

Mass Transfer during Andalusite Replacement by Kyanite in Al- and Fe-Rich Metapelites in the Yenisei Range

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Abstract—Information on the textures, mineralogy, and chemistry of rocks was used to study the behavior of material during dislocation metamorphism of Al- and Fe-rich metapelites in the Yenisei Range. Metamorphism of the kyanite–sillimanite type was associated with rock deformations. The replacement of andalusite by kyanite and development of new microtextures and mineral assemblages were related to an increase in the lithostatic pressure near the Panimbinskii overthrust. The compositions of minerals and their volumetric proportions in the rocks were utilized to calculate the equations of chemical reactions responsible for the origin of *Ky–St–Ms–Qtz* pseudomorphs and mineralogical transformations that brought about staurolite and garnet crystallization. Analysis of mass balance and changes in the mineralogical composition indicate that the general scheme of mass transfer during andalusite replacement by kyanite is the sum of two isochemical local reactions. It is determined that the minimum volume within which mass transfer proceeded and the full balance of major components between the reacting phases was maintained did not exceed $\sim 1.6 \pm 0.4 \text{ cm}^3$. As the deformations became more intense, the minimum volume increased due to the full pseudomorph replacement of andalusite crystals. Our results are in agreement with the estimated mass-transfer scale during metamorphic reactions in metapelites under similar *P–T* metamorphic conditions elsewhere.

INTRODUCTION

An important task of metamorphic petrology is to analyze the factors controlling compositional and textural transformations in rocks during their *P–T* evolution. One of the most uncertain issues therein is the relations between deformational and metamorphic processes, which is the key point in understanding the genesis of microtextures and tectonites and their petrogenesis (Knipe and Wintsch, 1985). Mineralogical transformations coupled with deformations affect the mechanical properties of rocks (Rubie, 1983), and deformational processes play an important part in the mechanisms of mineral reactions in deformed aggregates (Brodie and Rutter, 1985). Insight into these processes is provided by microtextures. Microtextural transformations in metamorphosed rocks are often interpreted with the aid of the mechanisms of phase reactions with the participation of cation exchange (Carmichael, 1969; Fisher, 1970). Within the framework of this mechanism, it is possible to explain several particular reactions within microscopically distinct rock volumes that can exchange their chemical component by means of diffusion. The compounds dissolved in the interstitial fluid come from different loci of the rock, and their movements are controlled by diffusion and the gradient of chemical components. Reactions between compounds and the growth of newly formed minerals take place at sites with the highest gradients (Fisher, 1978). Solutes diffuse for different distances,

with the nearest dissolving grains contributing most significantly to the growth of a mineral crystal. The rates of metamorphic reactions are so high compared to that of diffusion as to maintain local equilibria virtually everywhere within a rock volume that is controlled by a certain level of chemical potentials and in which newly formed minerals grow (Fisher, 1978; Lasaga, 1983; Fisher and Lasaga, 1983).

Metamorphic reactions are widely studied with the use of an approach involving calculations of mass transfer between dissolving the nearby newly formed grains. There is a number of models making use of this approach and explaining the development of the textures and mineralogical composition of rocks. The occurrence of earlier phases included in newly formed minerals in structurally and texturally heterogeneous coarse- and medium-grained rocks and the presence of reaction textures (kelyphites, coronites, and others) offers a possibility of inspecting the *P–T* evolution of these rocks (Vidale, 1969; Eugster, 1970; Joesten, 1974, 1977, 1991; Reverdatto and Kolobov, 1987; Ashworth *et al.*, 1998; Johnson and Carlson, 1990; Carlson and Johnson, 1991; Messiga and Bettini, 1990; Cesare, 1999). Fine-grained structurally and texturally homogeneous rocks without large porphyroblasts sometimes bear no armored relics if mineral reactions in the rocks were completed during variations in the *P–T* conditions. In this situation, the character of reactions can be inferred only from the transitions between alternative

