22 | 0.35 | 0.10 | 0.29 |
| OH      | - | - | - | - | - | 1.72 | 1.79 | 1.65 | 1.90 | 1.71 |
| Σ X     | - | - | - | - | - | 0.90 | 0.86 | 0.92 | 0.84 | 0.93 |
| Al IV   | 1.01 | 1.14 | 0.87 | 0.85 | 1.19 | 1.15 | 1.18 | 1.15 | 1.19 | 1.15 |
| Al VI   | 0.07 | 0.08 | 0.08 | 0.07 | 0.07 | - | - | - | - | - |
| C site total | 5.01 | 4.96 | 4.96 | 4.87 | 4.94 | - | - | - | - | - |
| Na₂     | 0.22 | 0.07 | 0.12 | 0.13 | 0.08 | - | - | - | - | - |
| Na₃     | 0.13 | 0.28 | 0.12 | 0.21 | 0.27 | - | - | - | - | - |
| A site total | 0.22 | 0.42 | 0.21 | 0.32 | 0.41 | - | - | - | - | - |
| MgO c   | 0.67 | 0.52 | 0.64 | 0.59 | 0.54 | - | - | - | - | - |
| Fe (Ann) b | 39.14 | 45.74 | 41.13 | 43.2 | 42.97 | - | - | - | - | - |
| Mg (Phil) | 49.40 | 43.28 | 47.95 | 47.35 | 46.79 | - | - | - | - | - |
| Al (Mus) | 2.34 | 2.53 | 2.78 | 2.41 | 3.20 | - | - | - | - | - |
| Mn (?)  | 1.63 | 0.86 | - | - | 0.80 | 0.07 | - | - | - | - |

a Numerals in panel stand for: 1 = quartz monconodiorite; 2 = syenite biotite-hornblende; 3 = quartz monconite biotite-hornblende; 4 = quartz monconidiorite biotite-hornblende.
b Numerals in braces show number of analyses.

c (-) is below detection limit.
Atoms per formula units (apfu) are based on \( A_{0.6}B_{2}C_{4}[T_{4}O_{11}]_{2}(OH, O, F, Cl) \) (amphibole) and \( \ce{XY_{2.3}AlSi_{3}O_{10}}(OH, F, Cl)_{2} \) (mica).

\[ \text{Mg}^\# = \text{Mg}/(\text{Mg}+\Sigma \text{Fe}). \]

Ann = annite minale (molecule), Phl = phlogopite, Mus = muscovite, (?) = abstract molecule.

**Figure 3.** Chemistry of amphiboles from the rocks of contact zone of the Shivey and Chadal massifs. Classification diagram, after [14]

**Figure 4.** of micas from the rocks of contact zone of the Shivey and Chadal massifs

Numerals in panel figure 3 and 4 stand for: 1 = quartz moncodiorite; 2 = syenite biotite-hornblende; 3 = subalkaline diorite biotite-hornblende; 4 = quartz monconite biotite-hornblende; 5 = quartz moncodiorite biotite-hornblende.

4. Geochemical characteristics of contact zone rocks

Geochemistry of contact zone rocks indicates the process of chemical mixing (figure 5). Granitoids of the Shivey massif are enriched with incompatible elements especially Th, K, Zr (up to 1086 ppm) and Hf, less and unevenly with Ta and Nb (0.49–7.07 and 4.94–69.8 ppm) and rare earth elements (ΣREE = 142–420 ppm) especially with light REE [2, 13, 14]. The presence of positive anomalies Ba, Th, U and K, Sm and negative anomalies Nb-Ta and Zr-Hf are characteristic for contact rocks (both leuco-and mesocratic).

Geochemical feature of contact zone rocks is a weak europium minimum and gentler slope in comparison with the case of REE distribution in rocks of the Shivey massif (figure 5b).

5. Results discussion and conclusion

Analysis of mineral associations of contact rocks of the Shivey and the Chadal massifs and their geochemical features showed that a reactionary effect occurred between the crystallized melt products and melts. Crystallization of minerals is occurred in two ways according to texture relationships. Manifestation of accessory and ore minerals occurred firstly: small crystals apatites, then zircon, ilmenite and magnetite. Aluminosilicates and silicates are abundantly formed later: titanite, orthoclase, medium plagioclase, hornblende, biotite and quartz. Secondly reverse situation is obvious where the rock-forming minerals are crystallized in the beginning and ore minerals are crystallized after.
Earlier formation of apatite (fluoroapatite) suggests high acidity at initial stages of crystallization because $\text{[PO}_4\text{]}^{3-}$ is one of the strong acid anions. Another fact indicates on increased acidity of the melt with the presence of orthosilicic acid – feldspars formation is later than apatite and zircon. Aluminum forms an aluminosilicate anion as an amphoteric element in alkaline silicate melts resulting in formation of feldspars and feldspathoids.

Another feature of mineral formation is the presence of exsolution texture in ilmenite which is characteristic of ilmenite from gabbro. It is worth noting that apatite inclusions are not found in these ilmenite individuals. Fact considering this ilmenite as a relic product of crystallization of a basic magma composed of the Chadal massif remains unclear because no other signs have been found. Typochemical characteristic of second-generation magnetite forming isometric crystals and presenting with ilmenite in one paragenesis let suggest that it could crystallize from the melt of basic composition of both normal and increased alkalinity. The increased content of pyrophanic molecule in ilmenite is also a typomorphic feature of crystallization of a mineral species from alkaline melts.

Change of acidic situation to alkaline could occur against the background of an oxygen fugacity increase. This process is occurred in replacement borders of ilmenite with titanite. Ilmenite becomes unstable that could result to its replacement with calcium and orthosilicic acid in the system as well as ferric oxide.

Geochemical analysis of rare and scattered elements contents in contact zone rocks showed strongly marked character of hybridization. These rocks are characterized by a sharp predominance of light over heavy lanthanides. Negative Zr-Hf anomalies and positive anomalies Th and U are especially strongly marked. Contact zone rocks occupy an intermediate position between REE distribution curves in rocks of the Shivey and the Chadal massifs according to REE content.

Results of raster electron microscopy and X-ray microanalysis let consider the probable sequence of mineralization in contact zone of massifs of bimodal association of gabbroic and alkaline granitoids of the Kaakhem magmatic areal. Relationship established between microtexture and geochemical inherity indicate the interaction of basic and acid melts with rock formation of middle group.

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