Petrochemical Criteria of Staurolite Stability in Metapelites at Medium-Temperature Low- and Medium-Pressure Metamorphism

E. B. Borisova[a, b,]* **and Sh. K. Baltybaev[a, b,]****

[a] *Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, St. Petersburg, 190034 Russia*
[b] *St. Petersburg State University, St. Petersburg, 199034 Russia*
*e-mail: jenyaborisova98@gmail.com
**e-mail: shauket@mail.ru

Abstract—Staurolite stability in rocks of zonal metamorphic complexes and the subsequent decomposition of this mineral in the rocks at increasing temperature is a criterion for distinguishing the staurolite metamorphic zone. Along with other metamorphic zones, this zone reflects the temperature distribution configuration when the metamorphic zoning was formed. Staurolite-bearing mineral assemblages are formed in metapelites of appropriate chemical composition at metamorphic temperatures of ~500−650°C. The fact that staurolite is stable within a relatively narrow temperature range makes it possible to predict the presence or absence of this mineral in rocks if representative data on the composition of their protoliths are available. We propose a method for identifying potentially staurolite-bearing rocks using computational petrochemical modules, whose values are calibrated on natural rocks and modeled rock compositions that can occur in nature. Four petrochemical modules are proposed in the form of specified proportions of major chemical components in metamorphic rocks: Al_2O_3/SiO_2, CaO/FM (where $FM = FeO_t + MgO$), K_2O/FM, and Na_2O/FM. They can be used as criteria for estimating the possibility of staurolite crystallization in rocks when a suitable temperature (and pressure) is reached. These modules make it possible to select and more reliably specify the boundaries of the staurolite zone when, for example, maps of metamorphism are produced.

Keywords: staurolite, metamorphic zoning, petrochemical module, metamorphism, mineral assemblage
DOI: 10.1134/S0869591121040020

INTRODUCTION

Iron−magnesium staurolite $(Fe^{2+}, Mg, Zn)_2Al_9[(Si, Al)O_4]_4O_4(OH)_2$ is a typical metamorphic index mineral of aluminous rocks, such as metapelites, because it is stable within a relatively narrow *P–T* field in medium-temperature metamorphic complexes (Barrow, 1893; Korikovsky, 1979; Ballèvre et al., 1989; Chopin et al., 2003; and others).

We have studied staurolite-bearing rocks in the northern Ladoga area, which was affected by zoned high-gradient metamorphism of the andalusite−sillimanite facies series, where, the mineral assemblages of the rocks systematically evolving from andalusite, staurolite−andalusite, sillimanite−muscovite, sillimanite−K-feldspar, and cordierite−K-feldspar to high-temperature garnet−cordierite−K-feldspar ones (Nagaitsev, 1974; Sudovikov et al., 1970; Baltybaev et al., 2000).

This zonal metamorphic complex has been studied by many geologists starting from the mid-20th century (Sudovikov, 1954; Nagaitsev, 1965, 1974; Kitsul, 1963; Predovskii et al., 1967; Sudovikov et al., 1970; Veliko-slavinskii, 1972; Baltybaev et al., 2000, 2009). Although the geology of this territory was thoroughly studied and mapped in much detail, the distinguishing of the staurolite isograd in the northern part of the metamorphic complexes turned out to be ambiguous. Various interpretations of the metamorphic zoning were proposed in the 1970s (Figs. 1a, 1b), and differences between them are most clearly seen in positioning the low-temperature boundary of the staurolite zone (and, correspondingly, the affiliation of the rocks with certain metamorphic facies).

When mapping the metamorphic zoning, Yu.V. Nagaitsev (1965, 1974) and D.A. Veliko-slavinskii (1972) determined mineral isograds based on petrographic studies, i.e., as inferred from the appearance and disappearance of critical mineral assemblages at the systematic evolution of the mineral assemblages from those with muscovite to higher temperature assemblages with biotite and staurolite

Fig. 1. Schematic map of metamorphic zoning in the northern Ladoga area. (a) According to (Nagaitsev, 1965, 1974), (b) according to (Predovskii et al., 1967), (c) according to (*Geological ...,* 1980). Metamorphic zones: *I*—biotite, II—garnet, III—staurolite–andalusite, IV—sillimanite–muscovite (–almandine) and biotite–sillimanite, V—zone of ultrametamorphism. Metamorphic facies: GSF—greenschist, EAF—epidote-amphibolite (staurolite zone), EA-AF—epidote-amphibolite–amphibolite, undifferentiated. In Fig. 1c, metamorphic facies were distinguished according to the systematics of metamorphic in facies (Dobretsov, 1969), the *P–T* parameters of the epidote-amphibolite facies correspond to the staurolite facies in (Korikovsky, 1979). The ambiguous position of the low-temperature boundary of the staurolite zone is obvious from the comparison of Figs. 1a and 1b.

$$Ms^1 + Chl \rightarrow Bt + And \pm St + Qtz + \text{H}_2\text{O};$$

$$Ms + Chl \pm Mgt \rightarrow Bt + St + Qtz + \text{H}_2\text{O}.$$
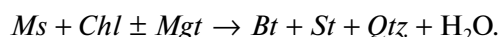
Based on the geology and composition of rock sequences in the area, A.A. Predovskii and his colleagues (Predovskii et al., 1967) have determined that the boundary at which staurolite starts to be stable in the rocks occurs to the north of the area, in a lower temperature zone (Fig. 1b).

The later fieldwork under Project GDP-200, which involved mapping of the metamorphic rocks, (*Geological ...,* 1989), also has not clarified this issue but instead resulted in a still another schematic map of the metamorphic zoning, in which the field of the staurolite-bearing rocks is mapped not as specified above (Fig. 1c).

The ambiguous interpretation of the position of the staurolite isograd is explained, in our opinion, by some features that control staurolite stability in rocks: in addition to suitable *P–T* parameters, its stability requires a suitable chemical composition of the protolith. If a rock did not contain staurolite, it could have been attributed to a lower temperature metamorphic zone, assuming that the temperature was not high enough for staurolite to crystallize.

Due to the fact that the stability of mineral assemblages with staurolite depends not only on the temperature of metamorphism (~500–650°C in Fe–Mg metapelite systems) but also on the chemical composition of the protolith (favorable protoliths are aluminous, with some other compositional features), we propose a method for identifying potentially staurolite-bearing rocks by using calculated *petrochemical modules*, which values are calculated to predict which medium-temperature rocks in metamorphic
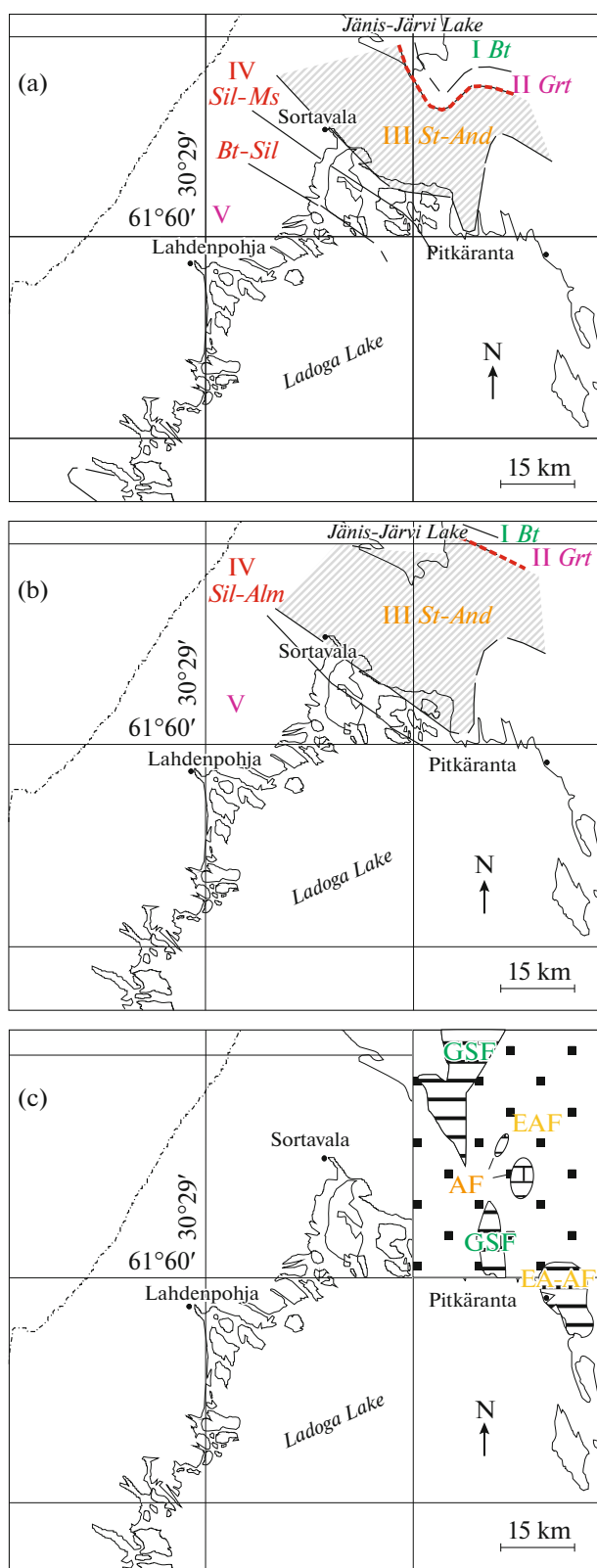
[1] Mineral symbols: *Alm*—almandine, *Amph*—amphibole, *Als*—Al$_2$SiO$_5$ minerals, *An*—anorthite, *And*—andalusite, *Bt*—biotite, *Chl*—chlorite, *Crd*—cordierite, *Fib*—fibrolite, *Fsp*—feldspar, *Grt*—garnet, *Ilm*—ilmenite, *Kfs*—K-feldspar, *Ky*—kyanite, *Mgt*—magnetite, *Ms*—muscovite, *Opx*—orthopyroxene, *Pl*—plagioclase, *Qtz*—quartz, *Ru*—rutile, *Sil*—sillimanite, *Sp*—spinel, *St*—staurolite, *Ta*—talc, *Tit*—titanite.
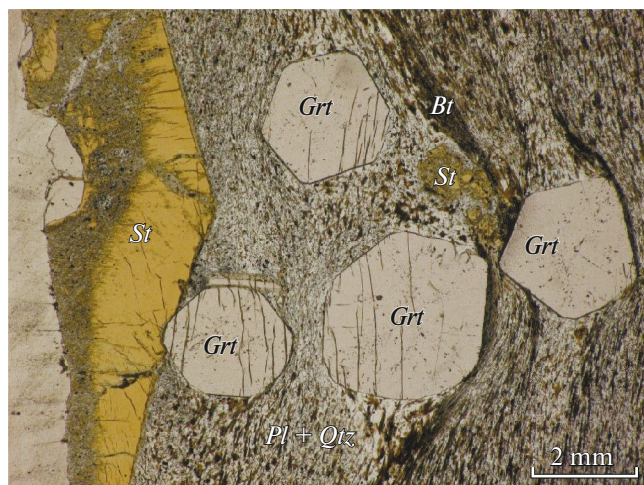
Fig. 2. Microphoto of a thin section of garnet–staurolite schist, sample B-05-177, magnification 40×, plane-polarized light, one polarizer.