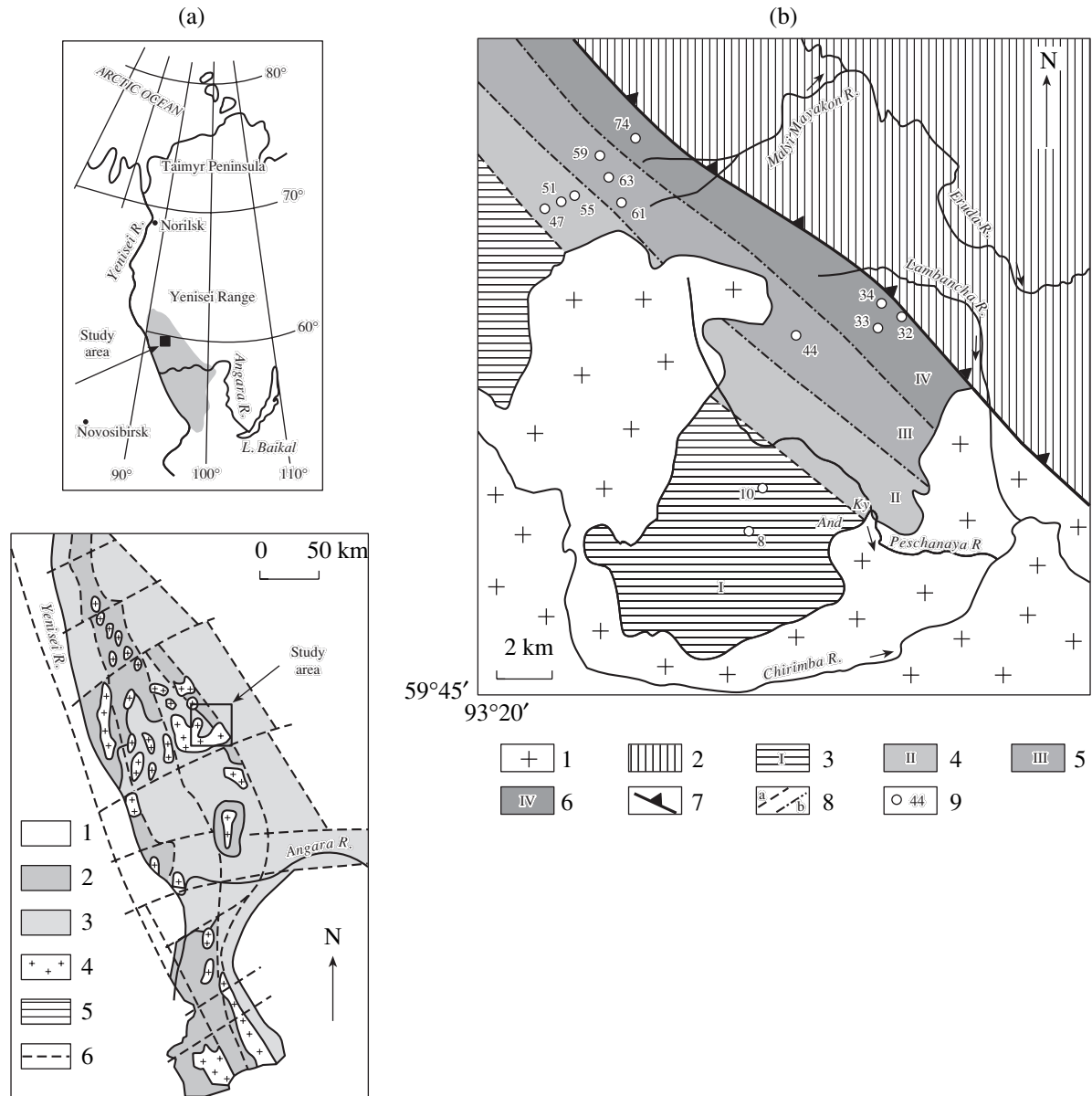


Fig. 1. (a) Regional geological map of the Yenisei Range (Kornev, 1986) and (b) metamorphic map of the watershed area between the Eruda and Chirimba rivers in the Transangarian part of the Yenisei Range (based on 1 : 50 000 geological survey materials provided by the Tsentral Party, Angara Geological Survey and Prospecting Expedition, and revising surveying of some areas in the southern part of the Northern Yenisei district, prepared by Yu.F. Avdievskii, A.I. Vyazu, and P.S. Kozlov).

(a) (1) Quaternary deposits; (2) pre-Riphean metamorphic complexes; (3) Riphean volcanic, sedimentary, and metamorphic complexes; (4) granitoids; (5) geologic boundaries; (6) faults.

(b) (1) Granite of the Chirimba Massif; (2) metamorphosed siltstone and carbonate rocks of the Pechenginskaya Formation; (3) metapelites of the Kordinskaya Formation metamorphosed to the (I) *And-Sil* and (II-IV) *Ky-Sil* facies series; zones: (4) inner (IV), (5) intermediate (III), (6) outer (II); (7) suture of the Panimbinskii overthrust (sawteeth are directed down-dip); (8) (a) *And-Ky* isograd and (b) boundaries between the zones of *Ky-Sil* metapelites of the Kordinskaya Formation; (9) rock sampling sites. The shaded area in the geographical map in the top left corner indicates the location of the Yenisei Range.

inconsistent mineral assemblages that mark certain isogrades (Foster, 1977, 1981, 1986; Yardley, 1977; Ferry, 1983, 1984; Menard and Spear, 1996; Likhanov *et al.*, 1994, 1995, 1999, 2001a, 2001b). If metamorphism proceeded simultaneously with strong deformations, spatiotemporal variations in mineral assemblages are correlated with textural transformations.

This paper is centered on employing information on the chemistry of coexisting minerals and their textural relations in an attempt to assay the effect of deformations on the character of mass transfer during metamorphism of Al- and Fe-rich metapelites of the Transangarian part of the Yenisei Range. The relations between an increase in the intensity of deformations and the scale

of mass transfer during metamorphism are still very rarely discussed in the literature (one exception is Dipple *et al.*, 1990).

GEOLOGICAL OVERVIEW

The Transangarian part of the Yenisei Range is characterized by variations in the metamorphic pressure and, as a consequence, regional metamorphism of two facies series: andalusite–sillimanite and kyanite–sillimanite (Kozlov and Lepezin, 1995). The kyanite–sillimanite type of metamorphism was locally overprinted on low-pressure metamorphic rocks.

The regionally metamorphosed low-pressure rocks of the Kordinskaya Formation (Likhanov *et al.*, 2000, 2001) in the basin of the Eruda and Chirimba rivers (Fig. 1) have a Middle Riphean age and are thought to be genetically related to the crustal evolution of the granite-gneisses of the Teya Complex, dated at 1100 ± 50 Ma (U–Pb zircon age; Volobuev *et al.*, 1968; 1973). The metapelites of the andalusite–sillimanite type contain the assemblage muscovite + chlorite + biotite + chloritoid + andalusite + quartz \rightarrow graphite + ilmenite \rightarrow cordierite (some of the minerals can be absent from some petrographic varieties) and were produced under greenschist and epidote-amphibolite facies conditions. Near the overthrust, the rocks were affected by medium-pressure metamorphism of the kyanite–sillimanite type in the Late Riphean (850 ± 50 Ma, K–Ar dating of biotite and muscovite; Zvyagin, 1989). The medium-pressure metapelites of the kyanite–sillimanite type contain the assemblage muscovite + chlorite + biotite + quartz + kyanite + staurolite + garnet + graphite + ilmenite + plagioclase \rightarrow andalusite \rightarrow sillimanite and correspond to the kyanite-schist facies. They compose a zone from 5 to 7 km wide and no less than 20 km long, which is bounded by the northwest-trending Panimbinskii overthrust in the east. The area east of the thrust is composed of Lower Proterozoic (1600 Ma, U–Pb zircon dating; Volobuev *et al.*, 1968, 1973) metacarbonates of the Pechenginskaya Formation, which were metamorphosed to the epidote-amphibolite and amphibolite facies (Fig. 1). The magmatic rocks of the Tatarskii–Ayakhtinskii Complex comprise granitoids of the Chirimba Massif of Late Riphean age (Datsenko, 1984). They are younger than both the andalusite–sillimanite and kyanite–sillimanite types of metamorphism.

The low-pressure Middle Riphean metamorphism of the andalusite–sillimanite type proceeded at $P = 3.5\text{--}4$ kbar, $T = 540\text{--}560^\circ\text{C}$ (Likhanov *et al.*, 2001). The Late Riphean was marked by a high-pressure metamorphic event ($P = 4.5\text{--}6.7$ kbar, $T = 540\text{--}600^\circ\text{C}$), which resulted in andalusite replacement by kyanite and the development of new microtextures and mineral assemblages of the medium-pressure kyanite–sillimanite type. This zonal metamorphism was clearly restricted to the Panimbinskii overthrust.

