

Physicochemical Crystallization Conditions of Al–F Spheue in Metasomatic Rocks with Ore Mineralization at the Berezitovoe Deposit

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Abstract—Al–F sphene (grothite) was found in mineralized rocks at the Berezitovoe Deposit in the Russian Far East. The paper is devoted to the mineral assemblages and composition of the mineral and its thermodynamic crystallization conditions. The average Al and F concentrations (p.f.u., microprobe data) in the grothite are 0.45 and 0.42 in sample 1374, 0.32 and 0.32 in sample 1306, and 0.35 and 0.33 in sample 96. Grothite was found in the rocks in association with chlorite, ilmenite (pyrophanite), and magnetite, and this mineral assemblage was obviously overprinted on the primary garnet–biotite assemblages. We estimated the temperature of grothite crystallization at 400–500°C. With regard for available experimental data on the mineral equilibrium between Al–F sphene, fluid, and anorthite, a tool is proposed for evaluating F concentrations in fluids by the equilibrium of Al–F sphene with plagioclase, rutile, and F-bearing aqueous fluid. Our model simulations indicate that the maximum F concentration in fluid during the crystallization of Al–F sphene richest in F at the temperatures and pressures of metasomatic rocks at the Berezitovoe deposit could reach 300–500 mg per kg of the aqueous solution. The level of F concentration in the fluid during the crystallization of Al–F sphene at the deposit is comparable with the F concentration in fluid during the development of greisens and rare-metal pegmatites, but these high F concentrations were reached only during the final evolutionary stages of the deposit.

Keywords: grothite, mineral assemblages, Berezitovoe deposit, thermodynamic simulations, crystallization conditions, fluorimeter.

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INTRODUCTION

Sphene or titanite, (Ca,REE)(Ti,Al,Fe)SiO₄(O,OH,F), is a mineral that is contained in magmatic, metamorphic, and metasomatic rocks that were formed within broad ranges of physicochemical environments and *P–T* parameters. The structure of the mineral allows for a wealth of anion and cation substitutions. For example, the Ca site can accommodate Na⁺, Mn²⁺, Sr²⁺, Ba²⁺, and REE³⁺; the Ti site can be partly occupied by Mg²⁺, Fe²⁺, Fe³⁺, Al³⁺, Cr³⁺, Zr⁴⁺, Sn⁴⁺, V⁵⁺, Nb⁵⁺, and Ta⁵⁺; and the Si site can incorporate P⁵⁺ and 4H⁺. Anionic isomorphism occurs at the O1 site, which can include F[–], Cl, and OH[–] [1]. The main isomorphous substitutions typically take place at the Ti site, which can contain Al³⁺ and Fe³⁺, with the excess positive charge counterbalanced according to the following two schemes: Al, Fe³⁺ + F[–] = Ti⁴⁺ + O^{2–} and Al, Fe³⁺ + OH[–] = Ti⁴⁺ + O^{2–} [1–4].

The former isomorphous substitution scheme pertains to a system with the CaTiSiO₄O and CaAlSiO₄F end

members, with the aluminous sphene variety referred to as grothite, which was named after the famous German mineralogist Paul Heinrich von Groth, the first one to describe this mineral in syenite in the vicinity of Dresden [5]. The substitution of this type is isostructural [1], and complete miscibility between the CaTiSiO₄O and CaAlSiO₄F was proved experimentally [6, 7]. The other type of isomorphism is described by the system with the CaTiSiO₄O and CaAlSiO₄(OH). The CaAlSiO₄(OH) component was named vuagnatite after the Swiss professor Mark Vuagnat [8]. This mineral has, however, a different structure from that of titanite, and hence, the miscibility between these end members is limited [1]. Thereby appreciable vuagnatite amounts were detected only in titanite that crystallized at low temperatures [2, 3].

Sphene with high Al and F concentrations was found in high-pressure rocks, which were reportedly formed under pressures of up to 30 kbar [4, 9, 10], with the high pressures confirmed by the occurrence of coesite and diamond in these rocks. This seemed to suggest

that Al- and F-rich titanite is an indicator of high pressures of metamorphic rocks. However, F–Al sphene was later found in metamorphic rocks of the amphibolite and granulite facies [11], in granitoids and F-bearing skarns [2], and in siliceous mineralized metasediments at the Berezitovoe gold–base metal deposit in the upper reaches of the Amur River [13]. The Al and F concentrations of sphene from these various low-pressure rocks were proved to be comparable with those in the mineral from high-pressure metamorphic rocks, and this suggests that the main factor facilitating the formation of Al–F sphene in various mineral assemblages is the F activity in the mineral-forming fluid. Here we consider more closely the mineral assemblages, composition, and thermodynamic crystallization conditions of Al–F sphene first found at the Berezitovoe deposit in the Russian Far East. We demonstrate that the F concentration of the fluid can be estimated with the use of our sphene “fluorimeter”, which is suggested below.

GEOLOGY

The Berezitovoe gold–base metal deposit in the northwestern part of Amur oblast, in the basin of the lower reaches of the Khaikt River, a large right-hand tributary of the Bol'shoi Ol'doi River, differs from other currently developed gold deposits in the Russian Far East in that it belongs to the gold–sulfide type of ore mineralization whose geology has no proximate analogues among currently known base-metal and gold deposits in Transbaikalia and the Russian Far East.

The deposit is restricted to the northeastern flank of the Amur gold province [14] and is hosted in structures of the southeastern part of the North Asian craton, in its junction zone with structures surrounding the northern part of the Tukuringra–Dzhanginskii terrane of the Mongolia–Okhotsk orogenic belt [15]. The ore field of the deposit is an uplifted block of ancient metamorphic and magmatic rocks, which is bounded by Triassic volcanic and volcano-sedimentary rocks of the Desovskii Complex in the east, north, and west and by large bodies of the Khaikt Early Cretaceous intrusion [16].

The orebody of the deposit is a large submeridionally trending zone of metasomatic rocks with sulfide ore mineralization in a massif of Early Proterozoic (?) porphyritic granite and gneissose granodiorite of the Late Stanovik Complex (?). The zone consists of two high-dipping funnel-shaped bodies, which converge near the surface and taper with depth (Fig. 1). In map view, the zone has a complicated lens-shaped morphology and dips at 70°–75° to the southwest. The exposed length of the zone reaches 950 m, and its thickness varies from 10–15 to 110 m.

The ore-hosting rocks of the deposit are pale gray and greenish gray massive or, more rarely, schistose quartz–muscovite metasomatites with disseminated almandine–spessartine garnet and tourmaline. The rocks may occasionally contain variable amounts of

orthoclase, chlorite, biotite, anorthite, Zn-bearing spinel (Fe-rich gahnite), sphene, zircon, epidote, allanite (orthite), prehnite, fluorapatite, fluorite, and graphite.

The ores of the deposit contain much sulfides. The predominant ore minerals are sphalerite, galena, pyrite, pyrrhotite, and magnetite.¹ The minor and rare minerals are marcasite, chalcopyrite, arsenopyrite, ilmenite, native gold, As-bearing pyrite*, pyrophanite*, jordanite*, tennantite*, boulangerite*, jamesonite*, Bi-bearing meneghinite, Sb-bearing bursaite–cosalite*, gersdorffite*, cervandonite-(Ce)*, scheelite*, stannite, molybdenite, argentite, hematite, chalcocite, native bismuth, patronite, altaite, calaverite, cinnabar, and cassiterite.

The two major ore types of the deposit remarkably differ in geological setting, mineralogy, and gold content [17]. One of them (predominant) is gold-bearing base-metal ore (with average gold concentrations from 1 to 4 ppm), which is localized in the axial part of the metasomatic zone as a complicated mineralized stockwork. The ores are classified into three major types: pyrite–pyrrhotite–sphalerite, pyrite–galena–sphalerite, and predominantly pyrite. The pyrite–pyrrhotite–sphalerite mineralization with the Zn/Pb ratio of the ores ranging from 8/1 to 2/1, is hosted by tourmaline–garnet–quartz–muscovite metasomatites in northern funnel-shaped body. The pyrite–galena–sphalerite ores with Zn/Pb of approximately 1/1 are localized in tourmaline–garnet–muscovite–quartz metasomatites of the central funnel-shaped body. The pyrite-dominated ores are hosted by tourmaline–garnet–orthoclase–muscovite–quartz metasomatites in the southern part of the zone, by the metasomatites surrounding this zone and having a more complicated garnet–orthoclase–biotite–anorthite–muscovite–quartz composition, and by dikes of garnet-bearing metaporphyrites.

The other type of the ores is very sparse at the deposit. It is hosted in the mineralized metasomatic rocks (which bear gold–base metal ore mineralization) and in the mineralized granodiorite hosting the metasomatites. This type comprises thin mineralized veins with thin veinlets of sulfide (predominantly galena), tourmaline, tourmaline–quartz, garnet–quartz, quartz–sulfide, and quartz–garnet–sulfide composition. The vein and veinlet orebodies are constrained to cutting sublatitudinal faults. This type of ores typically has fairly high Au concentrations, from a few to a few hundred ppm.

The metasomatic zone is cut across by intramineral metasomatized garnet-bearing metaporphyrite dikes and rare postmineral spessartite and diorite porphyry dikes, which are not metasomatized.

