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MINERAL REACTIONS IN HIGH-ALUMINA FERRIFEROUS METAPELITIC HORNFELSES: THE PROBLEM OF STABILITY OF RARE PARAGENESES OF CONTACT METAMORPHISM

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A detailed petrological study has been given to high-alumina ferriferous hornfelses characterized by the development of mineral associations (Cld + Bt, Cld + Bt + And, and Crd + Grt + Ms), quite rare for contact metamorphism. The sequence and stability of the observed parageneses were thoroughly analyzed in terms of the Harte-Hudson, Spear-Cheney, and Powell-Holland petrogenetic grids. It has been shown that in the contact aureole of the Ayakhta Massif: (1) the formation of chloritoid atypical of thermal metamorphism and the stability of rare parageneses (Cld + Bt and Cld + And + Bt) are explained by a rare combination of appropriate pressure (≥3 kbar) with a specific type of rocks enriched in both Al and Fe; (2) the appearance of the Grt + Crd + Ms paragenesis is caused by specific chemical compositions of Mn-enriched garnet and high-Al high-Fe rocks; (3) the development of Crd-And parageneses and staurolite-free associations at the intermediate steps of contact metamorphism is explained by the simultaneous expansion of the Grt + Chl field with participation of Mn-garnets and narrowing, up to complete disappearance, of the St + Bt stability field; (4) the sequence of the observed parageneses and reactions in high-Al Fe-rich hornfelses of the Ayakhta aureole is in agreement with the Spear-Cheney thermodynamic petrogenetic grid.

Metapelites, chloritoid, mineral reactions, petrogenetic grids

INTRODUCTION

One of the main concerns of metamorphic petrology is to reveal regularities of changes in the set of parageneses and the chemical composition of their minerals depending on the physicochemical conditions of their formation. The results of this research are used for constructing quantitative petrogenetic grids for various chemical systems. Modern petrogenetic grids for metapelites correctly and thoroughly describe mineral equilibria in rock complexes that occur at moderate- and high-pressure depths. Nevertheless, they are too contradictory and provide information insufficient for analysis of parageneses in low-pressure metapelites and hornfelses, particularly in hornfelses with a specific chemical composition and parageneses rare for thermal metamorphism. Therefore, we carried out a detailed petrological study of high-Al high-Fe hornfelses to recognize the cause of the formation and development of these parageneses and to determine their stability fields. The obtained petrological data on the *PT*-stability of parageneses were analyzed in terms of the available petrogenetic grids for metapelites. This helped to estimate the feasibility of these grids for interpreting the actual mineral transformations during contact metamorphism of high-Al high-Fe metapelites as well as to recognize and substantiate the cause of the formation and development of rare parageneses in the study aureole.

To solve the posed problems, we considered the thoroughly described contact aureole of the Ayakhta granitoid massif [1, 2], chosen for study for the following reasons: (1) Special petrochemical investigations showed that the mineral transformations in metapelites were isochemical processes and the evolution of mineral chemical compositions during contact metamorphism was governed by the *PT*-conditions of formation of the initial rocks [2]. (2) The formation of chloritoid atypical of thermal metamorphism and the stability of rare parageneses

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(chloritoid + biotite, chloritoid + biotite + andalusite, and cordierite + garnet + muscovite) in the Ayakhta aureole arouse much interest to the study hornfelses. Mineral associations including chloritoid are often found in regional metamorphic metapelites [3–7] and seldom in typical contact aureoles [8–13]. The rare occurrence of these parageneses is explained by the lithologic specifics of the rocks in which they form [14–16] and by the narrow temperature range of their stability at low-pressure thermal metamorphism [17]. Droop and Harte [18] reported only three findings of the Cld + Bt + And paragenesis in contact aureoles: Tono, Japan [19], Karatash, Russia [20], and Insh, Scotland [21]. The rare Crd + Grt + Ms paragenesis is also missing from most of the thoroughly studied hornfels aureoles; there are only five publications reporting reliable evidence for the coexistence of muscovite, cordierite, and garnet [12]. (3) The Cld + Bt paragenesis always creates complications in constructing petrogenetic grids for metapelites, in which this association has different stability limits. For example, on the Harte-Hudson [22] petrogenetic grid for metapelites, this paragenesis is stable in terms of the system K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O (KFMASH) in a narrow temperature range at low pressures in contrast to the KFMASH of the Kepezhinskas-Khlestov [23] and Spear-Cheney [24] petrogenetic grids, in which this association is stable over a narrow temperature range at elevated pressures and over broad temperature and pressure ranges, respectively. Moreover, these petrogenetic grids differ seriously in the position of the Cld + Bt = Grt + Chl equilibrium (with the participation of Mu and Qtz) in the *PT*-field. The Spear-Cheney petrogenetic grid [24] implies the stability of the Cld + Bt paragenesis in the low-temperature side of the reaction in contrast to the Harte-Hudson grid [22], in which this association results from the Grt + Chl paragenesis with increasing temperature. Thus, the thermal aureole of the Ayakhta granitoid massif yields unique material for studying phase relations during the formation of rare parageneses. The drawn petrological conclusions permit one to critically analyze the body of information provided by the available petrogenetic grids for low-pressure metapelites formed under the contact-metamorphism conditions.