The temperatures of metamorphic rocks of the andalusite–sillimanite type were estimated with the use of three geothermometers: *Bt–Cld* (Perchuk, 1991, *Bt–Ms* (Hoisch, 1989), and *Chl–Cld* (Vidal *et al.*, 1999; mineral symbols are after Kretz, 1993). The pressures were evaluated by two modifications of the *Bt–Ms–Chl* geobarometer (Powell and Evans, 1983; Bucher-Nurminen, 1987). The temperatures in the garnet-bearing metamorphic rocks of the kyanite–sillimanite type were quantified using the following calibrations of the *Grt–Bt* geothermometer and the corresponding mixing models: (1) Ferry and Spear (1978) with the mixing models from (Hodges and Spear, 1982), (2) Perchuk and Lavrent'eva (1983), (3) Kleeman and Reinhardt (1994), and (4) Holdaway *et al.* (1997). The pressures of these rocks were estimated by various calibrations of the *Grt–Bt–Ms–Pl* geobarometer (Hoisch, 1990; Ghent and Stout, 1981). The calculations were conducted with the use of the model–activity relations from (Hodges and Crowley, 1985) for the biotite ideal solid solutions and the nonideal solid solutions of other phases and from (Hoisch, 1991) for the nonideal solid solutions of garnet and plagioclase and nonideality in the distribution of cations between the tetrahedral sites of micas. The *Grt–Bt–Ms–Pl* geobarometer was chosen for pressure estimates because its equilibrium constant is not as strongly sensitive to temperature as is the constant of the *Grt–Pl–Als–Qtz* geobarometer (Avchenko, 1988) and allows for the presence of more than one Al_2SiO_5 polymorphs in the sample. The P – T parameters of the rocks were calculated by the simultaneous utilization of all geothermometers and geobarometers. The geothermobarometric results (Likhanov *et al.*, 2001) suggest that the pressure gradually increased toward the Panimbinskii overthrust: 3.5–4 kbar in zone I, 4–5 kbar in zone II, 5–5.6 kbar in zone III, and 6.2–6.7 kbar in zone IV (Fig. 1). A slight temperature increase (from 560 to 580°C) closer to the Panimbinskii overthrust implies a fairly low geothermal gradient (1–7°C/km). The highest temperatures (up to 600°C) were detected in two sillimanite-bearing mineral associations (Samples 61 and 44, Fig. 1) from zone III (Likhanov *et al.*, 2001a). The accuracy of the geothermobarometric results was assayed by comparing these results with P – T estimates yielded by the THERMOCALC computer program (Powell and Holland, 1988, 1994), which makes use of an internally consistent thermodynamic database and utilizes a variety of mixing models (Holland and Powell, 1990). All results are in satisfactory agreement within the accuracy of the geothermobarometers ($T = \sim 50^\circ\text{C}$ and $P = \sim 1$ kbar). The metamorphic trajectories calculated based on P – T data on different zones demonstrate that the pressure always gradually increases (by 1 to 2 kbar) closer to the Panimbinskii overthrust, while the temperature remains virtually unchanging (increases by $20 \pm 15^\circ\text{C}$), which suggests a nearly isothermal subsidence of the rock sequence in the course of the kyanite–sillimanite metamorphism (Likhanov *et al.*, 2000, 2001).

The increase in the lithostatic pressure is interpreted as resulting from the tectonic thickening of the crust, when the Lower Proterozoic metacarbonate Pecheneginskaya Formation was thrust over the Riphean metapelites of the Kordinskaya Formation. Heat-transfer computations within the guidelines of the tectonic crustal thickening model indicate that the thrusting of one block over another with different thermal properties and heat generation characteristics results in a noticeable temperature increase only within the depth range of 12–18 km. The evolution of geotherms in the overthrust zone was determined using the calculated values of heat generation and data compiled from the literature on the thermal conductivity of metapelites and metacarbonates.

The modern erosion level supposedly corresponds to a depth of 18 km, below which the temperature of the rocks practically did not increase during the thrusting. This enabled us to use a geodynamic model with a nearly isothermal increase in the lithostatic pressure (Likhanov *et al.*, 2001).

METAMORPHIC ZONING AND MICROTEXTURES

The spatial transition from the regionally metamorphosed low-pressure (andalusite–sillimanite type) rocks to higher pressure rocks is marked by a kyanite isograd. The four metamorphic zones, trending parallel to the suture of the Panimbinskii overthrust, differ by characteristic textural and mineralogical transformations of their metapelites (Fig. 1).

Zone I: unaltered metapelites of the andalusite–sillimanite type. The low-pressure metapelites of the Kordinskaya Formation at a distance of 5–7 km from the Panimbinskii overthrust are not affected by metamorphism of the kyanite–sillimanite type (Kozlov and Lepезin, 1995) and bear the stable assemblage $And + Cld + Bt + Ms + Chl + Qtz + Pl + Ilm$. These are dark gray rocks with a fine- and medium-grained lepidoblastic or lepidogranoblastic mica–chlorite–quartz–plagioclase groundmass and chloritoid and andalusite porphyroblasts. In thin sections, andalusite crystals are often clearly idioblastic, with chiasolite and hourglass structures of graphite inclusions. The crystals attain 1.5 cm across. Euhedral prismatic and tabular chloritoid crystals up to 1 mm occur in physical contact with andalusite and biotite (Fig. 2a), which is a petrographic rarity. Quartz develops as equant, elongated, or ellipsoidal grains with even or scalloped outlines, ranging from 0.1 to 1 mm. Muscovite is present as single flakes from 0.05 to 0.5 mm long or as interstitial aggregates between quartz grains. Plagioclase was encountered in the form of anhedral grains up to 0.5 mm across or in the form of grains elongated in the schistosity plane of the rock. Biotite and chlorite occur as flakes up to 0.4 mm across. The opaque mineral is ilmenite, which composes platelets in the schistosity plane and anhedral

grains. The accessory minerals are graphite, tourmaline, margarite, and calcite.

Closer to the Panimbinskii overthrust, the rocks are affected by dislocation metamorphism. The spatial transition from regionally metamorphosed low-pressure rocks to those metamorphosed under elevated pressures is marked by the simultaneous appearance of kyanite, staurolite, and garnet (kyanite isograd). The principal textural feature of these rocks is the development of pseudomorphs after andalusite. The main minerals of the pseudomorphs are kyanite, staurolite, quartz, and muscovite. The groundmass of the rocks consists of the $Grt + Bt + Chl + Ms + Qtz + Pl \rightarrow St$ assemblage (with or without *Ky*). Rocks closer to the overthrust can be subdivided into three zones of overprinted medium-pressure metamorphism: (II) outer, (III) intermediate, and (IV) inner with different proportions of relict and newly formed minerals and the deformation grades of the rocks. The amounts of andalusite in the rocks decrease closer to the Panimbinskii overthrust up to its absolute disappearance in the inner zone, whereas the contents of kyanite, staurolite, and garnet simultaneously increase.

The outer zone II is distinguished by the appearance of newly formed assemblage of kyanite, staurolite, and garnet. The rocks of this zone contain the assemblage $Ms + Chl + Bt + Qtz + Ky + And + St + Grt + Ilm + Pl \rightarrow Cld$ and can be ascribed to the andalusite–kyanite–staurolite subfacies of the kyanite schist facies (Dobretsov *et al.*, 1974). This zone is characterized by the initial resorption of andalusite porphyroblasts, which are locally replaced by Ky – Ms – St – Qtz aggregates in the margins at contacts with chloritoid and biotite (Figs. 2b, 2c, 2d). The prismatic shapes of the grains remain preserved, as are the chiasolite crosses inside them. Staurolite composes euhedral grains in the matrix, often with small inclusions of chlorite and chloritoid, which were captured during the growth of staurolite grains in the first metamorphic stage (andalusite–sillimanite type). The muscovite replacing andalusite (together with staurolite, kyanite, and quartz) consists of randomly oriented flakes, while the matrix muscovite flakes lie in the secondary schistosity plane. Both varieties occur in intergrowths with margarite. Small garnet grains (2 mm), which grew only in the matrix, are euhedral. Mineral inclusions in garnet are ilmenite, muscovite, biotite, chloritoid, and quartz. Biotite flakes typically have kink bands with uneven margins, which are twisted in the secondary schistosity direction.