sequences of broadly variable composition can contain staurolite.

The petrochemical moduli in the form of ratios of major components can serve as unbiassed and quantitatively unambiguous criteria for metamorphosed rocks that enable the researcher to determine whether staurolite can crystallize at the metamorphism of certain lithologies when specified temperatures and pressures are reached. It is important that the occurrence of metamorphic staurolite is possible only within a fairly narrow temperature range, although the staurolite-bearing rocks can thereby occur in zoned metamorphic complexes over large areas, whose size may range from tens of and to a few hundred square kilometers. In addition to clarifying the boundaries of the staurolite zone, this method can also be applied to determine the metamorphic grade of the staurolite facies (subfacies) even if staurolite is not found in the rocks. Evidently, the erroneous attribution of staurolite-free rocks to pre-staurolite zones has affected how the boundaries of metamorphic zones were shown in maps of metamorphism in the northern Ladoga area (Nagaitsev, 1965; Predovskii et al., 1967; Velikoslavinskii, 1972; *Geological ...,* 1989).

This study was focused on determining and justifying the ranges of proportions of major components in metapelites that can be used as criteria for distinguishing the staurolite zone and metamorphic facies both in the northern Ladoga area and in other medium-temperature metamorphic complexes elsewhere.

MATERIALS AND METHODS

To understand which compositions of protoliths are potentially favorable for staurolite stability, we used staurolite-bearing metapelites from the northern Ladoga area. The chemical composition of staurolite-free gneisses and schists sampled not far from the staurolite-bearing rocks were used as reference samples whose major-component and trace-element parameters were unsuitable for staurolite stability in them, although these rocks occurred under $P–T$ parameters of the staurolite facies.

Moreover, based on empirical data on the composition of rocks vs. the presence/absence of staurolite in them, we conducted computer modeling of mineral formation. The simulated results on staurolite presence or absence turned out to be exactly (with 100% probability) consistent with the natural observations, and in rocks that do not contain staurolite, it was not reproduced. This made it possible to conduct computer modeling for a broad range of the compositions of the protoliths and, hence, to predict whether this mineral shall or shall not occur in a diversity of "theoretical" compositions of protoliths that can be generated based on the compositions of naturally occurring metapelites.

We used 74 samples of staurolite-bearing metapelites from different regions, 22 staurolite-free rocks surrounded by staurolite-bearing ones, and also 574 theoretical compositions of the protoliths which is close to the metapelite composition. Of the 47 rock samples from the northern Ladoga area, 25 contained staurolite-bearing mineral assemblages, and 22 did not. In selecting 27 samples of staurolite-bearing rocks from 11 areas elsewhere, we did not give preference to samples from a single region (because they were usually of similar composition) but instead tried to select samples from various area to cover as broad as possible compositional ranges of the rocks.

We did not use staurolite assemblages from mafic metamorphic complexes (these were usually highly calcic and magnesian rocks) and those from high-pressure geodynamic environments. Hence, the applicability of the petrochemical moduli is limited to metapelite rocks in medium- and low-pressure metamorphic complexes.

The numerical simulations of mineral assemblages are based on the minimization of the Gibbs energy. In the course of this study, the simulations were carried out with the PERPLEX v. 6.88 and v. 6.90 software (Connolly, 1990, with updates up to 2020) and a thermodynamic database for minerals and solid solutions of biotite, plagioclase, amphiboles, chlorite, garnet, spinel, orthopyroxene, white micas, chloritoid, staurolite, cordierite, and ilmenite in the system MnNCK-FMASH ($MnO–Na_2O–CaO–K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O–CO_2$) hp02ver (Holland and Powell, 2011).

MINERALOGY AND PETROGRAPHY OF THE GARNET–STAUROLITE–BIOTITE SCHISTS

To determine the petrochemical moduli, we selected dominant rock varieties from the medium-temperature metamorphic zone in the northern Ladoga area: biotite, biotite–muscovite, garnet–biotite, staurolite–biotite, garnet–staurolite–biotite, and amphibole-bearing gneisses and schists. Compositional parameters were determined for all of the samples, but below we describe in detail only rocks that contained staurolite.

The *garnet–staurolite–biotite schists* are lepido- and porphyroblastic rocks with a fine-grained matrix and a linearly foliated structure. The porphyroblast minerals are euhedral staurolite and garnet crystals (Fig. 2). The foliation is defined by oriented biotite, quartz, plagioclase, and muscovite grains in the matrix.

Staurolite. The mineral occurs as flattened prismatic crystals up to 1 mm long (occasionally longer). The crystals are poikilitic, with their cores hosting inclusions of quartz, monazite, and ilmenite, and with cutting veinlets of secondary minerals (muscovite, biotite, chlorite, and plagioclase). The Fe mole fraction of this mineral varies relatively little ($X_{Fe} = 0.85$–0.90), but the TiO_2 concentration decreases from cores to margins (0.64–0.27 wt % TiO_2), the ZnO concentration increases unsystematically (within 0.09–0.56 wt % ZnO), and the MnO concentration varies (0.0–0.16% MnO).

Garnet. The porphyroblasts of this mineral are large rhombododecahedrons 2–10 mm across, typically with S-shaped growth and crystallization structures. The garnet porphyroblasts abound in small quartz and ilmenite inclusions. The chemical composition of the garnet grains is homogeneous, and their zoning is weak. The garnet consists (in end-member terms) of 86.00–88.93% *almandine*, 0.00–1.83% *spessartine*, 5.83–9.50% *pyrope*, and 3.40–4.73% *grossular*. The staurolite and garnet commonly do not show evidence of reaction replacement of one another, although the contacts of these minerals are sometimes lined by thin (~50 nm) quartz rims with small ilmenite needles.

The *biotite* occurs as platy crystals (~0.2×0.03 mm) and often envelops garnet porphyroblasts. The Fe mole fraction of biotite is the same in contact with garnet and in the matrix ($X_{Fe} = 0.58$–0.62), but the former is poorer in TiO_2 (0.87–1.48 wt %) than the latter (1.50–1.72 wt %).

Plagioclase. Plagioclase makes up the rock matrix, together with quartz and biotite, and was also found in replacement zones of staurolite in association with muscovite, biotite, and quartz. The plagioclase is oligoclase ($An_{13–17}$).