The nearby occurrence of gold and base-metal ore mineralization of different age and type is one of the

¹ Asterisks mark minerals whose identification was confirmed by chemical analyses.

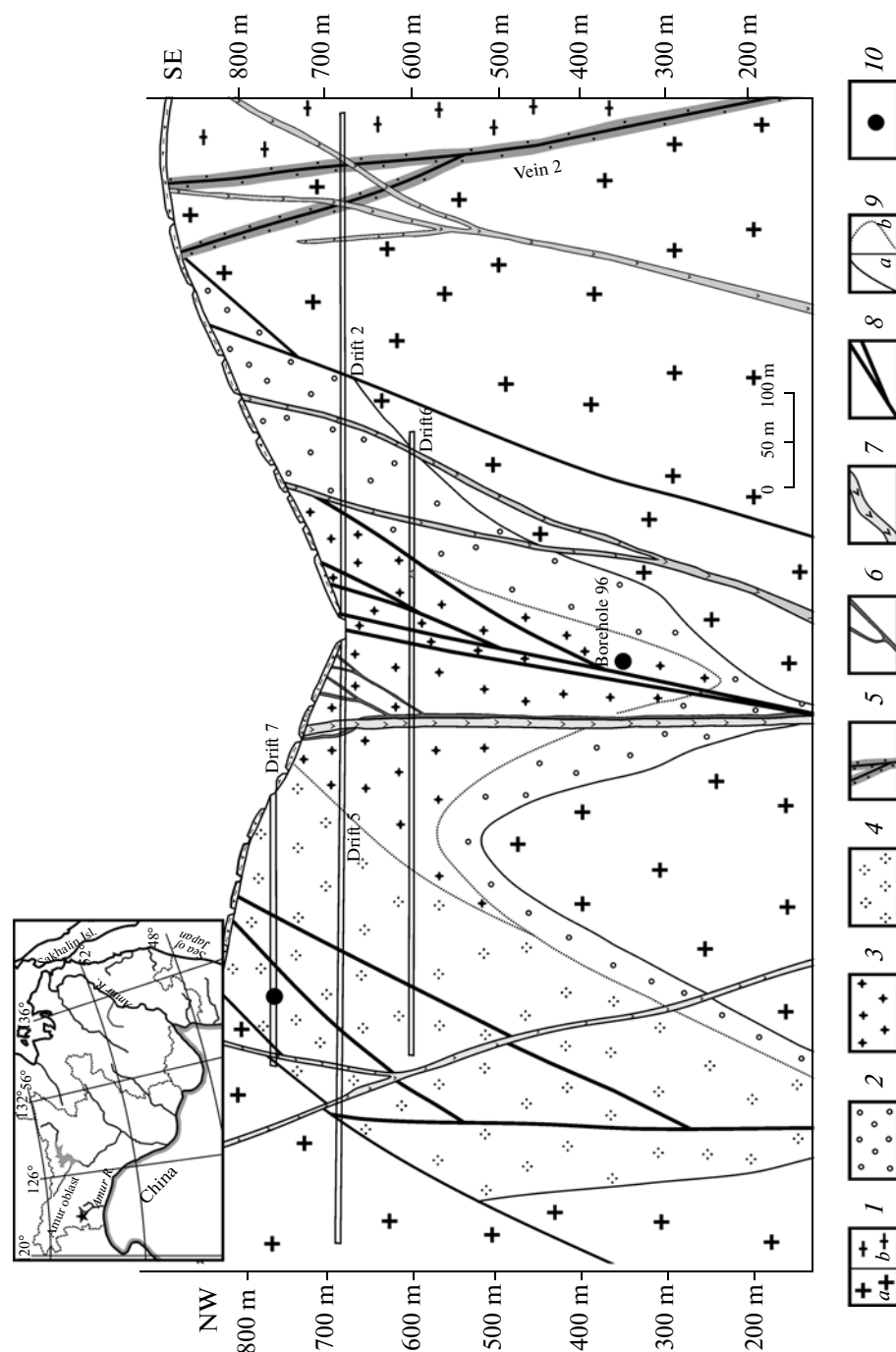


Fig. 1. Vertical section through the mineralized metasomatic zone of the Berezitovoe gold–base metal deposit.

(1) Early Proterozoic (a) porphyritic granodiorite–granite and (b) gneissose granodiorite; (2–4) predominant types of ore-hosting metasomatic rocks: (2) tourmaline–garnet–orthoclase–muscovite–quartz rocks with predominantly pyrite mineralization, (3) tourmaline–garnet–muscovite–quartz rocks with pyrite–galena–sphalerite mineralization, (4) tourmaline–garnet–quartz–muscovite rocks with pyrite–pyrrhotite–sphalerite mineralization; (5) quartz vein with low-grade gold mineralization and wall-rock muscovite–quartz metasomatic rocks; (6) garnet–muscovite–biotite–quartz–anorthite metaporphyrite dikes; (7) postmineral speckled and diorite porphyry dikes; (8) major faults; (9) (a) boundaries between major types of mineralized metasomatic rocks and (b) fields of mineralized metasomatic rocks; (10) sampling sites of graphite-bearing rocks. The asterisk in the location map (see inset) marks the Berezitovoe deposit.

distinctive features of the Berezitovoe deposit and indicates that the deposit belongs to a complicated polygenetic type, with its mineralization produced in several stages [17].

The ore field of the deposit includes, along with the Berezitovoe deposit itself, also about 20 morphologically similar mineralized metasomatic zones (Beregovaya, Flangovaya, Vostochnaya, Dioritovaya, Geofizicheskaya, and others) of predominantly muscovite—quartz, feldspar—quartz—muscovite, and chlorite—muscovite—feldspar—quartz rocks. Among them, the Beregovaya zone is commonly thought to be the closest analogue of the mineralized zone at the Berezitovoe deposit.

The Beregovaya zone in the right-hand side of the middle reaches of Orogzhan Brook, approximately 2 km south of the mineralized zone of the Berezitovoe deposit, is composed of extensively silicified and altered granite (with well preserved original brecciated textures) and chlorite—biotite—muscovite—feldspar—quartz metasomatites with locally abundant almandine—spessartine garnet. The ore mineralization of the zone is dominated by pyrite or, more rarely, chalcopyrite, pyrrhotite, sphalerite, galena, ilmenite, and rutile.

METHODS

The chemical composition of the grothite and accompanying minerals in mineralized metasomatic rocks from the Berezitovoe deposit and Beregovaya zone was examined on an JXA8100 (JEOL, Japan) microprobe equipped with three wave-dispersive spectrometers (WDS) and an INCAx-sight (OXFORD Instruments, United Kingdom) energy-dispersive spectrometer (EDS). The range of analyzable elements was from B to Pb. The accelerating voltage was 20 kV, the crystal analyzers were LiF, PET, TAP, and LDE2, and the standards were pure elements, compounds, or minerals provided by Micro-Analysis Consultants Ltd., Oxford, UK. The F concentrations of sphene and other minerals were determined with the use of both an INCAx-sight EDS and an WDS.

MINERAL ASSEMBLAGES OF THE GROTHITE-BEARING ROCKS

Sphene with high Al and F concentrations (grothite) was found and closely examined in three samples of metasomatic rocks of different geological setting and mineralogy from the Berezitovoe deposit and Beregovaya zone. Sample 96 was taken from the mineralized metasomatic rock of the Berezitovoe deposit, and samples 1306 and 1374 were collected outside the deposit: sample 1306 is from the altered granite that hosts the Berezitovoe deposit, and sample 1376 is from mineralized garnet-bearing metasomatic rock from the Beregovaya zone. Figure 1 shows the sampling sites of the

former two samples with grothite in a longitudinal vertical section of the Berezitovoe deposit.

Sample 96 was taken from the core material of Borehole 96, from the depth section of 372.2 m. The hole was drilled in 1976, in the course of exploration operations at the deposit to aimed at lower levels of the central orebody. The sample is one of the fragments of mineral segregations of unusual composition, with occur as occasional pockets (no more than a few centimeters across) in the groundmass of the tourmaline—garnet—muscovite quartz metasomatite with disseminated and veinlet galena—sphalerite mineralization. These are predominantly massive quartz—garnet rocks and individual numerous clearly euhedral garnet porphyroblasts up to 2 mm across submerged in a quartz—orthoclase—chlorite groundmass. In contrast to the host metasomatite, the mineral assemblage in question contains much orthoclase and chlorite, and the content of garnet is as high as 20–30%. This association typically contains no muscovite. The ore mineralization in this association consists of cleiophane (containing 2–4.5 wt % Fe), which is generally atypical of most sphalerite varieties at the deposit. The other ore minerals are pyrite, chalcopyrite, and minor galena. The pyrite contains abounds in small galena inclusions and contains rare small (<10 µm) inclusions of native gold. Table 1 reports the chemical compositions of the main minerals of the assemblage. Regardless of their morphologies, the garnet aggregates are composed of almandine—spessartine garnet, whose composition is identical to that of Mn-rich garnet in the host quartz—muscovite metasomatites. Single garnet aggregates in chlorite are composed of euhedral garnet grains with clearly pronounced zoning: the Fe and Ca concentrations increase from their cores to margins, and that of Mn conversely decreases. The chlorite is a Mg—Fe variety with pervasively high Mn concentrations. Grothite was found in this association only in chlorite and occurs as numerous disseminated platy aggregates in the interstitial space (Fig. 2) or as complicated thin reaction rims that replicate the shapes of chlorite aggregates and are often spatially restricted to contacts between chlorite and orthoclase. The grothite aggregates are usually 20–50 µm across and are occasionally as large as 100 µm. Grothite aggregates are often accompanied by ferrous pyrophanite, which often seems to replace the latter.