The intermediate zone III is composed of the deformation products of metapelites, with andalusite recrystallized more significantly than in zone II and partly or fully replaced by $Ky + St + Ms + Qtz$ pseudomorphs (Fig. 2e). The square and elongated cross sections (in petrographic thin sections) of cataclastic pseudomorphs acquire oval or rhomboidal shapes, with the long axes oriented along the schistosity. All three Al_2SiO_5 polymorphs (*And*, *Ky*, and *Sil*) were detected together

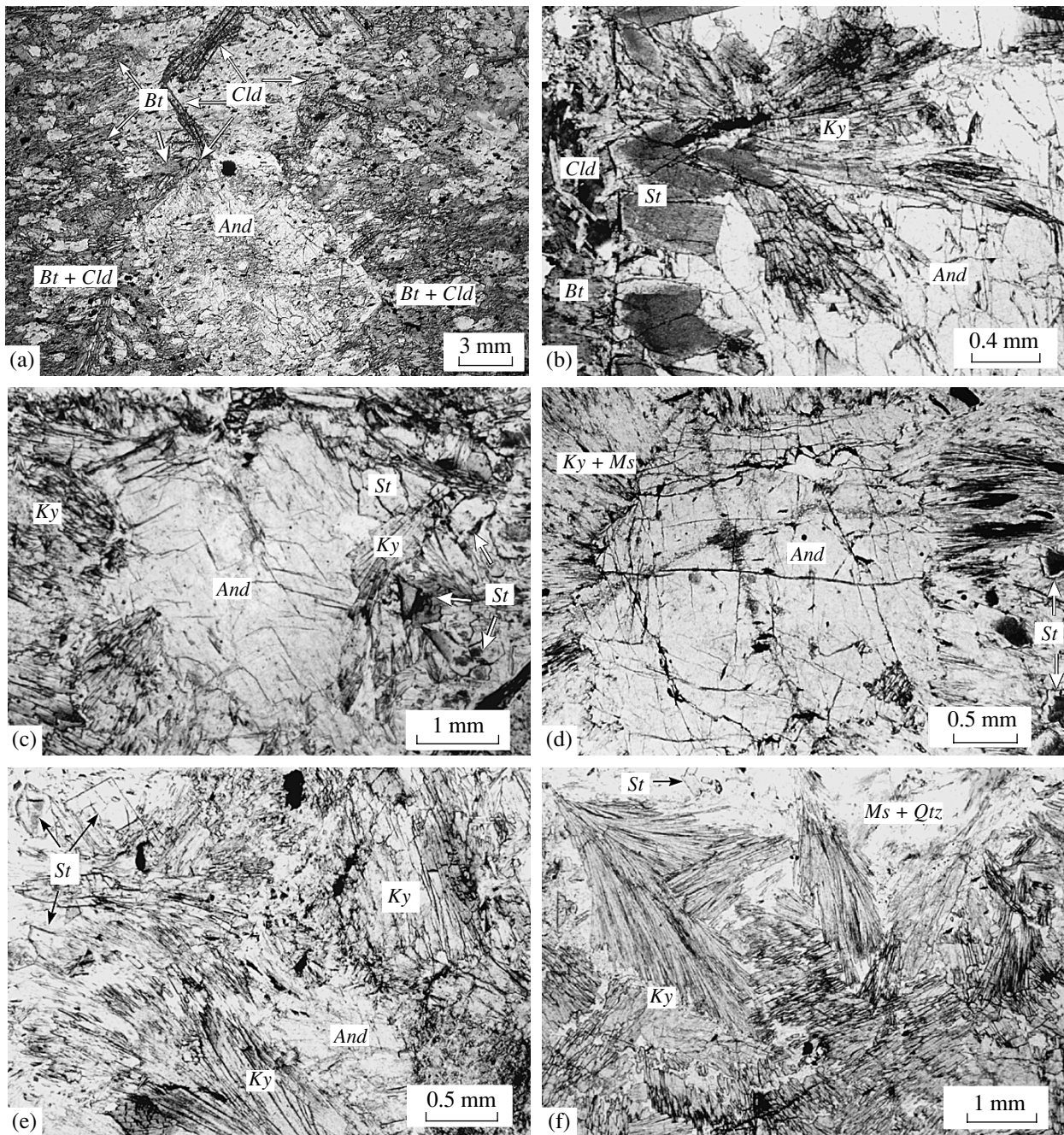


Fig. 2. Microphotographs of thin sections with microtextural relations between minerals in the pristine rocks (I) and rocks at different evolutionary stages of pseudomorphism.

(a) The *And-Chl-Bt* assemblage in a quartz-plagioclase-chlorite-mica matrix. The upper part of the andalusite crystal is in physical contact with chlorite and biotite. (b) Initial pseudomorphism at contacts between andalusite and a biotite-chlorite aggregate in outer zone II. (c, e) Incomplete pseudomorphing of the margins of an andalusite crystal by *Ky* and *St*. (d) Same, replacement by a *Ky-St-Ms* aggregate in intermediate zone III. (f) Full pseudomorphic replacement of andalusite crystals by a *Ky-St-Ms-Qtz* aggregate in inner zone IV.

only in rocks from this zone. The sillimanite is fibrolite, which developed in the margins of kyanite grains and, occasionally, in andalusite relics along cleavage planes. The rocks of this zone contain the assemblage *Ms + Chl + Bt + Qtz + Ky + And + Sil + St + Grt + Ilm + Pl* and can be attributed to the andalusite-kyanite-sillimanite-stau-

rolite subfacies of the kyanite schist facies (Dobretsov *et al.*, 1974). Farther toward the Panimbinskii overthrust, the last andalusite relics disappear, which marks the transition to the inner zone.