BRIEF GEOLOGICAL ESSAY AND METAMORPHIC ZONING

The contact aureole of the Ayakhta granitoid massif is located in the trans-Angarian part of the Yenisei Range, in the middle course of the Bol'shoi Pit River. The country rocks enclosing the massif are Middle Riphean deposits of the Sukhoi Pit series. In the study region, these are regionally metamorphosed pelites, which can be referred to the muscovite-chlorite subfacies of the greenschist facies judging from the stability of the hosted muscovite + chlorite + albite + quartz + rutile paragenesis. The contact-metamorphism aureole is revealed by the appearance of a new paragenesis including chloritoid and ilmenite in the enclosing graphite-bearing phyllites. Within the aureole, reaching 1 km in width, eight zones were recognized and the positions of seven contact-metamorphism isogrades were established (Fig. 1). From country rocks to intrusive contact, the parageneses change as follows (parenthesized are the number and name of zone and its apparent thickness):

(1) Chl + Ms + Pl + Qtz + Rut (0 — country rocks),
(2) Cld + Ms + Chl + Pl + Qtz + Ilm ± Rut (I — chloritoid zone, 45 m),
(3) Bt + Cld + Ms + Chl + Pl + Qtz + Ilm (II — biotite zone, 60 m),
(4) Grt + Bt + Cld + Ms + Chl + Pl + Qtz + Ilm (III – garnet zone, 35 m),
(5) And + Bt + Grt + Ms + Chl + Pl + Qtz + Ilm ± Cld (IV — andalusite zone, 300 m),
(6) Crd + And + Bt + Ms + Pl + Qtz + Ilm + Chl + Grt (V — lower cordierite zone, 400 m),
(7) Crd + And + Bt + Ms + Pl + Qtz + Ilm (VI — upper cordierite zone, 150 m),
(8) Sil + Kfs + Crd + Bt + Pl + Qtz + Ilm ± Ms ± And (VII — sillimanite-K-feldspar zone, 10 m).

The mineral symbols were taken from [25]. The parageneses found in hornfelses of each zone and the sequence of their change with increasing temperature are presented on the Thompson triangular diagrams [26] (Fig. 2). The mineralogical and petrographic characteristics of rocks of each zone, including detailed description of the microstructural relationships between the minerals and their chemical compositions, are given in [2, 27]. Some of these relationships are discussed below, where particular mineral reactions on the isogrades are considered.

According to the bulk chemical composition, the study rocks are initially inhomogeneous and are interpreted as ferriferous (FeO/(FeO + MgO + MnO) = 0.72–0.74 (molar ratio)) high-alumina (Al_2O_3–$3K_2O$–Na_2O/(Al_2O_3–$3K_2O$–Na_2O + FeO + MgO + MnO) = 0.30–0.32) metapelites [28]. On the AFM diagram [26], the chemical compositions of all rocks lie above the tie line of garnet-chlorite (Fig. 2).

MINERAL REACTIONS ON ISOGRADES

The isochemical nature of contact metamorphism was substantiated earlier; thus, the mass exchange between the reacting phases during metamorphism proceeded with maintenance of the mass balance (except for volatiles).

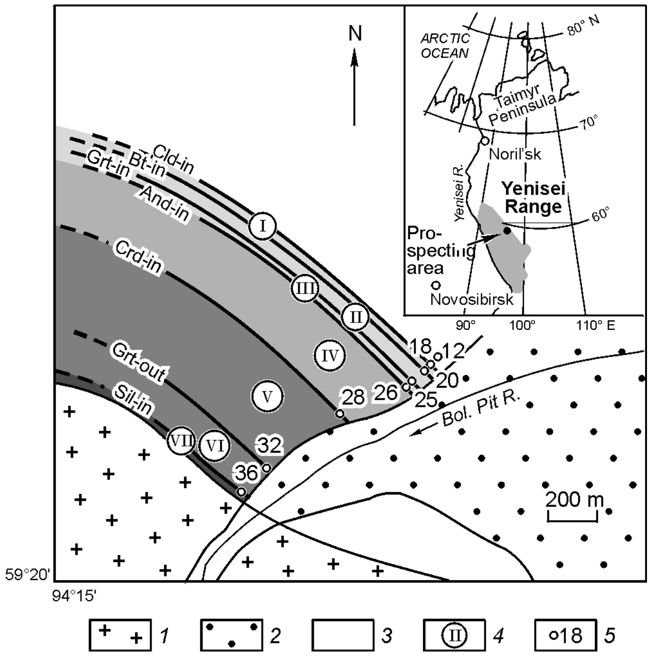

Fig. 1. Schematic metamorphic zoning of the northern exocontact of the Ayakhta granitoid massif (compiled using the data of geological survey (scale 1 : 50,000) by the Tsentral'naya team of the Angara geological-prospecting expedition and the results of geological study of the southern North Yenisei region (researchers Yu.F. Avdievsky, A.I. Vyzu, and P.S. Kozlov)). ***1*** **— granites;** ***2*** **— alluvium;** ***3*** **— country rocks;** ***4*** **— contact-aureole zones: I — chloritoid, II — biotite, III — garnet, IV — andalusite, V — lower cordierite, VI — upper cordierite, VII — sillimanite-K-feldspar;** ***5*** **— sampling localities with sample numbers. Isogrades are shown by solid lines dashed at the end.**

The equations of chemical reactions were calculated from the actual compositions of coexisting minerals (the systems K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O ± MnO ± TiO_2, i.e., KFMASH ± Mn ± Ti) using the MATHEMATICA 3.0 software (a matrix-algebra apparatus realized with the NullSpace technique). In each case, the number of components was determined by the actual composition of the system. The content of water in the chemical formulas of minerals was supposed to be stoichiometric; the content of structurally bound water in cordierite was taken equal to 0.5 moles, according to [29]. The calculated equations of chemical reactions were corroborated by the microstructural relationships between the mineral phases and changes in their contents and chemical compositions and then were discussed in complex with the literature experimental data on the *PT*-stability of minerals and their parageneses.