Muscovite. Occurs as elongate platy grains scattered in the rock matrix and replaces, together with biotite
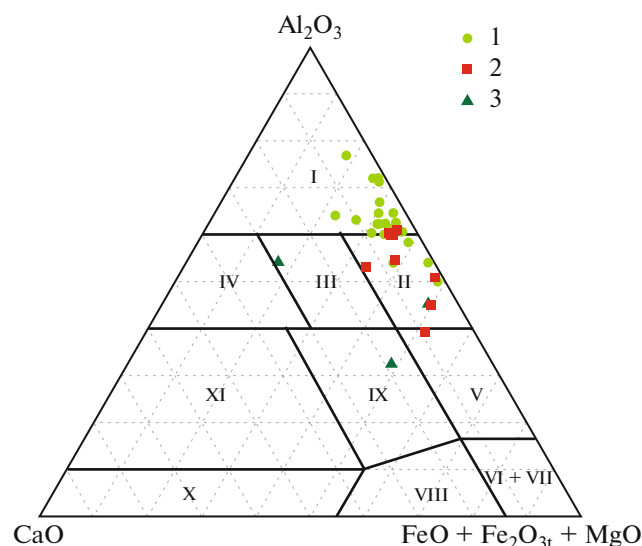

Fig. 3. A–C–F diagram for rocks of the medium-temperature metamorphic zone in the northern Ladoga area. (1) *Bt*, *Grt–Bt,* and *Bt–Ms* schists; (2) *St* and *St-Grt* schists, (3) *Amph* schists. Composition rock fields [according to N.P. Semeneko, quoted from (Efremova and Stafeev, 1985)]: I—aluminosilicate, II—iron-rich–magnesian aluminosilicate, III—alkali-earth–aluminosilicate, ortho-series, IV—calcic–aluminosilicate, V—aluminous–magnesian–iron-rich–siliceous, VI—iron-rich–siliceous, VII—magnesian ultramafic, VIII—alkali-earth–Al-poor, ultramafic orthoseries; IX—alkali-earth–aluminous, mafic orthoseries, X—calc–carbonate, XI—aluminous–calcic.

and plagioclase, staurolite. The muscovite has (Si + Ti) = 2.76–2.86 p.f.u., (Fe + Mg) = 0.08–0.14 p.f.u., and K/(Na + K) = 0.78–0.90. Muscovite found in veinlets in the staurolite is poorer in TiO_2 (0.10–0.24 wt %).

Chlorite. The chlorite is a secondary mineral, replaces the matrix biotite, and develops in cracks, together with muscovite, biotite, and plagioclase, in the staurolite.

Ilmenite. The ilmenite is found as equant and elongate grains (up to 50 nm) in the rock matrix and as inclusions in the staurolite and garnet. The mineral contains a Mn admixture (0.31–0.52 wt %).

Monazite. This mineral was found as small grains disseminated in the rock matrix and as inclusions in the staurolite and garnet.

PETROCHEMICAL SYSTEMATICS OF THE ROCKS

The compositions of the rocks were plotted in the Semenenko triangular plot (Efremova and Stafeev, 1995) to classify them and try to reproduce their protolith (Fig. 3).

We distinguish five rock groups reflecting rock varieties of the Ladoga Group. Most of the rocks plot within the aluminosilicate and ferro–magnesian–alu-

Table 1. Concentrations (wt %) of major oxides in rocks of the metapelite group

Oxide	Compositions of naturally occurring staurolite-zone rocks				Theoretical compositions			
	(*Materials…*, 1964)	(Predovskii et al., 1967)	our data on the northern Ladoga area	elsewhere	all	$\dfrac{max}{min}$	only *St*-bearing	$\dfrac{max}{min}$
SiO_2	$\dfrac{56.65}{6.87}$	$\dfrac{58.94}{3.58}$	$\dfrac{58.96}{4.21}$	$\dfrac{57.14}{7.51}$	$\dfrac{57.92}{4.69}$	$\dfrac{70.21}{40.15}$	$\dfrac{58.27}{4.58}$	$\dfrac{70.21}{40.15}$
Al_2O_3	$\dfrac{18.39}{2.81}$	$\dfrac{19}{2.03}$	$\dfrac{16.89}{1.93}$	$\dfrac{21.25}{3.91}$	$\dfrac{20.55}{3.34}$	$\dfrac{37.60}{9.95}$	$\dfrac{20.55}{3.23}$	$\dfrac{37.60}{12.98}$
FeO_t	$\dfrac{9.19}{2.35}$	$\dfrac{7.84}{0.87}$	$\dfrac{10.07}{2.30}$	$\dfrac{8.53}{2.37}$	$\dfrac{8.72}{2.28}$	$\dfrac{23.50}{1.25}$	$\dfrac{8.72}{1.93}$	$\dfrac{23.20}{2.42}$
MnO	$\dfrac{0.12}{0.06}$	$\dfrac{0.09}{0.04}$	$\dfrac{0.06}{0.07}$	$\dfrac{0.10}{0.03}$	$\dfrac{0.10}{0.04}$	$\dfrac{0.32}{0.01}$	$\dfrac{0.10}{0.04}$	$\dfrac{0.32}{0.01}$
MgO	$\dfrac{4.04}{1.08}$	$\dfrac{3.27}{0.56}$	$\dfrac{3.28}{0.65}$	$\dfrac{2.84}{1.13}$	$\dfrac{2.75}{0.94}$	$\dfrac{5.63}{0.20}$	$\dfrac{2.85}{0.91}$	$\dfrac{5.63}{0.41}$
CaO	$\dfrac{1.81}{0.94}$	$\dfrac{1.51}{0.68}$	$\dfrac{1.82}{1.05}$	$\dfrac{0.93}{0.68}$	$\dfrac{1.44}{0.91}$	$\dfrac{6.28}{0.00}$	$\dfrac{1.31}{0.77}$	$\dfrac{5.37}{0.00}$
Na_2O	$\dfrac{2.35}{0.84}$	$\dfrac{1.8}{0.96}$	$\dfrac{1.66}{0.71}$	$\dfrac{1.33}{0.85}$	$\dfrac{1.66}{0.68}$	$\dfrac{7.53}{0.00}$	$\dfrac{1.63}{0.66}$	$\dfrac{6.90}{0.00}$
K_2O	$\dfrac{3.25}{0.62}$	$\dfrac{3.67}{0.46}$	$\dfrac{3.03}{0.39}$	$\dfrac{3.39}{1.28}$	$\dfrac{3.52}{0.81}$	$\dfrac{7.30}{0.00}$	$\dfrac{3.45}{0.79}$	$\dfrac{5.99}{0.00}$
P_2O_5	$\dfrac{0.16}{0.08}$	$\dfrac{0.11}{0.03}$	$\dfrac{0.10}{0.05}$	$\dfrac{0.15}{0.08}$	$\dfrac{0.93}{0.15}$	$\dfrac{3.00}{0.00}$	$\dfrac{0.94}{0.15}$	$\dfrac{2.00}{0.00}$
TiO_2	$\dfrac{1.08}{0.22}$	$\dfrac{0.87}{0.13}$	$\dfrac{1.05}{0.28}$	$\dfrac{1.04}{0.28}$	$\dfrac{0.14}{0.06}$	$\dfrac{0.46}{0.03}$	$\dfrac{0.14}{0.06}$	$\dfrac{0.46}{0.03}$
Number of samples	7	10	8	27	574		514	

For samples of natural rocks, numerals and numerators and denominators are the arithmetic mean values and RMS deviations, respectively. For theoretical compositions, italicized numerals in numerators are the maximum concentrations of the component, and those in denominators are the minimum ones.

minosilicate composition fields (Fig. 3), and the composition points of the rocks are concentrated mostly along the boundary between the latter two fields. The amphibole and staurolite schists remarkably differ from the distribution of the rest of the rocks.

The amphibole schists are more calcic, and their protolith likely contained much mafic volcanic material, whose probable source was eroded Paleoproterozoic mafic volcanics of the Sortavala Group, which rests on the Archean rocks (*Ladoga …, 2020*).

Similar to most other paragneisses and paraschists in the area, the staurolite schists are interpreted as metamorphosed Paleoproterozoic turbidites of the Ladoga Group, which overlie the metavolcanics of the Sortavala Group (*Ladoga …, 2020*).