Sample 1306 represents weakly metasomatically altered Early Proterozoic granite that occurs at the contact between the granitoids and cutts gold—sulfide veinlet ores (Drift 7, Crossdrift 10). Portions of the gold-bearing sulfide veinlets near their selvages show clear indications of granite alterations: their replacement by potassic feldspar (secondary orthoclase replacing plagioclase) and biotite replacement by chlorite. The secondary feldspar is Ba-bearing orthoclase (Table 2). The chlorite that developed simultaneously with this orthoclase has a composition intermediate between those of biotite and chlorite and can thus be classed with mixed-layer biotite—chlorite micas with irregularly alternating

Table 1. Analyses and cation proportions in crystal chemical formulas of major minerals in association with grothite in mineralized metasomatic rocks from the Berezitovoe deposit

Component	Mineral								
	<i>gr-c</i>	<i>gr-r</i>	<i>chl</i>	<i>chl</i>	<i>chl</i>	<i>kfs</i>	<i>kfs</i>	<i>prf</i>	<i>prf</i>
	1	2	3	4	5	6	7	8	9
<i>Composition, wt %</i>									
SiO ₂	36.90	37.52	27.17	26.66	26.33	65.20	65.92	0.00	0.00
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	48.47	51.63
Al ₂ O ₃	20.14	20.18	18.99	19.36	19.12	19.07	18.84	0.00	0.00
FeO	8.82	11.87	23.04	23.04	23.31	0.00	0.00	17.42	22.29
MnO	30.24	22.16	1.77	2.10	1.56	0.00	0.00	26.49	23.61
MgO	0.39	0.42	15.67	16.08	15.61	0.00	0.00	0.00	0.00
CaO	2.71	8.24	0.00	0.00	0.00	0.00	0.00	0.46	0.49
K ₂ O	0.00	0.00	0.00	0.00	0.00	16.68	17.14	0.00	0.00
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.20	100.39	86.64	87.24	85.93	100.95	101.90	92.84	98.02
<i>Cation numbers</i>									
Si	3.04	3.02	2.90	2.82	2.83	2.98	3.00	—	—
Ti	—	—	—	—	—	—	—	0.99	0.973
Al	1.95	1.92	2.39	2.41	2.42	1.08	1.01	0.00	0.00
Fe ⁺²	0.61	0.80	2.06	2.04	2.10	—	—	0.40	0.48
Mn	2.11	1.51	0.16	0.19	0.14	—	—	0.61	0.51
Mg	0.05	0.05	2.49	2.54	2.50	—	—	—	0.00
Ca	0.24	0.71	—	—	—	—	—	0.01	0.01
K	—	—	—	—	—	0.97	0.99	0.00	0.00
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OH	—	—	8	8	8	—	—	—	—
O	12	12	10.19	10.06	10.09	8	8	3	3
$X_{\text{Fe}}^{\text{Gr}}$	0.92	0.94	—	—	—	—	—	—	—
$X_{\text{Ca}}^{\text{Gr}}$	0.08	0.23	—	—	—	—	—	—	—
$X_{\text{Fe}}^{\text{Chl}}$	—	—	0.45	0.45	0.46	—	—	—	—

Note: Minerals: *gr-c* and *gr-r* are garnet (core and rim, respectively), *chl* is chlorite, *kfs* is potassic feldspar, *prf* is pyrophanite; compositional parameters: $X_{\text{Fe}}^{\text{Gr}}$ is the Fe mole fraction of garnet $X_{\text{Fe}}^{\text{Gr}} = \text{Fe}/(\text{Fe} + \text{Mg})$, $X_{\text{Ca}}^{\text{Gr}}$ is the Ca mole fraction of garnet $X_{\text{Ca}}^{\text{Gr}} = \text{Ca}/(\text{Ca} + \text{Fe} + \text{Mg} + \text{Mn})$, $X_{\text{Fe}}^{\text{Chl}}$ is the Fe mole fraction of chlorite $X_{\text{Fe}}^{\text{Chl}} = \text{Fe}/(\text{Fe} + \text{Mg})$. Analyses were conducted on an JEOL 8100 microprobe at the Far East Geological Institute, Far East Branch, Russian Academy of Sciences. Sample 96.

biotite and chlorite layers. Micas of similar composition with a biotite to chlorite ratio of 1 : 1 were described as products of biotite chloritization. The replacement of the primary sphene by leucoxene in the granitoids is associated with the replacement of its aggregates by secondary magnetite, Mn-bearing ilmenite, fluorapatite, and the REE mineral allanite (Table 2). The latter mineral in titanite is pervasively restricted to domains with Mn-bearing ilmenite and develops around them in the

form of complicatedly shaped rims. This led us to believe that the two minerals replaced sphene roughly simultaneously. Grothite occurs in the mineral association of the altered granitoids only in aggregates with mixed-layer biotite–chlorite micas as elongated platelets arranged along cleavage planes (Fig. 3). The aggregates are never larger than 10–20 μm . The morphologies and character of grothite in the micas are largely analogous to those in chlorite in the first sample. The

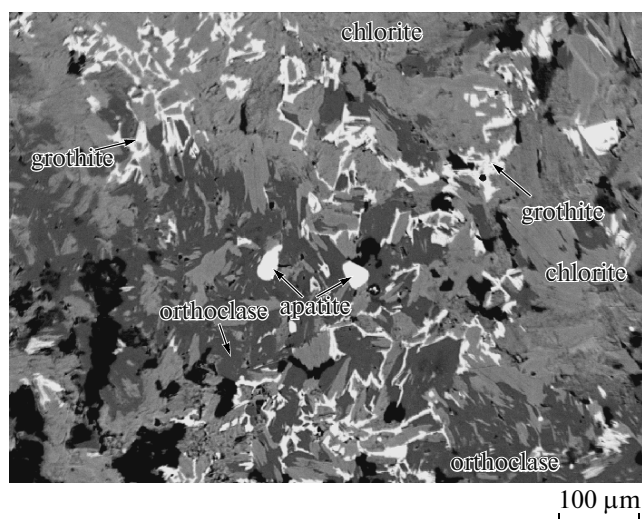


Fig. 2. BSE image showing grothite relations in the quartz-orthoclase-chlorite association.

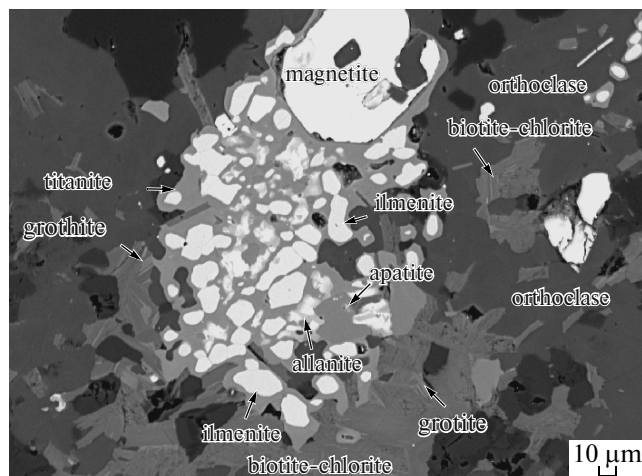


Fig. 3. BSE image showing orthoclase and mixed-layer mica of biotite-chlorite composition with grothite aggregates replacing primary plagioclase of granite and primary titanite (leucosene) replaced by magnetite, Mn-bearing ilmenite, and allanite.

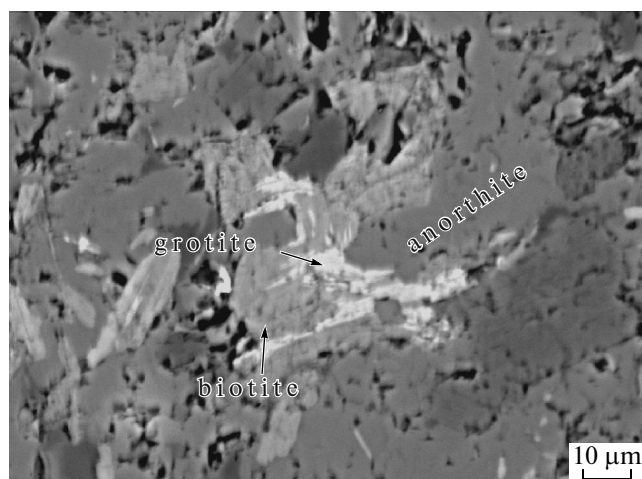


Fig. 4. Grothite and chlorite developing along a contact between biotite and anorthite.

mineral association of the altered granites is characterized by the simultaneous occurrence of grothite and sphene devoid of admixtures (Fig. 3). The latter is contained in the ores not only as an alteration product of the primary sphene but also (occasionally) as small (50–60 μm) inclusions in orthoclase. The Al_2O_3 concentration in these sphene aggregates are 1–2% (Table 2).

It is important to stress that the altered granitoids contain plagioclase (30% anorthite) and sometimes rutile, but these minerals have never been found in aggregates with grothite.