The first appearance of chloritoid in the contact aureole (Fig. 1, Cld-in isograde) can be described by the following mineral reaction for sample 18 in the KFMASHTi system:

$$0.704\mathrm{Ms_{c.r.}} + 0.023\mathrm{Chl} + 0.065\mathrm{Rt} =$$
$$= 0.657\mathrm{Ms_{c.z.}} + 0.029\mathrm{Cld} + 0.061\mathrm{Ilm} + 0.237\mathrm{Qtz} + 0.084\mathrm{H_2O}, \quad (1)$$

where $Ms_{c.r.}$ and $Ms_{c.z.}$ are muscovites from the country rocks and chloritoid zone, respectively. On the AKF diagram (Fig. 3), this reaction is reflected as the intersection of the $Ms_{c.r}$–Chl and $Ms_{c.z.}$–Cld tie lines. The formation of chloritoid on the aureole periphery from a chlorite mica + rutile aggregate is confirmed by the quantitative ratios of phases in microsections: An increase in chloritoid content is accompanied by a gradual decrease in chlorite and muscovite contents and a change in the chemical composition of muscovite. The formation of ilmenite from rutile is corroborated by the microstructural relationships between these minerals: The ilmenite grains on the chloritoid isograde often contain thin rutile lamellae. Chloritoid is usually produced in reactions involving pyrophyllite, kaolinite, or paragonite [30]. The X-ray patterns of white-mica fractions showed the complete absence

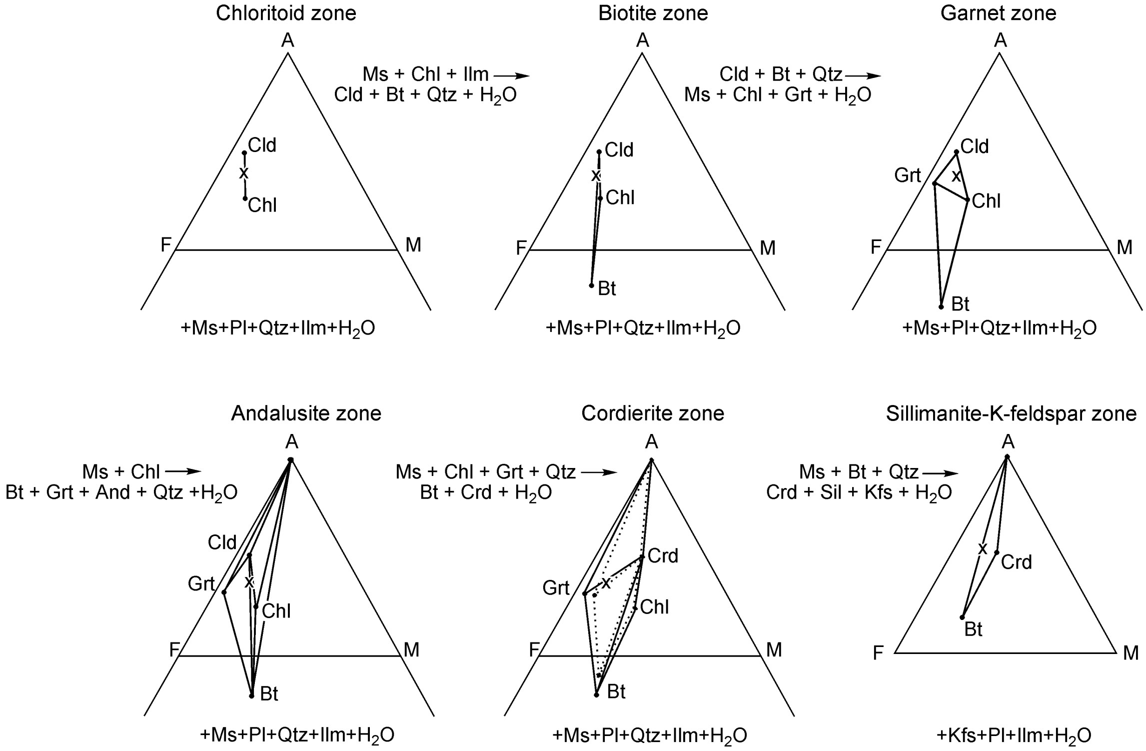

Fig. 2. Sequence of changes of parageneses with increasing temperature in metapelitic hornfelses of the Ayakhta contact aureole. The Thompson AFM diagram was constructed by projecting the compositions of minerals and rocks from Kfs, Pl, Ilm, and fluid onto the plane AFM (for the Sil-Kfs zone) at certain H_2O activity and from Ms, Qtz, Pl, Ilm, and H_2O (for the other zones). Dotted line shows the parageneses found in the upper cordierite zone.

of these minerals from the initial country rocks. Thus, the first chloritoid in the study aureole resulted from high-alumina chlorite, which agrees with mineral reactions of chloritoid formation described by Thompson and Norton [31] and Frey [32].