THERMODYNAMIC SIMULATIONS

In simulating the phase mineral equilibria with the PERPLEX software (Connolly, 1990), the input data were chemical analyses of the metapelites (Table 1). In solving the direct problem of the simulations, i.e., conducting searches for mineral assemblages corresponding to those found in nature, the rock composition and $P–T$ parameters were specified under the assumption that the system contains $H_2O–CO_2$ fluid, with its X_{CO_2} assumed to be 0.3 based on data derived from studying fluid inclusions hosted in synmetamorphic quartz veins in the metapelites (Baltybaev et al., 2000). Computations made for comparison for some parts of the phase diagrams at X_{CO_2} = 0.1 and 0.6 did

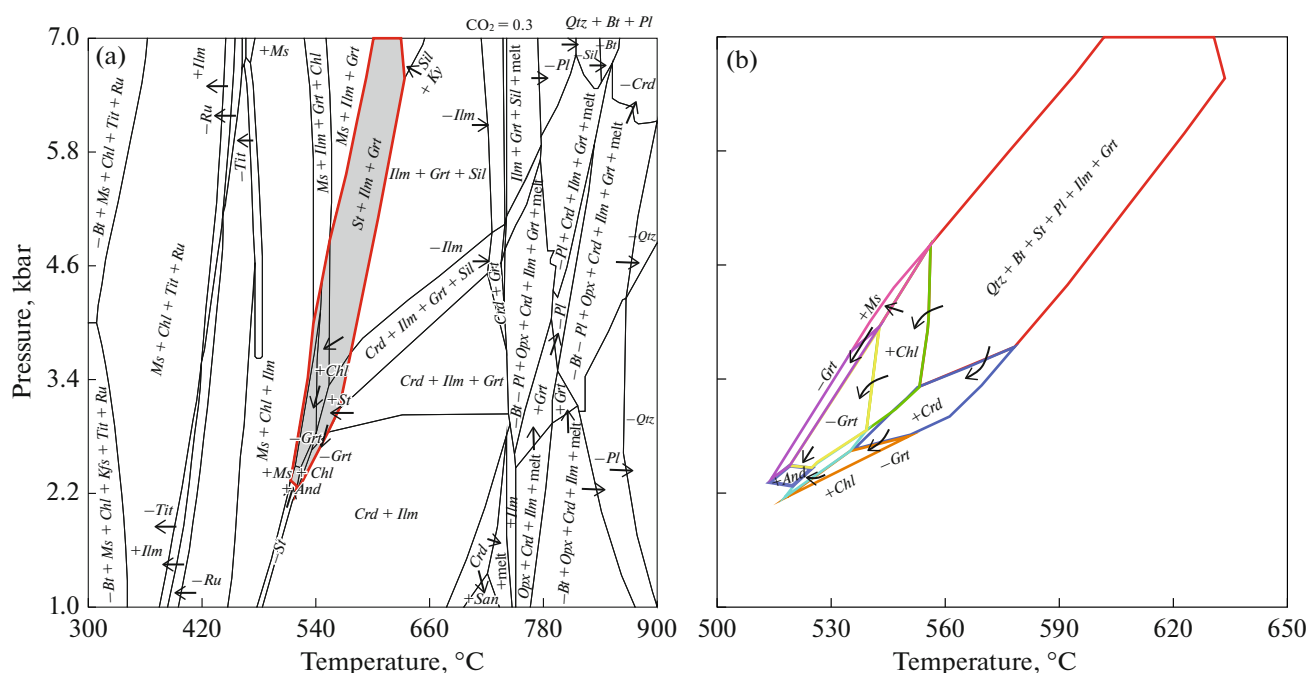**Fig. 4.** Numerically simulated mineralogical composition of metapelites, sample B-05-177. (a) $P–T$ diagram of the stability fields of minerals (for the composition of sample B-05-177, in wt %, $SiO_2 = 67.25$, $TiO_2 = 1.08$, $Al_2O_3 = 12.98$, $Fe_2O_{3t} = 9.85$, MnO < 0.01, MgO = 2.22, CaO = 0.45, $Na_2O = 1.52$, $K_2O = 2.84$, $P_2O_5 < 0.05$). The red contours are the field where staurolite is stable; (b) more detailed diagram for the stability field of staurolite-bearing mineral assemblages. The plus and minus signs denote the presence and absence, respectively, of the mineral phase indicated by an arrow in this field.

not show any significant differences in the simulated phase relations in the medium-temperature parts of the diagrams.

Below we discuss the mineral equilibria as illustrated by the simulations made with a typical metapelite composition (sample B-05-177).

In the $P–T$ diagram, the low-temperature (<500°C) region is made up of the assemblage $Qtz \pm Bt + Pl + Ms + Chl \pm Ilm \pm Tit \pm Ru$, and the high-temperature one (500–700°C) is characterized by assemblages with Crd, St, and Grt. The highest temperature assemblages contain Opx and Sil but no hydrous minerals, and melt appears because of anatexis of metapelites (Fig. 4).

Staurolite becomes stable at $T = 510–635°C$, $P > 2$ kbar (Figs. 4a, 4b). An increase in the $P–T$ parameters results in the $Qtz + Bt + St + Pl + Ilm + Grt$ assemblage, which is stable at $T = 550–630°C$, $P > 3.5$ kbar. As the $P–T$ parameters are further increased, first Chl disappears from the $Qtz + Bt + St + Pl + Crd + Chl + Ilm$ assemblage, and Grt is formed (at 540–550°C), then Crd disappears, and first And disappears from the $Qtz + Bt + St + Pl + Ilm + Chl + And$ assemblage and Grt is formed at pressures above 3.5–4 kbar, and then Chl disappears.

One of the critical parameters controlling the stability of St is the Mg fraction of the system $X_{Mg} =$ Mg/(Fe + Mg). Considering that the Ladoga

metapelite contain broadly varying MgO and FeO concentrations (Table 1), we have analyzed binary diagrams that show how the mineral assemblages vary depending on X_{Mg} of the rock (Fig. 5). The diagram shown as an illustrative example demonstrates the stability of assemblages with staurolite in $T–X_{Mg}$ space at $P = 4$ kbar, which was assumed for these rocks (Baltybaev et al., 2000).

In the binary plot, the position of sample B-05-177 with $X_{Mg} = 0.18$ is marked on the X_{Mg} axis with an arrow. The mineral assemblages corresponding to this bulk-rock composition evolve with increasing temperature as follows: $Qtz + Bt + Pl + Ms + Chl + Ilm \pm Ru \pm Tit \rightarrow + St$ (560°C) $\rightarrow -Ms$ (565°C) $\rightarrow +Grt$ (550–570°C) $\rightarrow -Chl$ (580°C) $\rightarrow +Crd$, $-St$, $+Sil$ (620°C) $\rightarrow$ partial melting (>670°C).

Had the protolith composition corresponded to another rock with, for example, $X_{Mg} = 0.3$, then the staurolite stability field would have significantly shrunk, the disappearance of Chl and subsequent appearance of Grt would have taken place at a higher temperature, and no Als would have been formed with increasing temperature.

For a Fe richer protolith (for example, with $X_{Mg} = 0.1$), a temperature increase leads to the following sequence of mineral assemblages: $Qtz + Bt + Pl + Ms + Chl + Ilm \rightarrow + Grt, -Chl$ (550–555°C) $\rightarrow +St, -Ms$ (560–565°C) $\rightarrow -St$, $+ Sil$ (600–605°C) $\rightarrow$ partial