The inner zone IV, which is bordered by the Panimbinskii overthrust in the northeast (Fig. 1), is noted

Table 1. Chemical composition of metapelites from different zones of the Kordinskaya Formation

Component	I (<i>n</i> = 6)		II (<i>n</i> = 7)		III (<i>n</i> = 8)		IV (<i>n</i> = 8)	
	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ
SiO ₂	59.57	3.14	59.81	2.83	60.11	3.02	59.34	2.17
TiO ₂	0.86	0.09	0.88	0.21	0.84	0.19	0.91	0.36
Al ₂ O ₃	21.12	3.02	21.35	2.43	21.25	3.42	21.52	3.14
FeO	7.62	1.86	7.94	2.31	7.74	4.62	8.24	1.99
MnO	0.08	0.07	0.14	0.18	0.14	0.11	0.13	0.09
MgO	1.99	1.10	2.04	1.05	2.08	0.96	2.01	1.26
CaO	0.28	0.38	0.56	0.44	0.52	0.31	0.47	0.59
Na ₂ O	0.66	0.46	0.69	0.55	0.61	0.34	0.51	0.31
K ₂ O	3.21	0.72	3.15	0.61	3.25	0.30	3.17	1.44
LOI	4.52	2.41	3.28	2.12	3.36	1.91	3.47	1.46
Total	99.91		99.84		99.90		99.77	

Note: *n* is the number of samples, \bar{X} and σ are the average and standard deviation. Oxides are given in wt %, all Fe is recalculated to FeO, LOI is loss on ignition.

for the full recrystallization of the mineral material with the origin of blastoporphyratic and blastomylonitic textures. Rhomboidal *Ky* + *St* + *Ms* + *Qtz* pseudomorphs are ubiquitously transformed to lenses, whose long axes are oriented along the schistosity, with the pressure shadows near them in the lepidogranoblastic groundmass composed of recrystallized quartz. The rocks of this zone bear the assemblage *Ms* + *Chl* + *Bt* + *Qtz* + *Ky* + *St* + *Grt* + *Ilm* + *Pl* and affiliate with the kyanite–staurolite subfacies of the kyanite schist facies (Dobretsov *et al.*, 1974; Fig. 2f). In contrast to euhedral grains in other zones, garnet in this zone has shapes of flattened porphyroblasts, which provide evidence of growth under stress. Some garnet grains were rotated and compose helical textures of the snowball type. The high intensity of the deformation is also evident from the lens–nodular structures of the rocks, veins of granulated quartz, and a decrease in the grain sizes of minerals.

METHODS

Our task was to examine the distribution character of material during metamorphism coupled with rock deformations. The analysis of mass transfer during the origin of the pseudomorphs and transformations in the matrix was based on calculations of the modal composition of the rocks and mineral reactions with the use of chemical analyses of the rocks (Table 1) and minerals (Table 2).

The modal concentrations of minerals were deduced from rock analyses in compliance with the procedure described by Ferry (1984). The amounts of element *i* relative to Al in a rock was expressed (in mole numbers) through the composition and relative amounts of

minerals as

$$i/Al = \left(\sum_j a_{i,j} n_j \right) / \left(\sum_j a_{Al,j} n_j \right), \quad (1)$$

where $a_{i,j}$ is the number of atoms of element *i* in the formula of mineral *j*, and n_j is the number of moles of mineral *j* in the rock. The calculations were made for a constant volume $V = 100 \text{ cm}^3$

$$\sum_j V_j n_j = 100, \quad (2)$$

where V_j is the molar volume of mineral *j*. The numerical values of n_j were obtained by the solving the set of Eqs. (1) and (2); the molar contents of minerals were recalculated to their volumetric concentrations with the use of the molecular volumes of these minerals from the thermodynamic database of Holland and Powell (1998). The results are summarized in Table 3.

The equations of chemical reactions were calculated using the actual compositions of minerals with the aid of matrix algebra techniques in the MATHEMATICA 4.0 program package by the NullSpace procedure for the system $K_2O\text{--}FeO\text{--}MnO\text{--}MgO\text{--}Al_2O_3\text{--}SiO_2\text{--}H_2O \pm TiO_2 \pm CaO \pm Na_2O$ (KFMnMASH $\pm T \pm C \pm N$). Matrices of the compositions of reacting minerals (with stoichiometric coefficients in their formulae) were constructed for each mineral assemblage. The matrices consisted of *n* columns, equal to the number of minerals in the assemblage, and (*n* – 1) rows, corresponding to the chemical components. In each case, the number of major component was determined by the actual composition of the system. The chosen reference configuration was the KFMnMASH system because of the

Table 2. Matrices of the stoichiometric coefficients of minerals used in the calculations of chemical reaction equations for (a) pseudomorphs and (b) rock matrix at the kyanite isograd

(a)											
Component	<i>Cld</i>	<i>And</i>	<i>Bt</i>	<i>Pl</i>	<i>Ilm</i>	<i>St</i>	<i>Ky</i>	<i>Qtz</i>	<i>Ms</i>	<i>Mrg</i>	H ₂ O
Si	1.99	0.98	2.68	2.89	0.00	7.87	0.98	1.00	3.04	2.01	0.00
Al	4.00	2.02	1.73	1.12	0.00	18.6	2.01	0.00	2.83	3.99	0.00
Fe	1.74	0.01	1.43	0.01	0.94	3.53	0.01	0.00	0.08	0.02	0.00
Mg	0.25	0.00	0.83	0.00	0.00	0.51	0.00	0.00	0.06	0.01	0.00
K	0.00	0.00	0.85	0.00	0.00	0.00	0.00	0.00	0.86	0.00	0.00
H ₂ O	2.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00	1.00	1.00	1.00
Mn	0.02	0.00	0.01	0.00	0.02	0.04	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.89	0.00
Na	0.00	0.00	0.00	0.87	0.00	0.00	0.00	0.00	0.10	0.12	0.00
Ti	0.00	0.00	0.17	0.00	1.02	0.02	0.00	0.00	0.03	0.00	0.00

(b)											
Component	<i>Chl</i>	<i>Cld</i>	<i>Bt</i>	<i>Pl</i>	<i>Ilm</i>	<i>St</i>	<i>Grt</i>	<i>Qtz</i>	<i>Ms</i>	<i>Mrg</i>	H ₂ O
Si	2.53	1.99	2.68	2.89	0.00	7.87	3.00	1.00	3.04	2.01	0.00
Al	2.86	4.00	1.73	1.12	0.00	18.6	1.94	0.00	2.83	3.99	0.00
Fe	2.84	1.74	1.43	0.01	0.94	3.53	2.62	0.00	0.08	0.02	0.00
Mg	1.75	0.25	0.83	0.00	0.00	0.51	0.24	0.00	0.06	0.01	0.00
K	0.00	0.00	0.85	0.00	0.00	0.00	0.00	0.00	0.86	0.00	0.00
H ₂ O	4.00	2.00	1.00	0.00	0.00	1.00	0.00	0.00	1.00	1.00	1.00
Mn	0.01	0.02	0.01	0.00	0.02	0.02	0.15	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.00	0.09	0.00	0.00	0.08	0.00	0.00	0.89	0.00
Na	0.03	0.00	0.00	0.87	0.00	0.00	0.00	0.00	0.10	0.12	0.00
Ti	0.02	0.00	0.17	0.00	1.02	0.02	0.01	0.00	0.03	0.00	0.00

Note: Cation numbers were calculated for the following sums of oxygen atoms: 48 for *St*, 14 for *Chl*, 12 for *Grt* and *Cld*, 11 for *Bt*, *Ms*, and *Mrg*, 8 for *Pl*, 5 for *And* and *Ky*, and 3 for *Ilm*.