The stability of the rare Cld + Bt association is controlled mainly by the bulk chemical composition of rocks. Wang and Spear [16] established that this paragenesis exists when the total value of Fe/(Fe + Mg) is higher than 0.6, which corresponds to the chemical compositions of the Ayakhta ferriferous hornfelses. For sample 20, the mineral reaction responsible for the first appearance of biotite (Bt-in isograde; KFMASH) is as follows:

$$0.439\text{Ms} + 0.285\text{Chl} + 0.322\text{Ilm} = 0.372\text{Cld} + 0.364\text{Bt} + 0.359\text{Qtz} + 0.472\text{H}_2\text{O}. \quad (2)$$

On the AKF diagram (Fig. 3), this reaction is represented as the intersection of the Ms-Chl and Cld-Bt tie lines. The calculated equation reflects the course of mineral transformations with decreasing chlorite and muscovite amounts and increasing biotite and chloritoid contents and agrees with the observed Fe/(Fe + Mg) sequence of minerals (Bt < Chl < Cld) on the isograde of the first appearance of biotite (Fig. 2).

The first appearance of garnet in metapelites (Grt-in isograde) might be the result of the following reaction for sample 25 in the system KFMASH:

$$0.207\text{Bt} + 0.368\text{Cld} + 0.800\text{Qtz} = 0.250\text{Grt} + 0.311\text{Ms} + 0.149\text{Chl} + 0.035\text{H}_2\text{O}. \quad (3)$$

On the AFM diagram (Fig. 2), this mineral reaction responsible for the formation of the Grt + Chl paragenesis is reflected as the intersection of the Bt-Cld and Grt-Chl tie lines. It is known, however, that garnet-bearing mineral associations seldom originate at low pressures, and their stability during contact metamorphism is due to the high values of Fe/(Fe + Mg) of the rocks (≥0.60) [24], commensurate with those of the Ayakhta granitoids. Another factor that broadens the *PT*-stability range of Grt-involving parageneses might be the high content of MnO in metapelites and, hence, in garnets [33]. During the formation of garnet, MnO-rich chloritoid might have been the source of the oxide. This is also suggested from the presence of chloritoid inclusions in garnet and the quantitative ratios of these minerals (up to 25 vol.% Cld and up to 3 vol.% Grt) on the Grt-in isograde. Similar conclusions

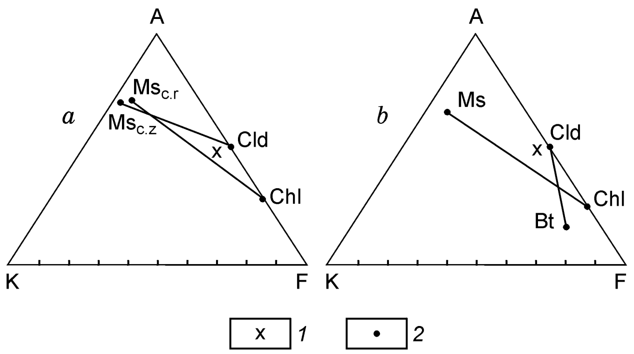

Fig. 3. AKF diagram for the chemical compositions of rocks (*1*) and minerals (*2*) on the isogrades of chloritoid (*a*) and biotite (*b*). The intersection of the $Ms_{c.r.}$–Chl and $Ms_{c.z.}$–Cld (*a*) and the Ms–Chl and Cld–Bt (*b*) tie lines is shown. A = Al_2O_3–K_2O–Na_2O; F = FeO + MgO + MnO; K = K_2O (in molar quantities).

were drawn by Whitney et al. [34], who reported the generation of garnet in the Dutchess County pelitic schists, USA, from chloritoid and biotite under the same *PT*-conditions of metamorphism.

Garnet and chlorite disappear simultaneously in the upper cordierite zone (Grt-out isograde), possibly, following the reaction (sample 32, KFMASH)

$$0.204\text{Ms} + 0.246\text{Chl} + 0.075\text{Grt} + 0.471\text{Qtz} = 0.422\text{Bt} + 0.166\text{Crd} + 0.682\text{H}_2\text{O}. \quad (4)$$

This equation corresponds to the observed sequence of the Fe/(Fe + Mg) values of minerals on the Grt-out isograde (Fig. 2): Crd < Chl < Bt < Grt. The reaction determines the upper bound of the stability of the Grt + Chl paragenesis in Ms-bearing metapelites. Above the Grt-out isograde, the major parageneses of the upper cordierite zone are Bt + Crd and Bt + Crd + And.