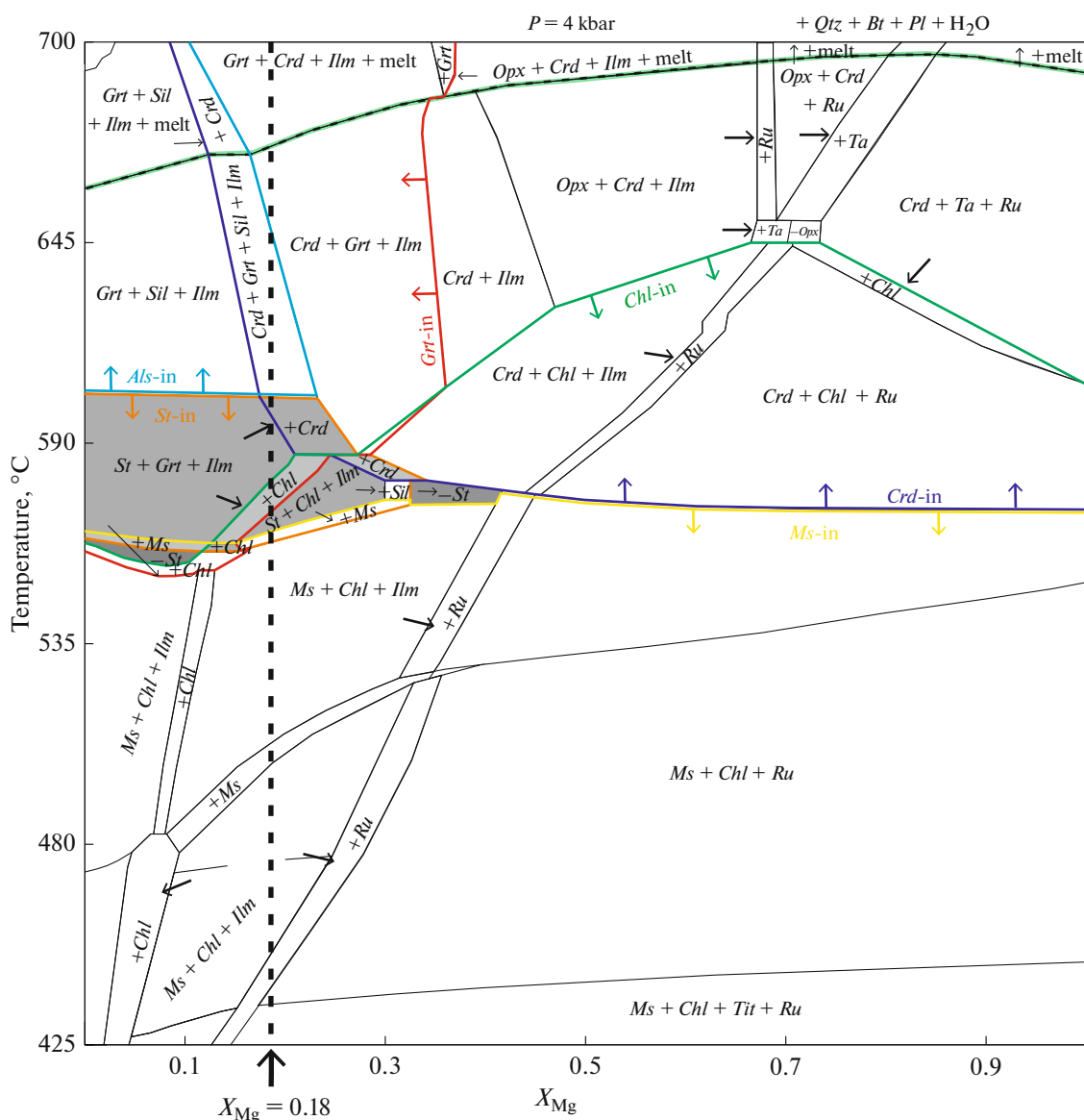**Fig. 5.** Binary T (°C)$-X_{Mg}$ diagram for variations in the mineral assemblages depending on X_{Mg} of the rock and temperature at $P =$ 4 kbar (sample B-05-177). Colored lines show the origin of: orange line—*St*, red—*Grt*, yellow—*Ms*, green—*Chl*, dark blue—*Crd*, and pale blue—*Als* (*Sil*). The projection of sample B-05-177 with $X_{Mg} = 0.18$ onto the X_{Mg} axis is indicated with an arrow. The composition of the sample yields the following sequence of mineral assemblages with increasing temperature: $Bt + Ms + Chl \rightarrow$ $+St$ (560°C) $\rightarrow -Ms$ (565°C) $\rightarrow +Grt$ (570°C) $\rightarrow -Chl$ (580°C) $\rightarrow +Crd, -St, +Sil$ (620°C) $\rightarrow$ partial melting (>670°C).

melting (>660°C). The staurolite stability field for this composition is the broadest, although X_{Mg} of the rock is still not high enough for *Crd* to be stable.

In protoliths whose composition corresponds to various X_{Mg} values, staurolite is stable in $P-T$ space within an almost rectangular field ($0 < X_{Mg} < \sim 0.3$) within a narrow temperature range of ~550 to ~605°C (Fig. 5). An increase in X_{Mg} of the rock to >0.3 leads to that the staurolite stability field narrows and wedges out rather quickly.

For the tested samples from the Ladoga group, thermodynamic simulations realistically reproduced the mineralogical compositions in the medium-temperature region: staurolite appears at $T = 510-635$°C, $P > 2$ kbar. Had the metamorphic temperature been higher, cordierite-bearing rock would have been formed instead of staurolite-bearing ones, and mica schists with chlorite would have been formed at lower temperatures.

For rock sequences with various lithologies, with staurolite-free rocks (biotite and garnet–biotite gneisses, schists, etc.), the thermodynamic simulations of the sequence of mineral assemblages well reproduced the natural assemblages: at the same $P-T$ parameters, the rocks (which have variable bulk compo-

sition) contain no staurolite. For example, a biotite gneiss contains the assemblage $Qtz + Bt + Fsp + Ilm + Chl$, and a garnet–biotite schist contains $Qtz + Fsp + Grt + Ilm \pm Crd \pm Sil$.

The thermodynamic simulations allowed us to exactly determine the composition of the protoliths controlling the stability of staurolite. First we tested a selection of all available metapelite compositions. Then the compositions of the Ladoga metapelites, which we named *reference compositions*, were modified sequentially, one by one, by varying the concentrations and proportions of elements in them. In modifying the compositions of the metapelites, the ranges of the varied concentrations of major components were specified according to variable grids with increments of 0.1–0.5 wt % in corresponding rectangular and triangular diagrams to more accurately determine the composition of the staurolite-bearing and staurolite-free rocks. For all of the reference compositions, various pseudosections were simulated in the medium-temperature region of 500–600°C at 2–10 kbar. Processing the naturally occurring and theoretical chemical compositions of rock samples allowed us to more accurately determine the ranges of concentrations of major components that control the stability of staurolite-bearing and staurolite-free mineral assemblages within a given $P–T$ region.

VERIFICATION OF THE SIMULATION RESULTS ON OTHER METAMORPHIC COMPLEXES WITH STAUROLITE-BEARING ROCKS

Staurolite-bearing rocks from some complexes worldwide were tested for the compatibility of their mineral assemblages with staurolite to our results of numerical simulations. The composition points of these rocks are plotted in Fig. 6.
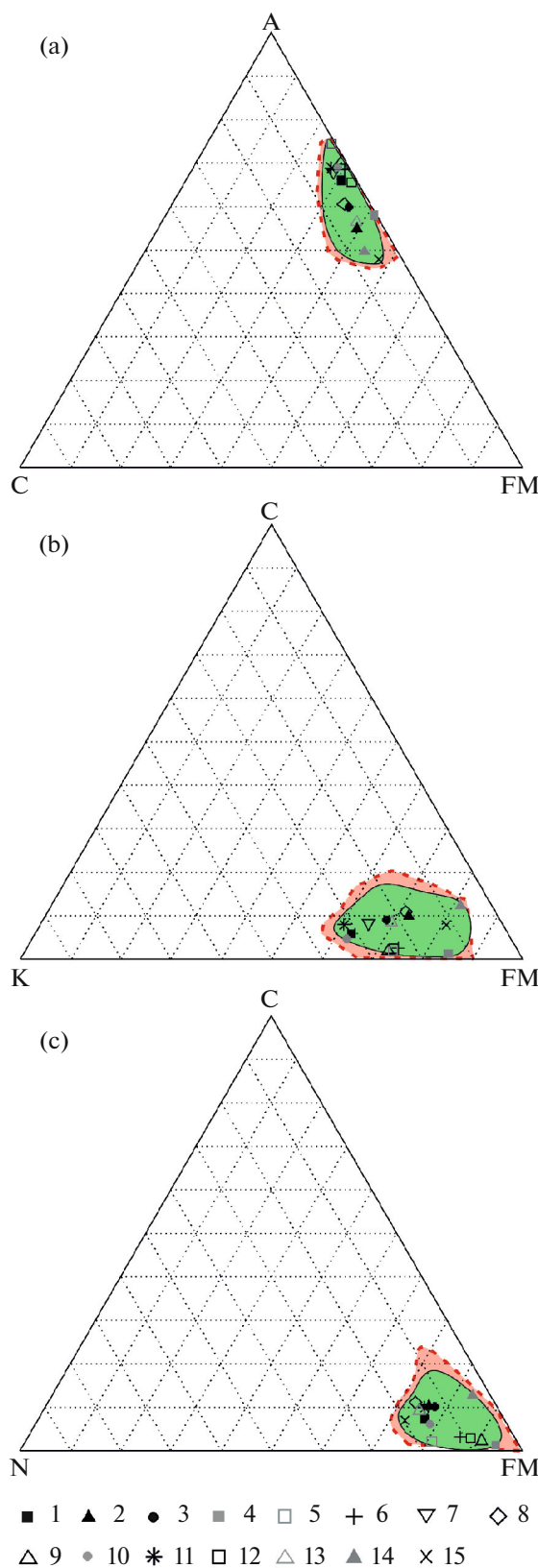

Fig. 6. CAFM [CaO–Al$_2$O$_3$–(FeO$_t$ + MgO)], KCFM [K$_2$O–CaO–(FeO$_t$ + MgO)], and NCFM [Na$_2$O–CaO–(FeO$_t$ + MgO)] diagrams for staurolite-bearing rocks in the northern Ladoga area and metamorphic complexes elsewhere worldwide. Average composition of the Ladoga-Group metapelites: (1) our data, (2) (*Material ...*, 1964), (3) (Predovskii, 1967). Composition of metapelites in other complexes elsewhere: (4) (Lal, 1970) India; (5, 6) (Baltatzis, 1979) Scotland, (7) (Garcia-Casco, 1999) Spain, (8) (Abu El-Enen, 2004) Egypt, (9) (Keller, 2005) western Alps, (10) (Corrie, 2008) North Caroline, United States, (11) (Pattison, 2009) British Columbia, (12) (Moynihan, 2012) Yukon, United States, (13) (Ugwuonah, 2017) Nigeria, (14) (Wang, 2018) southern China, (15) (Liu, 2020) northern China. The pale pink field is theoretical rock compositions (514 samples) in which staurolite can be formed upon the rocks reach the $P–T$ parameters of its stability, and the dark green field comprises the composition points of naturally occurring staurolite-bearing rocks in the northern Ladoga area and other metamorphic complexes worldwide (74 samples).