Table 3. Calculated volumetric and molar concentrations of minerals in rocks from different zones

Mineral	Concentration, moles				Concentration, vol %			
	I	II	III	IV	I	II	III	IV
<i>Ms</i>	0.104	0.102	0.095	0.093	14.64	14.34	13.37	13.05
<i>Chl</i>	0.020	0.019	0.017	0.016	4.14	3.98	3.55	3.51
<i>Bt</i>	0.090	0.098	0.094	0.092	13.98	15.08	14.44	14.25
<i>Pl</i>	0.014	0.048	0.045	0.043	1.38	4.84	4.50	4.32
<i>Qtz</i>	1.551	2.080	2.162	2.283	35.20	47.20	48.94	51.74
<i>Cld</i>	0.030	0	0	0	4.06	0	0	0
<i>Ilm</i>	0.050	0.047	0.044	0.040	1.58	1.46	1.33	1.26
<i>Mrg</i>	0.0009	0.0005	0.0004	0	0.12	0.06	0.05	0
<i>And</i>	0.483	0.140	0.097	0	24.90	7.19	5.02	0
<i>Ky</i>	0	0.115	0.182	0.246	0	5.10	8.04	10.88
<i>St</i>	0	0.013	0.010	0.016	0	0.60	0.47	0.73
<i>Grt</i>	0	0.001	0.003	0.002	0	0.14	0.30	0.27

Note: Numbers of mineral moles were calculated for a rock volume of 100 cm³.

Table 4. Balance of major components in the rocks of the original and outer zones

Mineral	N	Original concentrations of components								
		n_{SiO_2}	$n_{\text{Al}_2\text{O}_3}$	n_{FeO}	n_{MgO}	$n_{\text{K}_2\text{O}}$	n_{MnO}	n_{CaO}	$n_{\text{Na}_2\text{O}}$	n_{TiO_2}
<i>Ms</i>	16.7	50.77	47.26	1.34	1.00	14.36	0	0	1.67	0.50
<i>Chl</i>	3.10	7.84	8.87	8.80	5.43	0	0.03	0	0.09	0.06
<i>Bt</i>	14.6	39.13	25.26	20.88	12.12	12.41	0.15	0	0	2.48
<i>Pl</i>	2.20	6.36	2.46	0.02	0	0	0	0.20	1.91	0
<i>Qtz</i>	248	248	0	0	0	0	0	0	0	0
<i>Cld</i>	4.60	9.15	18.40	8.00	1.15	0	0.09	0	0	0
<i>Ilm</i>	8.00	0	0	7.52	0	0	0.16	0	0	8.16
<i>Mrg</i>	0.14	0.28	0.56	0	0	0	0	0.12	0.02	0
<i>And</i>	77.3	75.7	156	0.70	0	0	0	0	0	0
<i>Ky</i>	0	0	0	0	0	0	0	0	0	0
<i>St</i>	0	0	0	0	0	0	0	0	0	0
<i>Grt</i>	0	0	0	0	0	0	0	0	0	0
Total		437	259	47.3	19.7	26.8	0.43	0.32	3.69	11.2
Mineral	N	Final concentrations of components								
		n_{SiO_2}	$n_{\text{Al}_2\text{O}_3}$	n_{FeO}	n_{MgO}	$n_{\text{K}_2\text{O}}$	n_{MnO}	n_{CaO}	$n_{\text{Na}_2\text{O}}$	n_{TiO_2}
<i>Ms</i>	16.3	49.55	46.13	1.30	0.98	14.02	0	0	1.63	0.49
<i>Chl</i>	3.00	7.59	8.58	8.52	5.25	0	0.03	0	0.09	0.06
<i>Bt</i>	15.7	42.08	27.16	22.45	13.03	13.35	0.16	0	0	2.67
<i>Pl</i>	7.70	22.25	8.62	0.08	0	0	0	0.69	6.70	0
<i>Qtz</i>	333	333	0	0	0	0	0	0	0	0
<i>Cld</i>	0	0	0	0	0	0	0	0	0	0
<i>Ilm</i>	7.50	0	0	7.05	0	0	0.15	0	0	7.65
<i>Mrg</i>	0.06	0.17	0.07	0	0	0	0	0.01	0.05	0
<i>And</i>	22.4	21.8	45.2	0.20	0	0	0	0	0	0
<i>Ky</i>	18.4	18.03	36.98	0.18	0	0	0	0	0	0
<i>St</i>	2.10	16.52	39.12	7.41	1.07	0	0.04	0	0	0.04
<i>Grt</i>	0.2	0.60	0.39	0.52	0.05	0	0.03	0.01	0	0
Total		511	212	47.7	20.4	47.1	0.41	0.71	8.47	10.9

Note: $N = V/V_j$ is the number of moles of minerals in 1.6 cm^3 of rock ($N \times 10^{-4}$ moles), $n_k = N \times a_{i,j}$ is the numbers of moles of major component i in mineral j ($n_k \times 10^{-4}$ moles).

importance of MnO for mineral reactions in medium-temperature metapelites (Droop and Harte, 1995). To estimate the reliability of the equation obtained, we compared the volumetric proportions of minerals calculated by the chemical reaction with those observed in the rocks. The volumes of the reacting phases were calculated by the formula $v = n_j V_j$, where n_j is the stoichiometric coefficients of minerals in the reaction equation.

An important procedure was the mass-balance calculation of the minimum rock volume within which equilibrium was attained between coexisting minerals. Such volumes within which metamorphic transforma-

tions occurred were estimated (in differently oriented thin sections) from the spatial distribution of minerals participating in reactions with regard for grain sizes and distances between them in the rock. Based on the chemistry of all phases and their volumetric proportions in the calculated minimum volumes of material redistribution, we calculated the numbers of moles of major components in the rock before and after the reactions (Table 4). Analysis of the redistribution of components and microtextural interpretations of phase relations provided us with insight into the characteristic features of the mineral transformations (see below).