Sample 1374 from the metasomatic rocks of the Beregovaya zone contains grothite together with anorthite, chlorite, garnet, biotite, muscovite, potassic feldspar, ilmenite, and rutile (Table 3). As in other samples, chlorite in this rock replaces biotite. Grothite (no larger than 10 μm) often occurs together with newly-formed chlorite at boundaries between anorthite and biotite (Fig. 4).

The chemistry of the mineral assemblages of the various grothite-bearing rocks and the character of mineral relations (as can be seen in thin sections) definitely imply that the grothite always appears in assemblage with chlorite, ilmenite (pyrophanite), and magnetite, and they are obviously overprinted on the primary garnet-biotite associations. This led us to conclude that the grothite-chlorite associations are younger (and most likely crystallized at a lower temperature) than the garnet-biotite one, because the primary biotite is often replaced by chlorite. As will be demonstrated below, this conclusion is very important for the analysis of the crystallization temperature of grothite in our mineral associations.

DISTINCTIVE COMPOSITIONAL FEATURES OF THE Al-F SPHENE AND THE PROBABLE *P-T* PARAMETERS OF ITS CRYSTALLIZATION

The most representative analyses of grothite from our three samples are presented in Table 4. The cation proportions of the mineral were calculated in compliance with [1]. This technique is underlain by a meticulous structural study and makes it possible to calculate the number of OH groups (or the vuaganatite end member) in Al-F sphene. According to their concentrations of OH and $(\text{Al} + \text{Fe}^{3+})$, our grothite samples can be reliably subdivided into three individual groups (Fig. 5). Our data also confirm compositional trends of the mineral, which were previously documented in [1, 2, 18]: an increase in the F concentration is positively correlated with the Al concentration (Fig. 6). The Al and F concentrations (p.f.u.) of our grothite are 0.45 and 0.42 on average in sample 1374 (from the Beregovaya zone), 0.32 and 0.32 in the mineral from the altered granite (sample 1306), and 0.35 and 0.33 in it from the mineralized metasomatite from the deposit (sample 96).

Table 2. Analyses and cation proportions in crystal chemical formulas of major minerals in association with grothite in metasomatized granitoids from the Berezitovoe deposit

Com- ponent	Mineral												
	<i>plag</i>	<i>kfs</i>	<i>bi-chl</i>	<i>bi-chl</i>	<i>bi-chl</i>	<i>sph</i>	<i>sph</i>	<i>sph</i>	<i>ilm</i>	<i>ilm</i>	<i>aln</i>	<i>aln</i>	<i>aln</i>
	1	2	3	4	5	6	7	8	9	10	11	12	13
<i>Composition, wt %</i>													
SiO ₂	60.22	63.73	28.19	29.81	30.05	31.04	31.30	30.43	0.00	0.00	31.47	33.81	34.08
TiO ₂	0.00	0.00	0.89	0.89	1.92	36.97	36.48	38.09	52.04	51.62	0.00	0.00	0.00
Al ₂ O ₃	24.29	18.59	18.02	18.70	18.10	1.83	1.71	1.34	0.00	0.00	17.10	19.52	20.13
FeO	0.00	0.00	25.50	21.86	23.48	1.55	1.28	1.37	37.09	37.52	0.00	0.00	0.00
Fe ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	13.99	13.07	12.99
MnO	0.00	0.00	0.91	0.97	0.92	0.00	0.00	0.00	10.32	9.72	1.42	1.04	1.10
MgO	0.00	0.00	11.96	12.57	12.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	6.24	0.00	0.00	0.00	0.00	27.81	27.54	27.33	0.00	0.00	11.94	15.68	15.85
BaO	0.00	1.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	7.94	0.93	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.00	15.95	1.07	2.51	2.85	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
La ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.89	3.05
Ce ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	8.37	6.19	6.04
Nd ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.16	2.79	2.37
Total	98.69	100.55	86.54	87.31	89.86	99.20	98.31	98.56	99.45	98.86	91.54	94.99	95.61
<i>Cation numbers</i>													
Si	2.71	2.97	3.08	3.19	3.14	1.01	1.05	1.00	—	—	3.08	3.05	3.04
Ti	—	—	0.07	0.07	0.15	0.91	0.90	0.94	1.00	0.99	—	—	—
Al	1.29	1.02	1.41	1.55	1.37	0.07	0.06	0.05	—	—	1.97	2.08	2.12
Fe ⁺²	—	—	2.33	1.95	2.05	0.04	0.05	0.05	0.78	0.80	1.03	0.89	0.87
Mn	—	—	0.08	0.09	0.08	—	—	—	0.22	0.21	0.12	0.12	0.08
Mg	—	—	1.95	2.00	1.96	—	—	—	—	—	—	—	—
Ca	0.30	—	—	—	—	0.97	0.97	0.96	—	—	1.25	1.52	1.52
Ba	—	0.02	—	—	—	—	—	—	—	—	—	—	—
Na	0.69	0.07	—	—	—	—	—	—	—	—	—	—	—
K	0.94	0.15	0.34	0.38	—	—	—	—	—	—	—	—	—
Ñe	—	—	—	—	—	—	—	—	—	—	0.30	0.20	0.20
La	—	—	—	—	—	—	—	—	—	—	0.11	0.10	0.10
Nd	—	—	—	—	—	—	—	—	—	—	0.15	0.09	0.08
OH	—	—	8	8	8	—	—	—	—	—	1	1	1
O	8	8	10.49	10.53	10.44	4.90	4.92	4.94	3	3	11.68	11.57	11.57

Note: minerals: *kfs* is potassic feldspar, *bi-chl* is mixed-layer mica of biotite–chlorite composition, *ilm* is ilmenite, *sph* is sphene, and *aln* is allanite. Analyses were conducted on an JEOL 8100 microprobe at the Far East Geological Institute, Far East Branch, Russian Academy of Sciences. Sample 1306.

We evaluated the *P–T* conditions under which metasomatic rocks were produced at the Berezitovoe deposit [19] at 520°C and 3.5 kbar. These evaluations were made using the garnet–biotite and garnet–muscovite mineral associations to estimate the temperature

and the garnet–biotite–plagioclase and garnet–biotite–muscovite–plagioclase associations to evaluate the pressure. Since the grothite–chlorite association is obviously overprinted on the garnet–biotite one, these estimates can be regarded as the upper limit for grothite

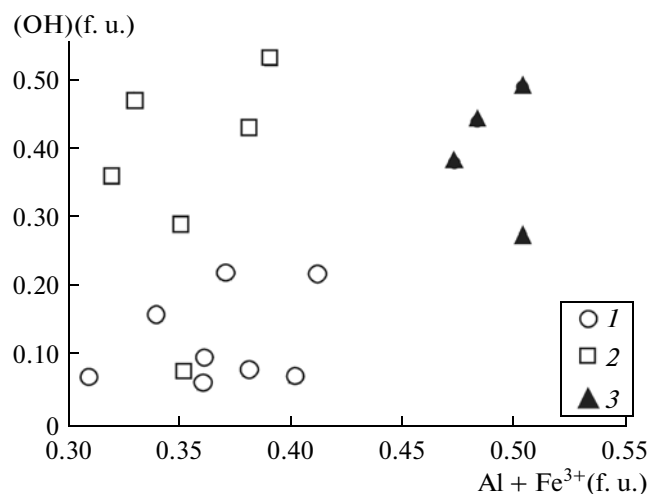


Fig. 5. Correlation between $(\text{Al} + \text{Fe}^{3+})$ and (OH) (p.f.u.) in the crystal chemical formula of grothite: (1) grothite from mineralized metasomatic rocks from the Berezitovoe deposit; (2) grothite from metasomatized host granitoids of the Berezitovoe deposit; (3) grothite from the mineralized metasomatic rocks from the Beregovaya zone.

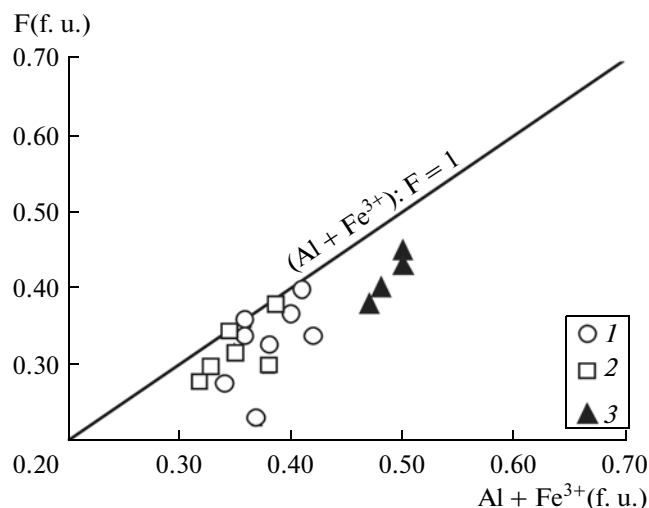


Fig. 6. Correlation between $(\text{Al} + \text{Fe}^{3+})$ and F (p.f.u.) in the crystal chemical formula of grothite. See Fig. 5 for symbol explanations.

crystallization conditions at the Berezitovoe deposit. The temperature of grothite crystallization can be further and more accurately constrained by the garnet–chlorite thermometer [20], although this leads to an insignificant uncertainty in the temperature estimate stemming from the uncertainty as to whether the garnet was in equilibrium with the chlorite. Tables 1 and 3 report the garnet–chlorite temperature estimates: 430–490°C. Our data led us to believe that grothite was likely formed in the metasomatic rocks at temperatures of 400–500°C and pressures of 3–3.5 kbar.