Staurolite schists of the Tabo Belt. This belt is one of the four pan-African metamorphic belts of the Sinai Peninsula, which make up the northern continuation of the East African Orogen. The critical mineral assemblages of the metapelites indicate that the regional metamorphism occurred at parameters of the amphibolite facies and define the following zoning: $(Qtz + Pl + Ilm) + Grt + Bt \pm Ms \rightarrow St + Grt + Bt \pm Ms \rightarrow Sil/And + St + Grt + Bt \rightarrow Crd + St + Grt + Bt \pm Ms \pm And$. The peak metamorphic parameters were $T \approx 590-640°C$ and $P = 5-6$ kbar, and the retrograde metamorphism proceeded at $T = 560-590°C$ and $P = 4.5-5$ kbar (Abu El-Enen et al., 2004).

Staurolite-bearing metapelites in Eastern Dalradian, Scotland. These schists are classic, meaning that they were the first rocks in which types of metamorphic zoning were distinguished (Barrow, 1893). The staurolite-zone rocks typically contain the mineral assemblage $St + Grt + Bt + Ms + Pl + Qtz$ and occur in metamorphic rocks of both the Barrovian and the Buchan type. The metamorphic parameters were estimated at $T = 540-580°C$, $P = 8-11$ kbar (Baltatzis, 1979).

Staurolite schists of the southern Appalachian metamorphic belt. The metapelite of the Great Smoky Mountains Group, which were metamorphosed during the Taconian orogeny (at 450 Ma), are now part of the West Blue Range Thrust, the westernmost metamorphic belt of the southern Appalachians. The metamorphic grades increase starting with the chlorite zone in the northwest through the biotite, garnet, and staurolite zones to the kyanite one in the southeast. The peak metamorphic parameters were evaluated at 600°C, 6–8 kbar (Corrie and Kohn, 2008).

Metapelites of the Torrox unit in the Betic Reaf Belt, southern Spain. These metapelites contain the following mineral assemblages: (1) $St + Bt + Grt + And \pm Crd$ for the andalusite schists; (2) $St + Bt + Grt + Fib + And \pm Crd$ for the fibrolite schists; (3) and $St + Bt + Grt + Ky + Fib + And \pm Crd$ for the kyanite schists. The metamorphism occurred in an extensional environment in the Late Paleogene−Early Neogene and gave way to rapid isothermal decompression. As a result, the high-pressure mineral assemblages were replaced by low-pressure ones. The peak metamorphic parameters were 600°C, 6–8 kbar (Garcia-Casco and Torres-Roldan, 1999).

Monte Rosa paragneisses. The gneisses make up one of the upper nappes in the western Alps. The nappes consists of high-grade metapelite gneisses, whose protolith was sedimentary rocks and which were metamorphosed to the amphibolite facies during the late Alpine episode at 9−12 kbar and 595−755°C (Keller et al., 2005).

Precambrian staurolite schists in the Kishangarh area, India. The rocks were metamorphosed to $P−T$ parameters of the staurolite−kyanite zone, make up an individual lithologic unit, and occur in association with micaceous quartzites, calcicates, graphite schists with marble beds, amphibolites, and some other rocks (Lal and Shukla, 1970). The staurolite was reportedly formed at medium pressures and a temperature of 500−675°C.

Metapelites of the Wutai complex. The complex is located in the central part of the Trans-North China Orogen and is dominated by metamorphosed volcano-sedimentary rocks and Late Archean gneisses of the tonalite−trondhjemite series. The metamorphism (at 1.97−1.80 Ga) of this complex was characterized by a clockwise $P−T$ path, from 3−7 kbar and $T = 570-630°C$ through 9−10 kbar and 615−660°C to 6−9 kbar and 655−680°C. The metapelites consist mostly of Grt, St, Bt, Fib, Pl, and Qtz (Liu et al., 2020).

Metapelites in the southeastern Yukon area. Metapelites in the Hyland River area make up rocks units consisting of an extensive group of schists and gneisses overlying the Logan Batholith and the eastern part of the Mount Billings Batholith. The metapelites of the group contain $Qtz + Pl + Bt + Ilm + St + Als$ (*Sil* and/or *And*) $\pm Ms \pm Grt \pm Sp$ assemblages. The metamorphic parameters were $T \approx 550-575°C$, $P = 3-4$ kbar (Moynihan, 2012).

Staurolite-bearing metapelites in the aureole of the Nelson Batholith. The batholith is a large Jurassic intrusive body in southeastern British Columbia, which is surrounded by a contact aureole 0.7−1.8 km thick in graphite-bearing clay host rocks. The contrasting prograde sequences of mineral assemblages around the aureole reflect the pressure variations. The staurolite metapelites occur within a broad zone, and their $P−T$ metamorphic parameters are 3.5−4 kbar and 500−650°C (Pattison and Vogl, 2005; Pattison and Tinkham, 2009).

Metapelites in the Keffi area, Nigeria. The metamorphic complexes including these metapelites are part of the Pan-African Trans-Saharan Belt and belong to the so-called Great Schist Belt of Nigeria. The metamorphic parameters of the staurolite-bearing schists ($Grt + Bt + St + Ms + Pl + Qtz + Ilm$) were evaluated at 6.4−7.7 kbar and 570−615°C, which is close to the peak parameters (Ugwuonah et al., 2017).

Metapelites in the Archean Yanpo Group. These metapelites belong to the recently distinguished Zhōngxiáng Complex in southern China, and their material was provided by the erosion of the Yangtze Craton. The metapelites consist of amphibolite-facies mineral assemblages of unvarying mineralogical composition, including Qtz, Bt, Pl, Kfs and lower amounts of Sil, Grt, St, and Ms. No exact parameters of the metamorphism are reported, but the mineral assemblages indicate that these parameters should have corresponded to the lower amphibolite facies of the andalusite−sillimanite facies series (Wang et al., 2018).

Simulations of mineral assemblages of the aforementioned rocks with the PERPLEX software yielded $P−T$ parameters of 500−650°C and <9 kbar and are obviously in good agreement with the mineral assem-

blages found in the rocks, with staurolite-bearing mineral assemblages reproduced for all of the mineral assemblages.

PETROCHEMICAL MODULI FOR THE METAPELITES

Analysis of the stability field of staurolite mineral assemblages in a broad range of the compositions of metapelites shows that the major-oxide ratios most informative for the description of these rocks are the Al_2O_3/SiO_2, CaO/FM (where FM = FeO + Fe_2O_3 + MgO), K_2O/FM, and Na_2O/FM ratios (Fig. 6).

To more accurately constrain the ranges of these ratios, all available chemical compositions of staurolite-bearing rocks were regarded as reference compositions, which were then modified by adding to them up to 10 wt % of each major oxide in some of the analyzed projections of the compositions. Thus we artificially expanded the ranges of the possible metapelite compositions to determine by simulations whether staurolite can be stable in any of them. If no staurolite was simulated in a given composition, then the composition of the protolith was modified in such a way as to determine the extreme concentration of the component that controlled the stability of this mineral. The increments in the concentrations of each major oxide did not exceed 10 wt % in order for the newly simulated bulk compositions not to extend outside the range typical of the metapelite group.

Analysis of the simulation results shows that staurolite can be stable only in metamorphic rocks of pelitic composition whose ratios (in wt %) of major oxides lie within the following ranges (Fig. 6):

1. Al_2O_3/SiO_2 = 0.19–0.92, with FeO + Fe_2O_3 + MgO within the range of 7–17 wt %;

2. CaO/FM = 0.01–0.44;

3. K_2O/FM = 0.07–0.83;

4. Na_2O/FM = 0.02–0.34.

The total of alkalis shall therewith not exceed 6–6.5 wt %, as is typical of metapelites.

The list of the applicable moduli can be extended by using, for example, the ratios CaO/K_2O, CaO/Na_2O, or Al_2O_3/FM, etc., but these ratios are linearly dependent on one another and thus cannot yield principally new results.