The mineral reactions calculated for sample 26 in the systems KFMASH (5) and KFMASHTi (6) determine the first appearance of andalusite in hornfelses (And-in isograde) for Grt- and (Cld + Ilm)-involving mineral associations, respectively:

$$0.329\text{Ms} + 0.180\text{Chl} = 0.272\text{Bt} + 0.089\text{Grt} + 0.404\text{And} + 0.082\text{Qtz} + 0.779\text{H}_2\text{O}, \quad (5)$$

$$0.399\text{Ms} + 0.236\text{Chl} + 0.028\text{Ilm} = 0.329\text{Bt} + 0.169\text{Cld} + 0.289\text{And} + 0.328\text{Qtz} + 0.676\text{H}_2\text{O}. \quad (6)$$

The occurrence of these mineral reactions and stability of the rare Cld + Bt + And paragenesis in the andalusite zone are supported by the relations of the initial phase and reaction products on the AFM diagram (Fig. 2), where the figurative composition point of chlorite lies inside the triangles formed by the composition points of the Grt + And + Bt and And + Cld + Bt parageneses. As the *PT*-stability range of rare garnet-involving mineral associations at low pressures significantly broadens with increasing MnO content in metapelite minerals [18, 28], we carried out the calculations with regard to all Mn-containing phases (ilmenite, chlorite, chloritoid, and garnet) in order to estimate the effect of MnO on the mineral transformations during the formation of andalusite. The latter process in the contact aureole is described for sample 26 in the system KFMASHTiMn by the reaction

$$0.395\text{Ms} + 0.231\text{Chl} + 0.028\text{Ilm} = 0.325\text{Bt} + 0.303\text{And} +$$
$$0.151\text{Cld} + 0.011\text{Grt} + 0.3\text{Qtz} + 0.693\text{H}_2\text{O}. \quad (7)$$

Thus, addition of Mn to the earlier considered systems virtually does not affect the mineral transformations during the formation of andalusite.

The mineral reactions calculated for sample 28 in the systems KFMASH (8) and KFMASHMn (9) determine the first appearance of cordierite in the contact aureole (Crd-in isograde) for Grt- and (Grt + And)-involving mineral associations, respectively:

$$0.263\text{Ms} + 0.213\text{Chl} + 0.018\text{Grt} + 0.452\text{Qtz} = 0.245\text{Bt} + 0.240\text{Crd} + 0.75\text{H}_2\text{O}, \quad (8)$$

$$0.403\text{Ms} + 0.164\text{Chl} + 0.083\text{Grt} = 0.442\text{And} + 0.190\text{Qtz} + 0.376\text{Bt} + 0.053\text{Crd} + 0.654\text{H}_2\text{O}. \quad (9)$$

These equations correspond to the observed Fe/(Fe + Mg) sequence of minerals on the Crd-in isograde (Crd <

Chl < Bt < Grt) and are supported by the quantitative ratios of phases in microsections: An increase in the contents of cordierite and biotite is accompanied by a decrease in the amounts of muscovite, garnet, and chlorite. The rare Crd + Grt + Ms paragenesis was discovered locally within the lower cordierite zone; the cause of its origin is discussed below.

The first appearance of sillimanite in the contact aureole cannot be treated as the result of simple polymorphic transition because it never forms on andalusite. Usually sillimanite appears near cordierite and K-feldspar in the groundmass consisting of quartz, ilmenite, plagioclase, and biotite, which supports its formation from these minerals. This is in agreement with data on the origin of sillimanite in the Ballachulish aureole, Scotland [35], and on the sillimanite-bearing pelites near Rangeley, USA [36], and contradicts the conclusions of Kerrick and Woodsworth [37] that the equilibrium boundary between andalusite and sillimanite always corresponds to a direct replacement of andalusite by sillimanite and that the findings of sillimanite in andalusite-bearing rocks are related to its metastable behavior in the *PT*-stability field of andalusite. Bearing this in mind, we can calculate the reaction for the first appearance of sillimanite, K-feldspar, and cordierite from muscovite and biotite (Sil-in isograde) in the aureole for sample 36 in the system KFMASH:

$$0.494\text{Ms} + 0.002\text{Bt} + 0.362\text{Qtz} = 0.024\text{Crd} + 0.435\text{Sil} + 0.448\text{Kfs} + 0.483\text{H}_2\text{O}. \quad (10)$$

THERMODYNAMIC CONDITIONS FOR MINERAL REACTIONS

The detailed studies including geothermobarometry and analysis of mineral equilibria [1] permitted estimation of the P-T-X_{H_2O}-conditions of contact metamorphism in the Ayakhta aureole (Table 1). Independent pressure estimates (P = 3.2 ± 0.3 kbar) were earlier obtained with four modifications of Grt-Bt-Ms-Pl geobarometers [38, 39] and from the projections of the normative compositions of granitoids onto the plane Ab–Kfs–Qtz [40]. They are supported by the intersection of the experimental curve for the reaction Ms + Qtz = Sil + Kfs + H_2O [41] with the And–Sil equilibrium line on the petrogenetic grid [35] (Fig. 4) and by the pressure estimates (P = 2.8–3.5 kbar) for other contact aureoles [19, 20, 42, 43] bearing the stable rare Cld + Bt and Cld + Bt + And parageneses. To estimate the validity of the geobarometric data, they were compared with the pressures evaluated by the THERMOCALC computer program [44] with an internally consistent thermodynamic dataset and mixing models [45]. The results obtained for different zones are in agreement with each other within the accuracy of the geobarometers (P = ±1 kbar) [46] (Table 1). According to classification in [12], the Ayakhta hornfelses belong to cordierite-andalusite of types 1c or 2a stable in the pressure range of 3–4 kbar.