THERMODYNAMIC MODEL FOR THE BINARY CaTiOSiO_4 – CaAlFSiO_4 SPHENE SOLUTION

To enable ourselves to calculate certain equilibria with Al–F sphene, estimate the maximum Al and F concentrations in our grothite, and develop a sphene fluorimeter, we needed a thermodynamic model for the binary sphene solution CaTiOSiO_4 – CaAlFSiO_4 . We borrowed experimental data required for studying the thermodynamic properties and stability of the sphene binary solution CaTiOSiO_4 – CaAlFSiO_4 from [6, 7].

Based on calorimetric and experimental data, thermodynamic properties of the AlF component were derived in [6], and two thermodynamic model were suggested for the sphene solid solution: a multi-site mixing model (MM model) and that of local charge balance (LCB model). According to the multi-site mixing model, the activity of the AlF component in the sphene solid solution is expressed as

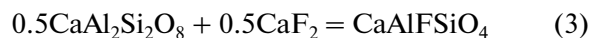
$$RT \ln a_{\text{CaAlFSiO}_4} = 2RT \ln X_{\text{CaAlFSiO}_4} + (W_H - TW_S + PW_V)(1 - X_{\text{CaAlFSiO}_4})^2, \quad (1)$$

where a_{CaAlFSiO_4} is the activity of the AlF component in the sphene solution, X_{CaAlFSiO_4} is its mole fraction, W_i is the Margules parameter, R is the universal gas constant, and P and T are pressure (bar) and temperature (K).

In the local charge balance model, the activity of the AlF component in sphene solution is formulated as

$$RT \ln a_{\text{CaAlFSiO}_4} = RT \ln X_{\text{CaAlFSiO}_4} + (W_H - TW_S + PW_V)(1 - X_{\text{CaAlFSiO}_4})^2. \quad (2)$$

The standard thermodynamic properties of the AlF component and the Margules parameters depend on the chosen model (Table 5). The dependence of the activity of the CaAlFSiO_4 component on the sphene composition was examined in [6] based on the reaction



anorthite + fluorite = Al–F sphene.

The experiments were carried out at a temperature of 800–1000°C and a pressure of 5–21 kbar, and the compositional range of the synthesized sphene encompassed 0.282–0.914 mole fraction of the CaAlFSiO_4 component. To calculate reaction (3), we compiled thermodynamic data from [21] for anorthite and from [22] for fluorite. According to [6], the MM model can much better than the LCB model approximate experimental data, and the W_V Margules parameter determined according to the former model is consistent with XRD data used to evaluate the excess mixing volume for the CaTiOSiO_4 – CaAlFSiO_4 solid solution. The thermodynamic properties of the CaAlFSiO_4 component of the sphene solution were experimentally studied at tem-

Table 3. Analyses and cation proportions in crystal chemical formulas of major minerals in association with grothite in metasomatic rocks from the Beregovaya zone

Com- ponent	Mineral																
	gr-c 1	gr-c 2	gr-c 3	bi 4	bi 5	plg 6	plg 7	chl 8	chl 9	chl 10	mus 11	mus 12	mus 13	kfs 14	kfs 15	ilm 16	ilm 17
	Composition, wt %																
SiO ₂	36.44	36.30	36.11	34.03	35.32	45.38	44.98	25.49	26.25	25.77	45.34	45.64	44.66	64.90	63.66	0.00	0.00
TiO ₂	0.91	0.00	0.00	1.5	2.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.63	0.00	0.00	48.31	50.09
Al ₂ O ₃	20.11	20.36	19.65	16.64	17.28	34.27	33.49	20.18	19.72	19.70	33.72	31.77	30.85	17.98	18.69	0.00	0.00
FeO	8.84	10.88	8.98	18.49	17.66	0.00	0.00	25.26	25.63	25.67	1.6	2.14	3.07	0.00	0.00	27.88	29.89
MnO	26.98	26.13	24.96	0.66	0.76	0.00	0.00	1.39	1.21	1.14	0.00	0.00	0.69	0.00	0.00	18.37	16.21
MgO	0.42	0.52	0.53	11.12	11.37	0.00	0.00	13.24	13.95	14.02	0.97	1.58	0.94	0.00	0.00	0.00	0.00
CaO	5.93	5.10	8.43	0.00	0.07	18.03	17.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.55	0.36
Na ₂ O	0.00	0.00	0.00	0.00	0.00	1.14	1.19	0.00	0.00	0.00	0.00	0.34	0.00	0.00	0.47	0.00	0.00
K ₂ O	0.00	0.00	0.00	10.38	10.99	0.55	0.57	0.00	0.00	0.00	11.20	11.17	10.02	16.24	16.58	0.00	0.00
F	0.00	0.00	0.00	0.42	0.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.63	99.29	98.66	93.34	96.00	99.37	97.71	85.56	86.76	86.30	92.83	92.64	90.86	99.66	99.40	95.11	97.21
	Cation numbers																
Si	2.97	2.97	2.96	2.69	2.70	2.11	2.12	2.77	2.81	2.78	3.11	3.15	3.15	3.01	2.97	—	—
Ti	0.06	—	—	0.09	0.12	—	—	—	—	—	—	—	0.03	—	—	0.96	0.97
Al	1.93	1.96	1.89	1.55	1.56	1.88	1.86	2.59	2.49	2.51	2.73	2.59	2.57	0.98	1.03	—	—
Fe ⁺²	0.60	0.65	0.42	1.22	1.13	—	—	2.30	2.30	2.32	0.09	0.12	0.18	—	—	0.53	0.62
Fe ⁺³	0.01	0.09	0.19	—	—	—	—	—	—	—	—	—	—	—	—	0.08	0.02
Mn	1.87	1.81	1.73	0.04	0.05	—	—	0.13	0.11	0.10	—	—	0.04	—	—	0.41	0.35
Mg	0.05	0.06	0.06	1.31	1.30	—	—	2.15	2.22	2.26	0.10	0.163	0.10	—	—	—	—
Ca	0.52	0.45	0.74	—	0.01	0.90	0.88	—	—	—	—	—	—	—	—	0.02	0.01
Na	—	—	—	—	—	0.10	0.11	—	—	—	—	—	—	—	0.04	—	—
K	—	—	—	1.05	1.07	0.03	0.03	0.00	0.00	0.00	0.98	0.99	0.90	0.96	0.99	—	—
F	—	—	—	0.10	0.10	—	—	—	—	—	—	—	—	—	—	—	—
OH	—	—	—	1.90	1.90	—	—	8	8	8	2	2	2	—	—	—	—
O	12	12	12	10	10	8	8	10	10	10	10	10	10	8	8	3	3
X _{Fe} ^{Gr}	0.92	0.91	0.87	—	—	—	—	—	—	—	—	—	—	—	—	—	—
X _{Ca} ^{Gr}	0.17	0.156	0.23	—	—	—	—	—	—	—	—	—	—	—	—	—	—
X _{An} ^{Pl}	—	—	—	—	—	0.90	0.89	—	—	—	—	—	—	—	—	—	—
X _{Fe} ^{Bi}	—	—	—	0.48	0.46	—	—	—	—	—	—	—	—	—	—	—	—
X _{Fe} ^{Chl}	—	—	—	—	—	—	—	0.52	0.51	0.51	—	—	—	—	—	—	—

Note: minerals: *gr-c* and *gr-r* are garnet (core and rim, respectively), *bi* is biotite, *chl* is chlorite, *plg* is plagioclase, *mus* is muscovite, *kfs* is potassic feldspar, *ilm* is ilmenite; compositional parameters: X_{Fe}^{Gr} is the Fe mole fraction of garnet $X_{Fe}^{Gr} = Fe/(Fe + Mg)$, X_{Ca}^{Gr} is the Ca mole fraction of garnet $X_{Ca}^{Gr} = Ca/(Ca + Fe + Mg + Mn)$, X_{An}^{Pl} is the anorthite content of plagioclase, X_{Fe}^{Bi} is the Fe mole fraction of biotite $X_{Fe}^{Bi} = Fe/(Fe + Mg)$. Analyses were conducted on an JEOL 8100 microprobe at the Far East Geological Institute, Far East Branch, Russian Academy of Sciences. Sample 1374.