DISCUSSION

Data on naturally occurring rocks (Korikovsky, 1979; Ballèvre et al., 1989; Chopin et al., 2003; and others) and experimental calibrations (Comodi et al., 2002; and others) indicate that staurolite-bearing mineral assemblages are stabile under pressures of 1–2 to ~32 kbar at temperatures of 450 to ~700°C. The temperature range in which staurolite and its assemblages are stable at pressures of 3–8 kbar is wide, but

it rapidly narrows as the pressures increases to 10–11 kbar, and the composition of the mineral shifts toward the more magnesian member of this solid solution. It is because staurolite is stable within a narrow $P-T$ field that makes this mineral so convenient to apply in mapping metamorphic complexes and in constructing maps and schematic representations of metamorphic zoning. Because of this, the concept of the staurolite zone of metamorphism was coined as long back as the mid-19th century (Barrow, 1893).

Metamorphic zonal complexes in which staurolite was found are widespread worldwide (Abu El-Enen et al., 2004; Baltatzis, 1979; Corrie and Kohn, 2008; Garcia-Casco and Torres-Roldan, 1999; Keller et al., 2005; Lal and Shukla, 1970; Liu et al., 2020; Moynihan, 2012; Pattison and Vogl, 2005; Pattison and Tinkham, 2009; Ugwuonah et al., 2017; Wang et al., 2018; and others). The broad variations in the composition of the protoliths of these rocks puts forth the problem as to how the metamorphic zones distinguished in these complexes are related to the $P-T$ parameters (metamorphic grades). In this context, it is important to find criteria for determining whether some $P-T$ parameters have been reached by a given rocks in spite of that the rock actually does not contain the indicator minerals (for example, staurolite). The fact that this mineral is stable within a fairly narrow temperature range opens, on the one hand, broad possibilities for modern thermodynamic simulations and, on the other hand, enables the researcher to successively apply criteria for estimating whether staurolite is or is not stable and thus constrain the boundaries of the metamorphic staurolite facies (subfacies).

Staurolite can be formed by decomposing chloritoid by the reaction $Cld + Qtz = St + Grt + H_2O$ (Whitney et al., 1996). In the presence of chlorite, the reaction $Grt + Chl + Ms = St + Bt + Qtz + H_2O$ can proceed, which continues until one of the three reactant minerals is completely exhausted (Yardley, 1989). If, for example, the first phase to be exhausted is garnet, then the reaction stops, and staurolite is further can be produced by a continuous reaction involving the remaining phases $Chl + Ms = St + Bt + Qtz + H_2O$ at a higher temperature than that of the aforementioned discontinuous reaction (Yardley, 1989). However, chloritoid can sometimes not to be produced at all if the $Grt-Chl$ assemblage is stable at lower temperatures. This can take place, for example, if the rock contains an elevated Mn concentration, which widens the stability field of garnet at relatively low temperatures (Karabinos, 1985).

Chloritoid was documented in numerous metamorphic complexes, in which it is stable in low- and medium-pressure metapelites, both enriched in and depleted in Al. High-pressure metapelites are often also characterized by elevated Mg concentrations.

The $P-T$ parameters under which chloritoid-bearing metapelites are stable range from those of the

greenschist to the mid-amphibolite facies, staurolite–kyanite zone. In greenschist-facies rocks, staurolite is a common mineral, which occurs, together with chlorite and muscovite, in rocks that contain more Fe and Al than is necessary to form the *Chl–Ms* assemblage (Turner and Verhoogen, 1960; Albee, 1983; Johnson et al., 2003).

Chloritoid is typical of metapelites affected by HP–HT metamorphism. This mineral is formed, together with chlorite, talc, and/or kyanite, in the course of early subduction by the decomposition of carpholite under parameters of the lower blueschist facies at 12−16 kbar and 450−550°C (Bucher, 2005; Palin and Dyck, 2021). As the metamorphic grade increases to the eclogite facies (>20 kbar and >600°C), chloritoid decomposes into magnesian garnet (pyrope) and kyanite, and magnesian staurolite can also be formed in lithologies richest in Al (Palin and Dyck, 2021).

Most researchers believe that the protoliths of chloritoid-bearing rocks consisted of the redeposited and metamorphosed material of ancient weathering crusts of the laterite (or kaolinite) type (e.g., Franceschelli et al., 2003). Such metamorphism produces pyrophyllite from kaolinite at a temperature close to 300°C, and pyrophyllite can, in turn, be replaced by chloritoid in associations rich in chlorite, and the complete decomposition of pyrophyllite to kyanite occurs at 400°C. At approximately 500°C, chloritoid decomposition results in staurolite and garnet, which marks the transition to the amphibolite facies (Bucher and Grapes, 2011).

The KFMASH system is characterized by prograde sequences of mineral assemblages depending on the chemical composition of the protoliths. The Fe-rich series is characterized by the following sequence of mineral assemblages: *Chl + Cld*, *Grt + Cld*, *Grt + St*, *Grt + Ky*, and *Grt + Sil*, without *Bt*. In magnesian rocks, the sequence is *Chl + Prl*, *Chl + Ky*, *Bt + Ky*, *Bt + Sil*, and neither garnet nor staurolite or hedenbergite are formed. The Fe richest association with *Bt* is *Grt + St + Bt*, with X_{Fe}(max) = 0.88. The low-temperature boundary of the stability field of these phases (560°C) occurs at a temperature 10°C higher than the maximum temperature of chloritoid stability (Richardson, 1968; Bucher and Grapes, 2011). In *P–T* diagrams, mineral assemblages with chloritoid (chloritoid zone) can be regarded, under some conditions, as in a zone analogous to the biotite zone (Spear, 1993). In the KFMASH system, chloritoid + biotite are stable within a narrow temperature range under relatively low pressures (Harte and Hudson, 1979), although some researchers (Spear and Cheney, 1989; Wang and Spear, 1991) are prone to think that the *P–T* field in which this association is stable is much larger.

The effect of oxygen partial pressure on staurolite origin by the reaction *Cld* + O_2 ↔ *St + Mgt + Qtz* is as follows: an increase in the oxygen pressure from that at the NNO to that at the QFM buffers decreases the staurolite crystallization temperature from 635 ± 15°C to 580 ± 10°C at $P_{tot} = P_{H_2O}$ = 10 kbar (Ganguly, 1968; Ganguly and Newton, 1968).

The staurolite stability field in the Fe−Al−Si−O−H at hydrothermal synthesis in the presence of the quartz−fayalite−magnetite (QFM) buffer lies at $P >$ 1.5−3.0 kbar and 530−700°C (Richardson, 1967, 1968). Similar parameters (540°C at 4 kbar and 565°C at 7 kbar) were obtained for staurolite origin by the reaction Chl_{40} + *Ms* ↔ *St + Bt + Qtz* + H_2O in the presence of QFM buffer at $P_{tot} = P_{H_2O}$ (Hoschek, 1969). The upper temperature limit for staurolite stability in the presence of muscovite and quartz in the reaction *St + Ms + Qtz* ↔ *Als + Bt* + H_2O was evaluated at 575°C at 2 kbar and 675°C at 5.5 kbar (Hoschek, 1969). Of course, if $P_{tot} > P_{H_2O}$, the temperature at which staurolite is formed and decomposes (because water is released in this reaction) shall be lower. According to calculations in (Hoschek, 1969), the temperature at which staurolite is formed at $P_{tot} = P_{H_2O}$ of 5 kbar shall be approximately 100°C lower, i.e., close to 450°C (Nagaitsev, 1974).

In the northern Ladoga area, metapelites of the pre-staurolite (biotite) zone do not contain chloritoid (Velikoslavinskii, 1972). It was previously thought that staurolite is formed in zonal metamorphic complexes only via chloritoid decomposition, but it was demonstrated (Hoschek, 1969) that chloritoid-bearing rocks are characterized by narrower variations in chemical composition than those of staurolite-bearing rocks, and staurolite can be formed not only by the decomposition of the assemblage *Cld + Qtz + Ms + Chl* but also at the expense of the assemblage *Qtz + Ms + Bt + Chl*. In G. Hoschek's AKF, ACF, and AFM triangular plots of mineral assemblages with the fields of chloritoid- and staurolite-bearing rocks, the composition point of staurolite rocks in the northern Ladoga area does not plot within the composition field of chloritoid. This provides grounds to think that the reason for the absence of chloritoid from the rocks in the area is their unsuitable composition, with their difference from chloritoid-bearing rocks being their elevated Mg and Ca concentrations (Velikoslavinsky, 1972).