ROCK AND MINERAL CHEMISTRY AND MINERAL REACTIONS

The bulk chemical compositions of the rocks were analyzed on a SRM-25 multichannel XRF spectrometer at the Joint Institute of Geology, Geophysics, and Mineralogy, Siberian Division, Russian Academy of Sciences. Analyses of metapelite samples from different zones (Likhanov *et al.*, 2001) revealed the following chemical variations: $\text{SiO}_2 = 57.14\text{--}62.59$ wt %, $\text{FeO} = 5.72\text{--}11.58$ wt %, $\text{Na}_2\text{O} = 0.29\text{--}1.13$ wt %, and $\text{CaO} = 0.26\text{--}1.06$ wt %. The variations in the concentrations of other components are insignificant, and the metamorphic processes were generally nearly isochemical. The differences in the concentrations of SiO_2 , Na_2O , and CaO can be explained by the primary lithological heterogeneity of the rocks (different contents of quartz, plagioclase, and calcite). Average chemical compositions of rocks from different zones are listed in Table 1. As follows from this table, although slightly heterogeneous in composition, most of the rocks are classified with Fe- and Al-rich metapelites [$X_{\text{Fe}} = \text{FeO}/(\text{FeO} + \text{MgO} + \text{MnO}) = 0.68\text{--}0.69$ and $X_{\text{Al}} = \text{Al}_2\text{O}_3\text{--}3\text{K}_2\text{O}/(\text{Al}_2\text{O}_3\text{--}3\text{K}_2\text{O} + \text{FeO} + \text{MgO} + \text{MnO}) = 0.38\text{--}0.41$] as compared with the average metapelites (Shaw, 1956; Ague, 1991).

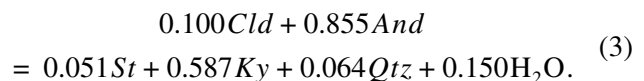
The chemistry of minerals from the metapelites was analyzed on an EDAX DX-4 energy-dispersive X-ray spectral microprobe attached to a Philips XL-30 scanning electron microscope at the university of Siena, on a Camebax-micro X-ray spectral microprobe at the Joint Institute of Geology, Geophysics, and Mineralogy, Siberian Division, Russian Academy of Sciences, in Novosibirsk, and on a Cameca SX-50 at the University of Bochum. The occurrence of graphite and virtually pure ilmenite in each rock sample means that the redox potential was relatively low, and the Fe^{3+} concentrations in the formulae of Fe-bearing phases are low (Holdaway *et al.*, 1988). The stoichiometry of minerals used in the further calculations was calculated in accordance with these considerations (Table 2). The reader can find a detailed description of the chemistry of all rock-forming minerals in (Likhanov *et al.*, 2001), so that below we mention only the general regularities in the compositional variations of minerals participation in chemical reactions.

Andalusite is one of the main rock-forming minerals of the pristine rocks (I), in which its concentrations are as high as ~25 vol %. In the outer (II) and intermediate (III) zones (Fig. 1), its concentrations in the rocks drastically decrease, and it fully disappears from the rocks of the inner zone. The decrease in the andalusite concentration is coupled with a simultaneous increase in the contents of kyanite in zones II–IV (Table 2). Chloritoid is a typical mineral of the pristine rocks (I) and is also present in zones II–IV in the form of small relics in staurolite and garnet. The mineral is chemically homogeneous and has a constant $X_{\text{Fe}} = \text{Fe}/(\text{Fe} + \text{Mg}) = 0.875$. Muscovite, chlorite, biotite, quartz, plagioclase, and

ilmenite are ubiquitously stable from zone I throughout zone IV. The amounts of plagioclase, quartz, and biotite gradually increase closer to zone IV, while the concentrations of muscovite, chlorite, and ilmenite simultaneously diminish (Table 2), and the composition of the micas and plagioclase progressively change (Likhanov *et al.*, 2001). With the transition from the pristine rocks of zone I to zone II and farther to zone IV, the Al^{IV} in biotite increases from 1.04–1.07 to 1.25–1.34 p.f.u., and the X_{Fe} decreases from 0.69 to 0.603. The muscovite is characterized by a slight enrichment in the celadonite component $(\text{Mg} + \text{Fe})/(\text{Mg} + \text{Fe} + \text{Al})$ from 0.08 to 0.16 at a significant change in the concentration of the paragonite end member X_{Na} from 0.085 to 0.255. The plagioclase composition changes from albite with $X_{\text{An}} = 0.063\text{--}0.094$ in the pristine rocks (I) to oligoclase with $X_{\text{An}} = 0.116\text{--}0.124$ in zones II–IV. The chlorite is chemically homogeneous in all zones and shows only slight variations in its $X_{\text{Fe}} = 0.608\text{--}0.621$. Garnet and staurolite simultaneously appear in the outer zone II and are present in mineral assemblages in the other zones (II–IV). The chemical composition of staurolite from different zones is practically the same, its X_{Fe} is constant and equal to 0.874, and the Mn and Zn concentrations vary insignificantly (0.02–0.04 and 0.2–0.21 p.f.u., respectively). The X_{Fe} of garnet is also nearly constant $X_{\text{Fe}} = 0.91\text{--}0.92$. The prograde (with a pressure increase) nature of the garnet zoning is determined by a gradual increase in the grossular concentration at a progressive depletion in spessartine from the cores to rims of grains (see, for example, Crawford and Mark, 1982) at a virtually unchanging concentrations of the almandine and pyrope end members.

Variations in the chemistry of the coexisting minerals and in their quantitative proportions in the rocks were controlled by variations in the compositions of the rocks and the thermodynamic conditions of metamorphism. Likhanov *et al.* (2000, 2001) have demonstrated that the evolution in the chemical and modal compositions of the minerals was controlled by an increase in the pressure (at a practically unchanging temperature) at the preservation of the original rock compositions. Inasmuch as mineralogical transformations in the metapelites were isochemical, the mass transfer between phases participating in metamorphic reactions occurred at the preservation of mass balance. Considering this fact and based on the microtextural and chemical information obtained, we calculated chemical reactions responsible for the development of *Ky–St–Ms–Qtz* pseudomorphs after andalusite and mineral transformations in the matrix at $P = 4\text{--}4.5$ kbar and $T = 550\text{--}570^\circ\text{C}$.

In a simplified form, the mineral transformations during the initial development of pseudomorphs at the kyanite isograd can be written as follows for the FMn-MASH system:



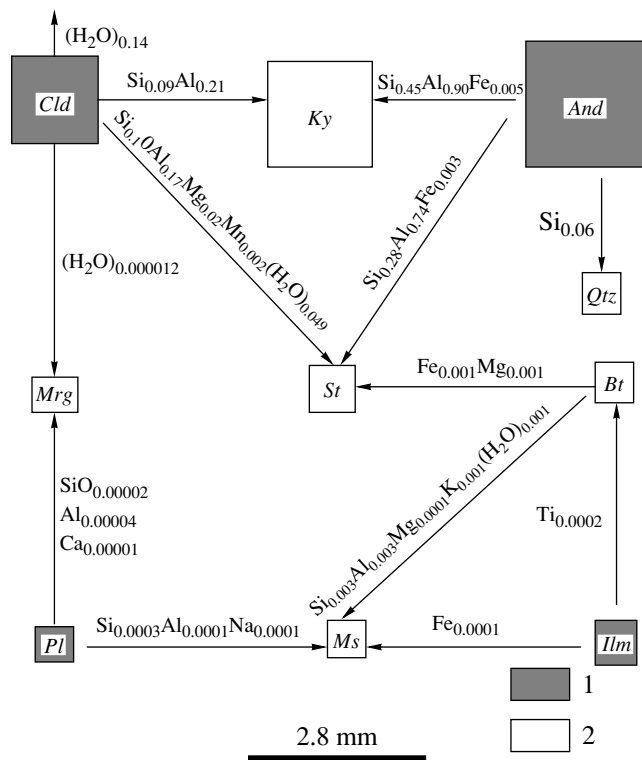
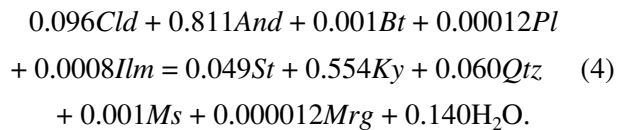


Fig. 3. Redistribution of components between reacting phases during the development of *Ky–St–Ms–Qtz* pseudomorphs after andalusite.