Table 4. Analyses and cation proportions in crystal chemical formulas of grothite in rocks from the Beregovaya zone

Com- ponent	Sample 96								Sample 1306						Sample 1374			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
<i>Composition, wt %</i>																		
SiO ₂	31.91	32.10	31.67	30.98	31.39	31.53	31.81	33.69	31.57	32.02	31.87	32.39	32.23	32.66	33.62	31.99	33.41	33.41
TiO ₂	27.98	28.29	24.68	24.88	26.4	27.06	24.00	23.26	27.12	27.54	26.78	26.62	25.39	22.52	20.21	20.51	22.84	22.84
Al ₂ O ₃	8.44	7.91	10.71	9.93	8.79	8.72	10.33	12.71	8.57	7.84	8.32	8.34	9.14	11.96	13.71	13.07	12.03	12.03
Fe ₂ O ₃	1.30	0.81	0.89	0.99	1.19	1.23	1.34	1.00	1.10	1.38	1.80	1.18	2.08	1.56	1.00	0.87	2.67	2.67
CaO	28.36	29.21	28.74	28.42	28.28	28.37	27.67	28.94	28.42	26.99	26.98	26.61	26.42	26.88	27.28	27.88	25.70	25.70
F	2.70	3.82	3.22	3.49	3.42	3.20	3.79	6.16	3.26	2.70	2.98	2.87	2.76	3.58	4.27	4.05	3.78	3.78
–O=F ₂	1.14	1.61	1.36	1.47	1.44	1.35	1.60	2.60	1.38	1.14	1.26	1.21	1.16	1.51	1.80	1.71	1.59	1.59
Total	99.55	100.5	98.55	97.22	98.03	98.76	97.35	103.2	98.66	97.33	97.47	96.80	96.85	97.65	98.29	96.66	98.83	98.83
<i>Cation numbers</i>																		
Ca	0.98	0.95	0.96	0.97	0.98	0.97	0.96	0.93	0.89	0.97	0.90	0.91	0.88	0.88	0.88	0.87	0.93	0.82
Ti	0.62	0.66	0.63	0.58	0.60	0.64	0.65	0.57	0.53	0.65	0.65	0.63	0.62	0.59	0.52	0.45	0.48	0.52
Al	0.35	0.31	0.34	0.40	0.38	0.33	0.33	0.38	0.35	0.32	0.29	0.31	0.30	0.33	0.43	0.48	0.48	0.42
Fe ⁺³	0.03	0.03	0.03	0.02	0.02	0.03	0.03	0.04	0.04	0.03	0.03	0.04	0.03	0.05	0.04	0.02	0.02	0.06
Si	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
F	0.33	0.28	0.23	0.34	0.37	0.36	0.34	0.40	0.38	0.34	0.28	0.32	0.30	0.30	0.38	0.45	0.43	0.40
OH	0.08	0.16	0.22	0.14	0.07	0.06	0.09	0.22	0.53	0.07	0.36	0.29	0.47	0.43	0.38	0.49	0.27	0.44
O	4.55	4.56	4.55	4.52	4.56	4.58	4.57	4.38	4.09	4.59	4.36	4.39	4.23	4.27	4.24	4.06	4.30	4.16

Note: Analyses: (1–14) grothite from rocks from the Berezitovoe deposit (1–8—mineralized metasomatites rich in Au, Ag, Pb, and Zn; 9–14—granitoids hosting the mineralized zone); (15–18) metasomatites from the Beregovaya zone. Analyses were conducted on an JEOL 8100 microprobe at the Far East Geological Institute, Far East Branch, Russian Academy of Sciences. Cation proportions of grothite were calculated in compliance with the technique [1].

peratures of 900–1100°C and pressures of 11–40 kbar [7]. To describe the thermodynamic properties of this solid solution, these authors applied a regular symmetrical mixing model, in which the activity coefficient of end member i is $RT \ln \gamma_i = W(1 - X_i)^2$, where i is an end member of the solid solution, and W is the Margules parameter. The equation for estimating W is as follows:

$$W(\text{Jmol}^{-1}) = -47672 + 34.956T. \quad (4)$$

The standard thermodynamic properties of the CaAlFSiO₄ component [7] are very close to those reported in [6]. Inasmuch as Al–F sphene in our samples of metasomatic rocks from the Berezitovoe deposit obviously crystallized at low P – T parameters, data in [6] are more suitable for extrapolating the properties of sphene solid solution to low temperatures and pressures, because these experiments were carried out at lower temperatures and pressures than the experiments in [7] and all results in [6], except only the mixing

model for the sphene solid solution, are in good agreement with the results in [7].

In Table 6, the experimental data [6] on reaction (3) are compared with the results of our calculations conducted by various mixing models for the solid solution of sphene, with regard to the thermodynamic properties of fluorite compiled from [22, 23]. The results clearly demonstrate that (i) the MM model better than the LCB model approximates the experimental data and (ii) the chosen thermodynamic properties of fluorite are crucial for the approximation accuracy of the experimental data. Because of this, all of our further simulations were carried out with the thermodynamic properties of fluorite from [22] and those for anorthite, rutile, and quartz from [21], and with the MM model for the sphene solid solution with $W = 13600 + P0.214 \text{ J/mol}$ (Table 5) and W_S assumed to be zero.

Table 5. Standard thermodynamic properties of the CaAlFSiO_4 component and its Margules parameters

Parameter	Value	Unit of measure
MM model		
Gibbs standard energy G^0	–2592900	J mol^{-1}
Standard enthalpy H^0	–2740800	J mol^{-1}
Standard entropy S^0	104.9	$\text{J mol}^{-1} \text{K}^{-1}$
Molar volume V^0	5.183	$\text{J mol}^{-1} \text{bar}^{-1}$
Margules parameter $W_H - TW_S$	13600	J mol^{-1}
Margules parameter W_V	0.214	$\text{J mol}^{-1} \text{bar}^{-1}$
LCB model		
Gibbs standard energy G^0	–2587800	J mol^{-1}
Standard enthalpy H^0	–2733800	J mol^{-1}
Standard entropy S^0	111.3	$\text{J mol}^{-1} \text{K}^{-1}$
Molar volume V^0	5.183	$\text{J mol}^{-1} \text{bar}^{-1}$
Margules parameter $W_H - TW_S$	–9100	J mol^{-1}
Margules parameter W_V	0.214	$\text{J mol}^{-1} \text{bar}^{-1}$

Note: Units of measure are quoted in [6] with misprints.

Table 6. Comparison of experimental results [6] with our model calculation results obtained with various mixing models for the solid solution

Experiment no.	$T(^{\circ}\text{C})$	P (kbar)	Mole fraction of the F–Al end member of sphene				
			Experiment	1	2	3	4
G-391	1000	5	0.282	0.271	0.259	0.419	0.170
G-392	1000	6	0.290	0.289	0.275	0.450	0.189
G-444	800	7	0.393	0.376	0.377	0.626	0.269
G-416	850	7	0.371	0.355	0.352	0.612	0.251
G-422	950	7	0.330	0.321	0.311	0.509	0.221
G-402	1000	7	0.309	0.308	0.297	0.471	0.208
G-389	1000	9	0.367	0.351	0.337	0.552	0.254
G-409	900	10	0.460	0.448	0.415	0.711	0.325
G-404	950	10	0.417	0.397	0.389	0.646	0.302
G-400	1000	10	0.394	0.376	0.361	0.590	0.280
G-395	1000	12	0.464	0.434	0.421	0.682	0.341
G-413	1000	15	0.605	0.543	0.520	0.833	0.458
G-403	1000	16	0.632	0.586	0.590	0.868	0.504
G-407	1000	17	0.679	0.633	0.596	0.917	0.555
S				0.0008	0.0018	0.0472	0.0143

Note: Models: (1) MM model, fluorite thermodynamics $G_{298} = -280903 \text{ cal/mol}$ [22]; (2) LCB model, fluorite thermodynamics $G_{298} = -280903 \text{ cal/mol}$ [22]; (3) MM model, fluorite thermodynamics $G_{298} = -277796 \text{ cal/mol}$ [23]; (4) ideal mixing. S is the mean square error of the estimate. Coefficients in Berman's equation for the calculation of the fluorite volume are borrowed from: V_1 and V_2 from [24], V_3 and V_4 from [7].

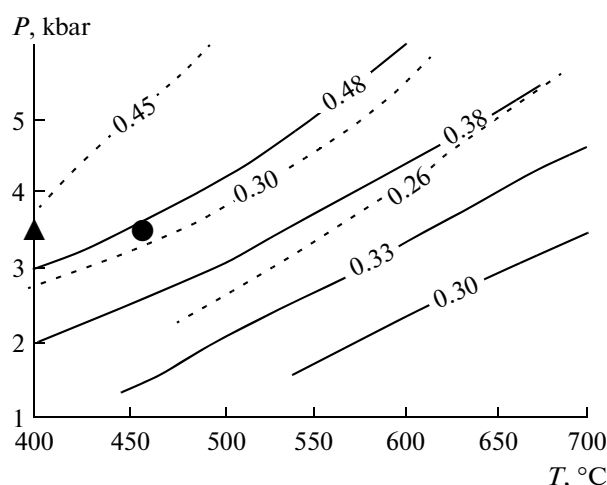


Fig. 7. Dependence of the concentration of the CaAlFSiO_4 end member in sphene in the sphene–plagioclase–fluorite–fluid equilibrium on temperature and pressure. Solid lines show Al concentration in sphene in equilibrium with anorthite, and dashed lines show these concentrations in sphene equilibrium with plagioclase (27–30% anorthite). The solid circle and triangle show grothite in granitoids of the Berezitovoe deposit (circle) and metasomatic rocks from the Beregovaya zone (triangle).