The temperatures were evaluated using eight geothermometers (Table 1). The temperature of regional greenschist metamorphism, estimated with the Ms-Chl [47] and Pl-Ms [48] geothermometers, is 400 °C. The temperatures of contact metamorphism are within 430–640 °C, which corresponds to the zone of transition from muscovite to amphibole hornfels facies. The initial temperature of contact metamorphism on the Cld-in isograde, determined by the Pl-Ms geothermometer [48], is 430 °C, which is close to the kinetic threshold of contact metamorphism under mesoabyssal conditions. The average temperature of metamorphism on the biotite-in isograde, evaluated with the Pl-Ms [48] and Bt-Cld [49] geothermometers, is 450 °C, which agrees with the temperature of the first appearance of biotite in association with chloritoid determined in studying high-Al high-Fe hornfelses of the Karatash Massif [20, 42] as well as from the petrogenetic grid in the system KFASH [24]. The average temperatures of metamorphism on the isogrades of the first appearance of garnet, andalusite, and cordierite, determined by four geothermometers — Pl-Ms [48], Bt-Ms [50], Crd-Grt, and Grt-Bt [28, 51], — are 480, 500, and 560 °C, respectively. They agree with the experimental data for the reactions of garnet [52] and cordierite [53] formation and the temperature and reaction curve for andalusite formation calculated by the THERMOCALC program (Table 1, Fig. 4). The above Grt-in temperature is commensurate with that obtained for ferriferous (Fe/(Fe + Mn) = 0.95) and Mn-bearing (Mn/(Mn + Mg + Fe) = 0.2) garnets from the monovariant Ms + Qtz + Bt + Chl + Grt + Cld paragenesis by the isopleth method on the petrogenetic grid considered in [24] — 470 °C, at P = 3 kbar and $X_{H_2O} = 1$. It is also close to the temperature of metamorphism on the isograde of ferriferous cordierite for graphite-bearing metapelites of the Ballachulish aureole [12, 54]. The average temperature on the Grt-out isograde, estimated with three geothermometers [28, 48, 49], is 620 °C, which agrees, within the accuracy of the geothermometers (T = ±50 °C), with the temperature and reaction curve for the disappearance of garnet calculated by the THERMOCALC program (Table 1, Fig. 4). The first appearance of sillimanite in paragenesis with K-feldspar was observed at T = 640 °C; this coincides with the THERMOCALC-estimated temperatures [44, 45] (Table 1). The resulting *PT*-trend of evolution of the Ayakhta mineral associations, proved and substantiated by experimental and calculated mineral equilibria, is shown by a bold arrow in Fig. 4.

Table 1

***PT*-Conditions of Contact Metamorphism Estimated with Various Geothermobarometers and the THERMOCALC Program**

Zone, sample no.	*T*, °C							*P*, kbar				
	[47]	[48]	[49]	[50]	[49]	[51]	[44, 45]	[38]	[39]	[39]	[39]	[44, 45]
0, 12	400	400										
I, 18		430										
II, 20		448	452				456 ±					3.0 ± 1.2
III, 25		480					491 ± 36					3.1 ± 1.1
IV, 26		490		510	500		499 ± 24	2.9	3.1			3.3 ± 0.9
V, 28		553		542	578	560	554 ± 44	3.2	3.1	2.9		3.5 ± 1.0
VI, 32		613			632	620		3.5	3.5		3.1	
VII, 36		640					638 ± 42					3.2 ± 1.2

Note. The bracketed geothermobarometer numbers follow the references. The results obtained with the THERMOCALC [44, 45] program are given with the confidence interval of ±2σ.

COMPARATIVE ANALYSIS OF THE REVEALED PARAGENESES WITH PETROGENETIC GRIDS AND CONCLUSIONS

The thorough petrological investigations in the contact aureole of the Ayakhta Massif have shown that: (1) the degree of contact metamorphism varies in transition from chloritoid to sillimanite-K-feldspar zone (T = 430–640 °C, P = 3.2 ± 0.3 kbar); (2) as the temperature grows, the Cld + Bt paragenesis is changed by the Grt + Chl association in the garnet zone, which is stable over a broad temperature range (480–620 °C); (3) in the lower cordierite zone, Grt reacts with Chl to produce the Crd + Bt paragenesis; (4) the rare Cld + Bt, And + Cld + Bt, and Crd + Grt + Ms parageneses are stable over narrow temperature ranges (~50 °C) within the biotite, andalusite, and lower cordierite zones, respectively.