Thermodynamic simulations with the PERPLEX software (Connolly, 1990) in the low- and medium-temperature region (<520°C) with the compositions of rocks of the Ladoga Group confirm the absence of chloritoid. However, chloritoid was obtained in the simulations with Fe- and Al-richer metapelites from elsewhere. Numerical simulations with a broader range of theoretical compositions led us to establish that chloritoid is stable in more aluminous and less magnesian compositions of the protoliths with the ratios (in wt %) Al_2O_3/MgO > 10 and FeO/MgO > 5.

The staurolite facies of metamorphism is distinguished based on a combination of critical mineral

assemblages of the staurolite zone, which is bounded by reactions involving other index minerals or their assemblages. Each metamorphic facies can be spatially compared with a certain zone or zones in a metamorphic zoning. Metamorphic facies commonly comprise a number of mineral subfacies, as was proposed, for example, by S.P. Korikovsky (1979), who distinguished the staurolite metamorphic facies as an individual rank. The authors of this publication adhere to this system of metamorphic facies.

The position of staurolite-bearing rocks in the system of metamorphic facies was extensively discussed in the literature. For example, the assemblage $St + Qtz$ was ascribed to the epidote-amphibolite facies (Ramberg, 1952; Francis, 1956), with its replacement by andalusite and kyanite assemblages with increasing metamorphic grade. N.G. Sudovikov (1964), A.A. Predovskii (1967), and Yu.V. Nagaitsev (1974) attributed the staurolite−andalusite subfacies, together with the sillimanite−almandine one, to the amphibolite facies. According to V.S. Sobolev (*Facies ...,* 1970), staurolite rocks are stable within the epidote-amphibolite under relatively low pressures and amphibolite facies and within the facies of kyanite schists (an analogues of epidote amphibolites) under high pressures.

One of the latest petrogenetic grids for Fe−Al metapelites in the KFMASH system was proposed by I.I. Likhanov and his colleagues (Likhanov et al., 2005). The medium and high-temperature parts of most currently used diagrams were determined to be practically exactly identical, with differences between them occurring only at low and intermediate metamorphic grades at $T < 570°C$. The reasons for the origin of some mineral assemblages is, first of all, the effect of the chemical composition of the metapelites (e.g., Hoschek, 1969), with the main role played by the X_{Fe} and X_{Al} of the coexisting minerals. According to the petrogenetic grid in (Likhanov et al., 2005), the stability field of the assemblage $St + Bt$ and $Bt + Als$ lies within a narrow temperature range, with the $St + Bt$ assemblage giving way to the $Bt + Als$ one with increasing temperature, and with the latter assemblages replaced by the $Grt + Bt + Als$ association, which is stable within a broad pressure range.

In the northern Ladoga area, staurolite-bearing schists are spatially associated with diopside marbles and andalusite schists of the amphibolite facies (Kitsul, 1963; Nagaitsev, 1974). This provides evidence in support of the conclusion (Sudovikov, 1964) that staurolite is formed at prograde metamorphism near the high-temperature boundary of the epidote-amphibolite facies, although most of its stability field occurs in the low-temperature portion of the amphibolite facies (Predovskii, 1967). It is worth mentioning that, in spite of some differences in their approaches, all researchers point out that the distinguished metamorphic zones are directly related to the corresponding facies and subfacies of metamorphism. It should also

be mentioned that we do not discuss herein the problem how isotherm lines are correlated with the stability isograds of certain minerals.

For model reconstructions with regard to the composition of the protoliths, it is important how much the rocks preserved their composition in the course of overprinted metamorphism. This problem was explored in much detail with reference to the Ladoga gneisses and schists to understand how various metamorphic grades may affect the original chemical compositions of the premetamorphic rocks (Lobach-Zhuchenko et al., 1972; Ronov et al., 1977). Sampling carried out according to a grid over an area covering all of the metamorphic zones in the northern Ladoga area, and analysis of the materials, led to the conclusion that the compositions of all rocks of the Ladoga Group (Formation) are practically exactly identical. This was interpreted as evidence of an isochemical character of the metamorphic processes in terms of major components.

Minor and trace elements in the protoliths and the role of these elements in staurolite were discussed in a number of papers. For example, it has been proved that Li concentrations in the rocks usually do not correlate with the modal contents of staurolite in these rocks (Dutrov et al., 1986). In metapelites with elevated boron concentrations (i.e., containing tourmaline), no appreciable changes have been detected in the properties and $P−T$ parameters when staurolite-bearing mineral assemblages are formed (Henry, 1985).

After its crystallization, staurolite is susceptible to various alterations. It is replaced by, for example, muscovite (e.g., Grew and Sandiford, 1984). This process was identified during retrograde metamorphism at $T = 300−370°C$ and $P = 3−5$ kbar, when muscovite is formed in a staurolite−talc−chlorite−corundum rock, together with clinozoisite, margarite, and pumpellyite (Grew and Sandiford, 1984). For example, staurolite in the northern Ladoga area is locally replaced by the quartz−muscovite assemblage, up to the development of almost complete pseudomorphs. Staurolite replacement by secondary minerals can usually be readily identified based on textural and structural features.

Staurolite is thus an informative mineral that can be used in solving a wide spectrum of problems. Understanding which features and parameters control its stability in rocks makes it possible to more reliably determine the facies to which certain rocks belong and facilitates in drawing reasonably justified boundaries between metamorphic zones corresponding to different metamorphic grades. The compositional diversity of the probable protoliths can be used to estimate whether staurolite can be formed in certain rocks when their $P−T$ parameters reach certain values (Fig. 7). A graphical (Fig. 7) or numerical representations of the petrochemical moduli in the form of ratios of major components, such as Al_2O_3/SiO_2, CaO/FM
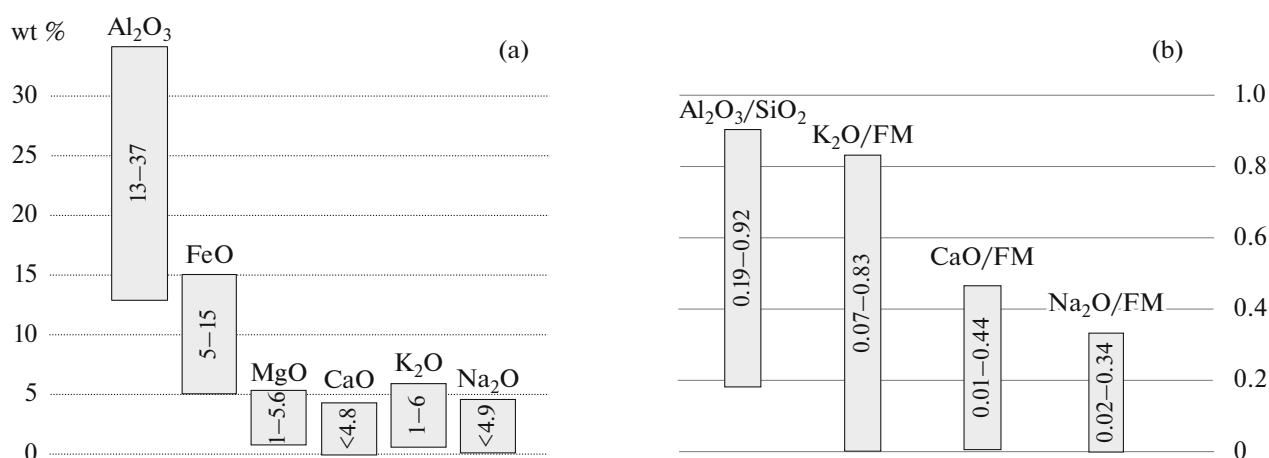
Fig. 7. Composition of the protoliths in which staurolite can be formed by metamorphism at 500−650°C under low and medium pressures. (a) Possible ranges of major oxide concentrations; (b) ranges of the values of the petrochemical modules.

(where FM = FeO$_t$ + MgO), K$_2$O/FM, and Na$_2$O/FM, enable the researcher to evaluate the potential possibility of staurolite crystallization at medium-temperature low- to medium-pressure metamorphism of metapelites. The problem of developing analogous criteria for mafic protoliths and for high-pressure staurolite-bearing rocks calls for further testing.

CONCLUSIONS

Natural and synthetic compositions of protoliths can be utilized to quantitatively characterize the ranges of major-component concentrations suitable for staurolite stability in the rocks within given temperature and pressure ranges. The four proposed petrochemical moduli, Al$_2$O$_3$/SiO$_2$, CaO/FM, K$_2$O/FM, and Na$_2$O/FM, are ratios of certain major components in metapelites whose values define the principal possibility of staurolite crystallization.

The petrochemical moduli serve as unbiased parameters of protolith compositions that can be applied to predict which mineral assemblages shall be stable in the rocks at certain $P-T$ parameters and to more accurately determine boundaries between low- and medium-temperature metamorphic zones (facies and subfacies) when metamorphic maps and schematic representations are created.

ACKNOWLEDGMENTS

FUNDING

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Translated by E. Kurdyukov