MAXIMUM CONCENTRATION OF THE CaAlFSiO_4 COMPONENT IN THE SPHENE SOLID SOLUTION UNDER P – T PARAMETERS OF METASOMATIC ROCKS AT THE BEREZITOVUE DEPOSIT

Reaction (3) can be expressed through the equilibrium constant and standard Gibbs energy as

$$(v\Delta G^0)_{P,T} = -RT \ln Kp_3. \quad (5)$$

whose equilibrium constant Kp_3 is

$$Kp_3 = a_{\text{alf}}/(a_{\text{fl}})^{0.5} (a_{\text{an}})^{0.5}. \quad (6)$$

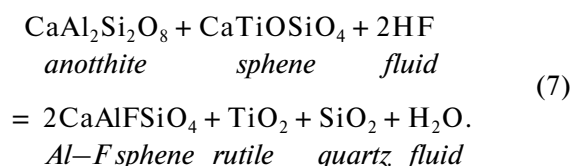
In (5) and (6), δG^0 is the standard Gibbs energy of reaction (3) as calculated from the properties of the anorthite, fluorite, and CaAlFSiO_4 end members, which is constant at given P – T parameters, a_{alf} , a_{fl} , and a_{an} are the activities of the CaAlFSiO_4 component, anorthite, and fluorite in the respective solid solutions, and v are stoichiometric coefficients of reaction (3).

It can be seen from the expression for the constant of reaction (6) that a decrease in the Ca mole fraction of plagioclase (anorthite activity) at any given P – T parameters should be associated with a decrease in the CaAlFSiO_4 activity in the sphene solid solution, and the maximum value of this activity is reached in equilibria with anorthite and pure fluorite. We have calculated the temperature and pressure dependence of the activity and concentration of CaAlFSiO_4 in sphene in the sphene–plagioclase–fluorite equilibrium based on the aforementioned thermodynamic data (Fig. 7). The cal-

culations were conducted with the MM model of the sphene solid solution and the model [25] for the plagioclase solid solution. The diagram clearly shows that the concentration of CaAlFSiO_4 in the sphene solid solution in its equilibrium with plagioclase and fluorite increases with increasing pressure and decreasing temperature, and the mole fraction of this component cannot be higher than 0.40–0.45 at the P – T parameters of metasomatic rocks of the Berezitovoe deposit ($T = 520^\circ\text{C}$, $P = 3500$ bar) (Fig. 7). If equilibrium (4) involves plagioclase with 27–30% anorthite (as in our rocks) instead of pure anorthite, then the CaAlFSiO_4 mole fraction in the sphene solid solution under the same P – T parameters should be no higher than 0.30. The average mole fraction of CaAlFSiO_4 in the sphene solid solution in metasomatic rocks and granites from the Berezitovoe deposit is, however, 0.32 and reaches 0.42 in the mineral from the Beregovaya zone. As is evident from the arrangement of the data points of these sphene samples in Fig. 7, their composition can be explained by the lower crystallization temperatures (approximately 400° – 450°) of this grothite compared to the temperatures at which the metasomatic rocks were generated. Obviously, the maximum concentration of the F–Al end member in sphene from the Berezitovoe deposit does not contradict the aforementioned temperature estimates.

SPHENE FLUORIMETER FOR EVALUATING F CONCENTRATION IN FLUID

The currently used biotite, muscovite, apatite, topaz, and topaz–andalusite fluorimeters are underlain by experimental data from [26]. Inasmuch as our rocks most probably contain Al–F sphene in equilibrium with plagioclase and rutile (ilmenite), a sphene-based fluorimeter can make use of the following stoichiometric relations:



The equilibrium constant of (7) has the form

$$Kp_7 = (a_{\text{alf}})^2 a_{\text{rt}} a_{\text{Q}} a_{\text{H}_2\text{O}} / a_{\text{an}} a_{\text{sf}} (a_{\text{HF}})^2. \quad (8)$$

The activities of the pure phases can be assumed to be unity, and hence, (8) can be simplified as

$$Kp_7 = (a_{\text{alf}})^2 a_{\text{H}_2\text{O}} / a_{\text{sf}} a_{\text{an}} (a_{\text{HF}})^2. \quad (9)$$

It can be seen from expression (9) that, at a constant anorthite activity and any given P – T parameters, the activity of the CaAlFSiO_4 component in the sphene solid solution is related to the F activity in the aqueous solution. Hence, the rutile–quartz–plagioclase–Al–F sphene assemblage can be utilized as a tool for quantifying the F concentration of a fluid.

Table 7. Composition (numbers of moles) of the systems in the first and second reservoirs before the reaction, for one problem

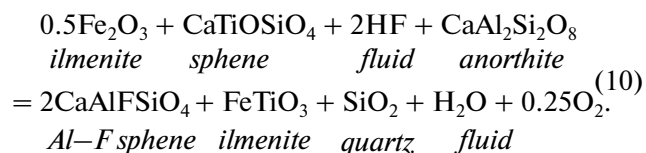
First reservoir					Second reservoir					
CO ₂	CH ₄	C	HF	H ₂ O	plagioclase		sphene		quartz	rutile
					NaAlSi ₃ O ₈	CaAl ₂ Si ₂ O ₈	CaAlFSiO ₄	CaTiOSiO ₄	SiO ₂	TiO ₂
0	0	0.03	0.11	0.195	5.2	1	0	1	1	0

Table 8. Composition (logarithms of mole concentrations) of fluid and solid phases in the second reservoir after the reaction. Solution conditions: $P = 3500$ bar, $T = 525^\circ\text{C}$

Fluid components									
AlO ₂ [−]	CO ₂ [*]	F [−]	HCO ₃ [−]	HF [*]	HSiO ₃ [−]	CO [*]	Na ⁺	NaF [*]	SiO ₂ [*]
−3.13	−0.290	−1.794	−2.84	−2.23	−3.3	−2.631	−1.7	−3.2	−1.0
Solid phases									
plagioclase		sphene		quartz	rutile				
NaAlSi ₃ O ₈	CaAl ₂ Si ₂ O ₈	CaAlFSiO ₄	CaTiOSiO ₄	SiO ₂	TiO ₂				
0.716	−0.025	−0.96	−0.025	0.023	−1.26				

Note: The table lists components whose logarithms of mole concentrations per 1000 g of solution are higher than −4.

Another mineral assemblage that can be used to evaluate F activity in aqueous fluid can be ilmenite–sphene–plagioclase–quartz, because the following stoichiometric expression can be written for these phases:



It is, however, much less convenient to evaluate F activity by equilibrium (10) than (7) because the application of the former requires the evaluation of the oxygen potential and the hematite activity in ilmenite.

In order to quantify F activity from the composition of Al–F sphene in the presence of plagioclase, rutile, and quartz [Eq. (7)], we have carried out thermodynamic calculations based on a model constructed with the application of the Selector-C program package. The model comprised two reservoirs. The first one contained HF, H₂O, and C, and the second one involved plagioclase (consisting of two end members: albite and anorthite), sphene (as the CaTiOSiO₄ end member), and quartz. F-bearing fluid was generated in reservoir 1 and then came to reservoir 2, in which equilibrium was reached between the F-bearing fluid and the gas phase generated by the reaction of Al–F sphene, plagioclase of given composition, rutile, and quartz. Varying the amounts of HF, albite, and anorthite in reservoirs 1 and 2 in the formulation of the problem, we were able to

obtain a certain plagioclase composition at various F concentrations in the fluid and Al–F sphene in equilibrium with this fluid and plagioclase. As an illustrative example of solving one of such problems, Tables 7 and 8 list the input (by the reaction) and output (after the reaction) values.

The thermodynamic system simulated with Selector-C consisted of 57 components, which composed possible minerals, aqueous electrolyte, and a gas phase. The gas phase consisted of eight components: CO₂, CO, F₂, HF, H₂, CH₄, O₂, and H₂O. The solid phases were fluorite, calcite, Al₂SiO₅ polymorphs, albite, anorthite, quartz, sphene (consisting of the CaAlFSiO₄ and CaTiOSiO₄ components), rutile, wollastonite, zoisite, clinozoisite, grossular, paragonite, prehnite, kaolinite, and graphite. The aqueous electrolyte solution contained 30 components: neutral species H₂O, SiO₂, O₂, NaOH, NaHSiO₃, NaF, CH₄, HF, H₂, HAlO₂, CaCO₃, CO₂, and CO; and ions Al(OH)⁺, Al³⁺, AlO⁺, AlO₂[−], CO₃^{2−}, Ca(HCO₃)⁺, Ca²⁺, CaF⁺, CaOH⁺, F[−], HCO₃[−], HF₂[−], HSiO₃[−], Na⁺, SiF₆^{2−}, OH[−], and H⁺. Thermodynamic properties of the gas components and solid phases were calculated from data in the databases [21, 22, 27, 28]. Thermodynamic properties of component of aqueous solution were accounted for by the a-Sprons.tdb database integrated into Selector-C. The activities of ions and neutral compounds in aqueous electrolyte were calculated

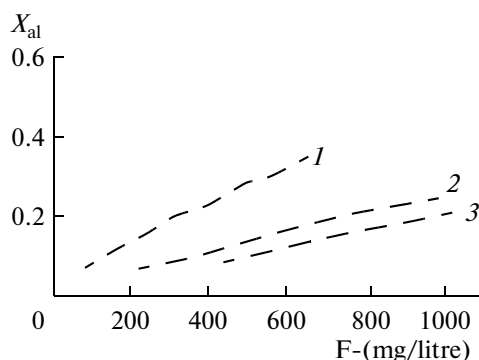


Fig. 8. Correlation between the bulk F concentration of aqueous fluid and the concentration of the CaAlFSiO_4 end member of sphene in the equilibrium sphene–plagioclase–rutile–quartz–fluid at a temperature of 550°C and pressure of 3500 bar. Each line corresponds to a constant concentration of the anorthite end member in plagioclase: line 1—60% anorthite, line 2—30% anorthite, and line 3—15% anorthite.

by a modified Debye–Hückel equation. As is shown by our calculations, the liquid phase in equilibrium with Al–F sphene, plagioclase, and rutile should contain the following compounds (listed in descending order of their concentrations): CO_2 , CH_4 , CO , SiO_2 , HCO_3^- , H_2 , F^- , HF , HSiO_3^- , Na^+ , NaF , NaHSiO_3 , CaF^+ , and AlO_2^- . The parameter assumed as a measure of F concentrations of the fluid was the bulk F concentration as a total of the F^- , HF , NaF , and CaF^+ concentrations recalculated to the F ion. Figure 8 shows that the CaAlFSiO_4 concentration in the sphene solid solution in equilibrium with plagioclase of constant composition, rutile, and quartz systematically increases with increasing bulk F concentration of the fluid. The pH value of the F-bearing fluid was 2–2.5 before its reaction with the components of the second reservoir and increased to 6.5–6.8 after the reaction. The simulation results exhibit a slight increase in the amount of the gas phase, which consisted of H_2O , CH_4 , H_2 , CO_2 , and trace concentrations of HF .