The first appearance of the Cld + Bt paragenesis from the Chl + Ms association on the periphery of the Ayakhta contact aureole at T = 430 °C corresponds to the position of this reaction on the Spear-Cheney petrogenetic grid [24] for metapelites in the KFMASH system. This grid implies that the Cld + Bt paragenesis is stable in the low-temperature side of the reaction Cld + Bt = Grt + Chl (with participation of muscovite and quartz) in contrast to the Harte-Hudson grid [22], where the Cld + Bt paragenesis results from the Grt + Chl association with increasing temperature. The Powell-Holland [55] petrogenetic grid does not allow for the appearance of the Cld + Bt and Cld + And + Bt parageneses in the ordinary KFMASH system. However, when adding small amounts of Fe^{3+} into the octahedral positions of biotite and chloritoid crystals, the above parageneses are produced from the Grt + Chl association and are stable over the temperature range of 460–550 °C at P = 3 kbar. The limited stability of the Cld + Bt and Cld + And + Bt parageneses (over a narrow temperature range) at low pressures was confirmed by natural observations and agrees with the model given in [55] as opposed to the Spear-Cheney petrogenetic grid [24] suggesting that these associations are stable over broad temperature and pressure ranges. As mentioned above, the ratios between the widths of the stability ranges for the Cld + Bt and Grt + Chl parageneses can vary significantly as a result of the effect of MnO on the natural parageneses. For example, for the garnet of the Ms + Qtz + Bt + Chl + Grt + Cld association with Fe/(Fe + Mg) = 0.95 and Mn/(Mn + Mg + Fe) = 0.2, the petrogenetic grid from [24] suggests a ~50 °C narrowing of the temperature stability range of the Cld + Bt paragenesis in the stability field of andalusite at the expense of broadening of the narrow stability range of the bordering Grt + Chl paragenesis. This is in agreement with natural associations found in ferriferous-aluminous rocks. Thus, the petrological investigations in the Ayakhta and other contact aureoles bearing rare Cld + Bt and Cld + And + Bt parageneses confirm the validity of the Spear-Cheney grid with the KFMASH system for analyzing the lowest-temperature phase equilibria in aluminous ferriferous hornfelses. Wang and Spear [16] comprehensively studied the stability of the Cld + Bt paragenesis in regional metamorphic rocks of the Barrow series and established that it is governed mainly by the bulk chemical composition of rocks (total Fe/(Fe + Mg) > 0.6) rather than the *PT*-conditions of

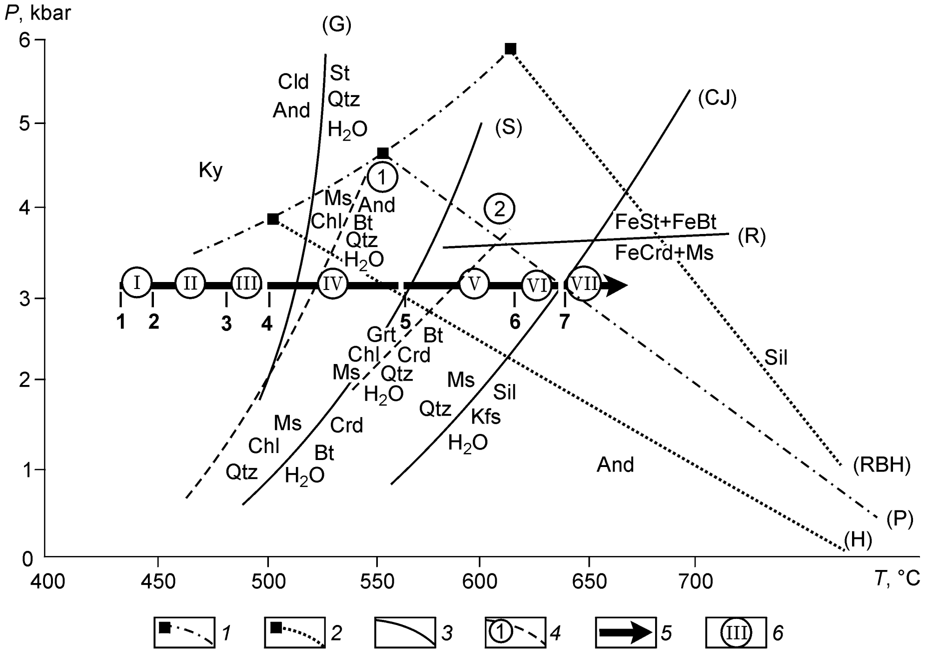

Fig. 4. Schematic *PT*-trend of evolution of the Ayakhta aureole mineral associations, showing the position of metamorphic zones and contact-metamorphism isogrades, and its correlation with the calculated and experimental mineral equilibria. *1* — coordinates of the triple point and the And-Sil equilibrium line by Pattison (1992) (P), *2* — coordinates of the triple points and the And-Sil equilibrium line by Holdaway (1971) and Richardson et al. (1969) (RBH), *3* — experimental data by Chatterjee and Johanes (1974) (CJ), Ganguly (1969) (G), Richardson (1968) (R), and Seifert (1970) (S), *4* — curves of monovariant equilibria calculated by the THERMOCALC program; *5* — *PT*-trend of evolution of mineral associations in the aureole; *6* — metamorphic zones. Arabic figures below the arrow correspond to the contact-metamorphism isogrades in Fig. 1: 1 — Cld-in, 2 — Bt-in, 3 — Grt-in, 4 — And-in, 5 — Crd-in, 6 — Grt-Chl-out, 7 — Sil-Kfs-in.

metamorphism. In less ferrous rocks (Fe/(Fe + Mg) <0.5), the Grt + Chl paragenesis is stable, and intermediate rocks show the following sequence of parageneses with increasing degree of metamorphism: Grt + Chl → Cld + Bt → Grt + Chl. Our and literature data evidence that the formation of chloritoid atypical of thermal metamorphism and the stability of rare parageneses (Cld + Bt and Cld + And + Bt) in the Ayakhta contact aureole are related to the rare combination of pressure (≥3 kbar) with the specific type of rocks enriched in both Al and Fe.

The stability of the Grt + Crd + Ms paragenesis locally appearing within the lower cordierite zone of the Ayakhta aureole is of great petrological importance as this association is usually not included into petrogenetic grids for metapelites described by equilibria in the KFMASH system [12]. When introducing Grt + Crd + Ms as a stable paragenesis into any petrogenetic grids, at P ≥3–4 kbar, the stability field of the alternative Bt + And + Qtz paragenesis either disappears at all or shifts to the higher-temperature region as compared with the Grt + Crd + Ms + Qtz paragenesis. For example, the schematic petrogenetic diagram for regional metamorphic rocks of the Tongulak complex [56] shows the stability field of the Grt + Crd + Ms paragenesis changed by the field of Bt + Al_2SiO_5 + Qtz with increasing temperature. But studying the metamorphic zoning in shallow-level and hornfels aureoles revealed that the Bt + Al_2SiO_5 + Qtz association is more typical and usually lower-temperature than the Grt + Crd one [33, 42]. The Harte-Hudson petrogenetic grid [22], based on field observations, does not regard this paragenesis as stable in the KFMASH system. On the Powell-Holland petrogenetic grid [55], this paragenesis can appear at T ≤575 °C in high-alumina (above the Grt + Chl tie line) ferriferous rocks only, which corresponds to the studied hornfelses. The Spear-Cheney petrogenetic grid [24] implies the stability of this paragenesis in the field of K-feldspar or without it only in the presence of Mn, Fe-garnets.

The literature data [57–60] on contact and regional aureoles where the Grt + Crd + Ms paragenesis originates in different *PT*-conditions show that the content of MnO in garnets is much (three to five times) higher than that of MgO. This proves that the above paragenesis can exist solely in the presence of Mn-containing garnets; Mn-free metapelites usually bear a stable Bt + Al_2SiO_5 paragenesis. This agrees with Korikovsky's conclusions [33] about the factors giving rise to the Grt + Crd + Ms paragenesis in regional metamorphic complexes. Analysis of the mineral equilibria between muscovite-bearing rocks of the staurolite facies has revealed that the Grt + Crd + Ms + Qtz and Bt + Al_2SiO_5 + Qtz parageneses do not exclude each other if regarding MnO as a virtual component. With regard to these factors and the fact that the Grt + Crd + Ms paragenesis has been found in various settings of contact and regional metamorphism proceeding over wide ranges of temperatures and pressures, we infer that the appearance of this paragenesis is related to the specific chemical composition of garnet (high Mn content) and the country rocks (high Al and Fe contents) rather than to the specific *PT*-conditions of contact metamorphism.

Another distinctive feature of the Ayakhta aureole is the presence of typical And-Crd hornfelses, though the composition of rocks (high Al and Fe contents) and the conditions of contact-metamorphism occurrence ($P > 3$ kbar) favor the formation of staurolite [12]. Hornfelses of the study aureole lack mineral reactions of staurolite formation (e.g., Cld + And = St + Chl or Grt + Chl = St + Bt with participation of muscovite and quartz) predicted from many petrogenetic grids, which is proved by the stability of the revealed And + Bt and Crd + Bt parageneses resulting from the Ms + Chl and Grt + Chl associations, respectively, with increasing temperature. The Crd + Bt paragenesis in the lower cordierite zone results from the Grt + Chl association (with participation of Ms and Qtz), stable to $T = 550$ °C at $P = 3$ kbar in terms of the Spear-Cheney petrogenetic grid [24]. The process is related to the simultaneous expansion of the Grt + Chl stability field (with participation of Mn-garnets) and narrowing, up to complete disappearance, of the wedge-shaped St + Bt field. This is in agreement with the *PT*-coordinates of the reaction Chl + Grt = Bt + Crd on the petrogenetic grid in [55]. Thus, the Grt + Chl stability over a broad range of contact-metamorphism temperatures in the Ayakhta aureole (480–620 °C) leads to wedging-out of the St + Bt field at $P = 3.2$ kbar, which agrees with the field observations for other Crd-And-bearing aureoles that lack St-containing parageneses [12]. All these data suggest that if the Grt + Chl paragenesis is disintegrated below the lower bound of staurolite stability, this mineral can form prior to Crd-containing associations, and if above this bound, Crd-containing parageneses appear instead of staurolite. This is consistent with the natural observations for the Ayakhta and other contact aureoles and with various petrogenetic grids. Thus, the predominance of Crd-And hornfelses and the absence of St-containing associations at the intermediate steps of contact metamorphism in the Ayakhta aureole are explained by the simultaneous expansion of the Grt + Chl stability field with participation of Mn-garnets and narrowing, up to complete disappearance, of the St + Bt field.

The obtained petrological data on the sequence of the observed parageneses and mineral reactions in high-Al ferriferous hornfelses of the Ayakhta aureole are best consistent with the data inferred from the Spear-Cheney petrogenetic grid [24], which takes account of the effect of MnO on the stability limits of parageneses [16]. This might be due to the fact that when the phase relations in the low- and moderate-temperature regions at low pressures were studied, this grid included the Berman thermodynamic data [61] for high-Al ferriferous chlorites and biotites composing many parageneses of regional and contact metamorphism [18, 34, 62, 63] and compositionally corresponding to minerals of the Ayakhta aureole.

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