Utilizing a set of problems formulated and simulated with Selector-C and the technique described above, we have derived an equation for the rough evaluation of F concentration in fluid that was in equilibrium with the assemblage rutile–quartz–plagioclase–alumina–F-bearing sphene at any given pressure and temperature. The problems were calculated for temperatures of 450 – 700°C and pressures of 3–7 kbar. The plagioclase composition was varied from 15 to 70% of the anorthite end member, and the mole fraction of the Al–F end member of sphene was 0.1–0.4. The data thus obtained were processed with the application of regression analysis and least-squares method, based on the Levenberg–

Marquardt algorithm [29]. We have processed 445 problems. The resultant equation has the form

$$F = X_{\text{al}}(-17522.9 - 84.0498N_{\text{an}} + 30.00026T + 38821.27X_{\text{al}} - 6.48414X_{\text{al}}P + 0.00302TP), \quad (11)$$

where F is the F concentration in the fluid (in mg/l), N_{an} is the plagioclase composition (percentage of its anorthite end member), P is pressure (bar), T is temperature ($^\circ\text{C}$), and X_{al} is the mole fraction of the F–Al end member of sphene. The latter parameter is calculated from the crystal-chemical formula of the sphene calculated according to [1] and is numerically equal to the number of F ions, i.e., $X_{\text{al}} = F(\text{p.f.u.})$. Thereby the total of Al and Fe^{3+} ions in the sphene crystal-chemical formula should be greater than or equal to the number of F ions. As can be seen from Table 4, this rule is complied with by all of the 18 analyses. The approach suggested for determining the mole fraction of the F–Al end member of sphene makes it possible to avoid errors related to the presence of the vuagnatite end member in sphene and possible overestimation of F concentration in microprobe analyses. The estimated accuracy of Eq. (11) by the least-squares method (squared deviations of the input and calculated values) is 82%, and the correlation coefficient between the Selector-C results and the equation is 91%.

Below we present an example of calculation by Eq. (11) for $N_{\text{an}} = 15$, $T = 500^\circ\text{C}$, $X_{\text{al}} = 0.1734$, $P = 3000$ bar, and a F concentration in the fluid of 712 mg/L. Equation (11) is applicable to temperature within the range of 500 – 700°C and can yield negative F concentrations in fluid at lower temperatures, in the region of relatively low concentrations of the F–Al end member of sphene ($X_{\text{al}} < 0.15$) and highly calcic plagioclase ($N_{\text{an}} > 60$).

F CONCENTRATION IN FLUID WHEN MINERALIZED ROCKS WERE FORMED AT THE BEREZITOVoe DEPOSIT

The data presented above allowed us to estimate the F regime when grothite-bearing mineral assemblages were produced at the Berezitovoe deposit. If the differences in the F concentrations of the fluid estimated by the sphene and biotite fluorimeters are ignored, i.e., it is assumed that $\log M_{\text{HF}}(\text{Bi}) \cong \log M_{\text{F}}(\text{Sph})$, where $\log M_i$ is the logarithm of the molar bulk F concentration recalculated to the F ion per 1000 g of the fluid, then the F concentration of the fluid during the generation of the AlF sphene at the Berezitovoe deposit should have been comparable with the F concentration in fluid during the development of greisens and rare-metal pegmatites: point 1 ($\log M_{\text{F}} = -1.6$, $T = 450^\circ\text{C}$, sample 1306) and point 2 ($\log M_{\text{F}} = -1.8$, $T = 420^\circ\text{C}$, sample 1374) (Fig. 9). These values of the F concentra-

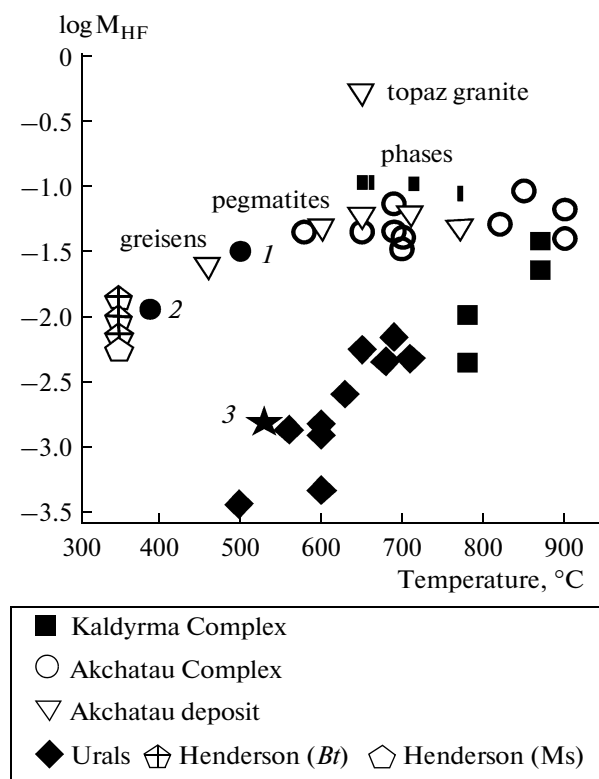


Fig. 9. Concentration F_{HF} ($\log M_{HF}$, mol/dm³) in fluids related to various types of granites (central Kazakhstan, the Urals, and the Akchatau and Henderson deposits) determined using the fluorimeter [26] and the F concentration of fluid at the Berezitovoe deposit [(1, 2) solid circles—by sphene (grothite), (3) asterisk—by biotite (see text)].

tion in the fluid were obtained by means of model simulations with Selector-C. If the F concentration of the fluid is estimated using the primary (pre-grothite) biotite, it turns out to be much lower. Generally speaking, microprobe analyses of all micas from the Berezitovoe deposit show low F concentrations, which are comparable with the microprobe detection limit (Table 3). The F concentration of the fluid was estimated using biotite and equation [26]

$$\log M_{HF}(Bt) = \log(X_F/1 - X_F)Bt - 1722/T(K) - 1.107 \quad (12)$$

$$\times X_{Mg} + 0.216(Al - 2) + 0.8958 + \log a_{H_2O}.$$

where $X_F = F/4$, $X_{Mg} = Mg/\Sigma oct$; F, Mg, and Al are the numbers of the respective ions in the crystal chemical formula of biotite calculated by normalizing to 44 negative charges.

Calculations by this equation yield a value of $\log M_{HF} = -2.77$ ($T = 525^\circ\text{C}$) based on the biotite composition from Table 3 (asterisk on the low-F trend in Fig. 9). Hence, the F concentration in the mineral-forming fluid evolved from low values when the metaso-

matic biotite- and muscovite-bearing associations were formed to high ones when the grothite—chlorite assemblages were produced. Hence, a “greisen” level of F concentrations in fluid was reached at the Berezitovoe deposit only very late during the development of the mineralized metasomatic rocks.

CONCLUSIONS

We were the first to find Al-F sphene (grothite) in mineralized metasomatic rocks and metasomatized granitoids at the Berezitovoe deposit and to demonstrate that the typical mineral assemblage of the grothite is grothite—chlorite—ilmenite—magnetite. This grothite—chlorite mineralization is younger and overprinted on the primary garnet—biotite—muscovite mineral assemblages. The P – T parameters of grothite crystallization were estimated at 400–500°C and 3000–3500 bar.

The composition of grothite from three samples was examined on a microprobe. The average Al and F concentrations (in f.u.) are 0.45 and 0.42 in sample 1374, 0.32 and 0.32 in sample 1306, and 0.35 and 0.33 in sample 96. Grothite from the granite is the richest in the vuagnatite $\text{CaAlSiO}_4(\text{OH})$ end member. Higher Al and F concentrations in grothite (in sample 1374) are demonstrated to be most likely accounted for by lower (400°C) crystallization temperatures of the mineral.

A sphene fluorimeter is developed for evaluating F concentrations in fluid, and quantitative estimations are provided for the F concentration in the fluid present when the grothite-bearing mineral associations were produced. These associations were proved to be formed by a F-rich fluid, whose F concentration roughly corresponded to that in greisenizing fluid.

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