(1) Original phases; (2) reaction products. The volumes are increased by a factor of two for *Bt* and *Ms*, by a factor of four for *Ilm* and *Pl*, and by a factor of six for *Mrg*; other phases are shown to scale.

For the KFMnMASHCNT system, which models metamorphic reactions with the participation of all of the probable phases, these mineral transformations assume the form



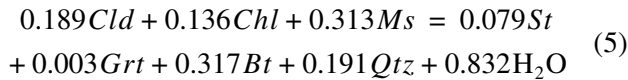
The stoichiometric coefficients of the phases in reactions (3) and (4) are quite similar, suggesting that the introduction of other components and phases will not significantly modify the character of the mineral transformations during the development of the pseudomorphs. The amounts of *Pl*, *Mrg*, and *Ilm* are negligibly small. The feasibility of reaction (4) receives support from microtextural features of the rocks, in which *Ky–St–Ms–Qtz* pseudomorphs are formed at contacts between andalusite and a biotite–chlorite aggregate in the groundmass (Fig. 2b). The redistribution of components between interacting phases according to reaction (1) is graphically represented in Fig. 3. In this situation, there is no simple polymorph transition but rather the replacement of andalusite by a complex of minerals with the participation of kyanite.

Replacements of this kind during the prograde metamorphic stage are rare, because the stationary continental geotherm usually does not intersect the andalusite–kyanite equilibrium line (Kerrick, 1990). The origin of such pseudomorphs is commonly attributed to retrograde metamorphic stages and hydration reactions (see, for example, Chinner, 1980). However, a few examples in the literature involve prograde andalusite transformation into kyanite explained by metastable andalusite behavior in the *P–T* region of kyanite stability (Hollister, 1969) or an increase in the lithostatic pressure under the effect of magmatic intrusions (Brown and Walker, 1993; Brown, 1996; Whitney *et al.*, 1999) or due to overthrusting (Bel'kov, 1963; Crawford and Mark, 1982; Barker, 1987; Beddoe-Stephens, 1990; Spear *et al.*, 1990). When mineral transformations responsible for the origin of *Ky–St* pseudomorphs after andalusite in aluminous metapelites are described in the literature, they are usually explained with calling upon well-known reactions producing staurolite at the sacrifice of chloritoid (without muscovite and biotite), coupled with the *And* → *Ky* polymorph transition (see, for example, Klaper and Bucher-Nurminen, 1987). However, in our case, the small stoichiometric coefficients of biotite and muscovite indicate that these minerals practically do not participate in the reaction. To test this concept, we introduced chlorite, a mineral present in the matrix (micas were ignored), into this reaction and obtained the following FMASH reaction: $0.001Chl + 0.800And + 0.301Cld = 0.193Qtz + 0.151St + 0.450H_2O$ (if $X_{FeCld} > X_{FeSt}$). The reaction has a very small coefficient of chlorite. Taking this into consideration, along with microtextural features of the rocks, in which *Ky–St–Qtz–Ms* pseudomorphs are formed at contacts between andalusite and biotite–chlorite aggregates (Fig. 2b), it can be concluded that reactions (3) and (4) are more probable for the rocks in question.

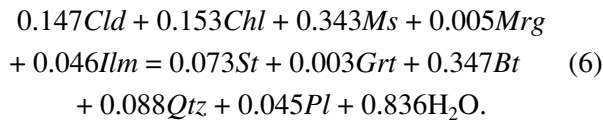
In this context, it is pertinent to stress that the *Cld* + *Bt* + *And* equilibrium assemblage is usually absent from *St*-bearing metapelites at $P > 2$ kbar, because their chloritoid is always decomposed and gives rise to the *Bt* + Al_2SiO_5 assemblage by reactions like $Cld + Qtz = St + Grt + Chl + H_2O$ or $Cld + Ms + Qtz = St + Grt + Bt + H_2O$ (Korikovskii, 1979). Nevertheless, this assemblage was occasionally encountered in high-Fe and high-Al hornfels both without staurolite (Okuyama-Kusunose, 1994; Likhanov *et al.*, 2001a) and with this mineral (Likhanov, 1988) at $P = 2–3.5$ kbar. The assemblage was also found in regionally metamorphosed pelites at $P = 3.5–4$ kbar (Dickenson, 1988; Bickle and Archibald, 1984). The stability of the *Cld* + *Bt* + *And* assemblage in our rocks seems to be explained by a rare combination of a narrow pressure range with the unusual chemistry of the rocks, which are high in both Al and Fe. Powell and Holland (1990) argued that the *And* + *Cld* + *Bt* assemblage can be stable within the temperature range of 520–570°C under $P \geq 3$ kbar

because of minor amounts of Fe³⁺ in the biotite and chloritoid.

The onset of pseudomorph development in the rocks coincided with mineral transformations in their groundmass with the crystallization of garnet and staurolite. Rare finds of staurolite inclusions in garnet and garnet in staurolite may be indicative of their simultaneous crystallization in the matrix. Taking into account these observations, it is possible to calculate mineral reactions in the matrix for the simultaneous formation of staurolite and garnet in the KFMnMASH system

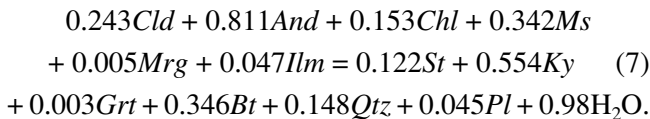


and, for the KFMnMASHCNT system,



The equations of reactions (5) and (6) are nearly identical and correspond to the usual succession of a decrease in the $X_{Fe} = Fe/(Fe + Mg)$ of minerals ($Grt > Cld \geq St > Bt > Chl$) in metapelites. The equations are justified by the quantitative proportions of phases in the rock: the growth of staurolite, garnet, biotite, quartz, and plagioclase is associated with a decrease in the amounts of chlorite, muscovite, and chloritoid. Additional arguments are provided by inclusions of mineral relics in the products of these reactions (staurolite and garnet) and the absolute absence of both kyanite and andalusite in the matrix assemblages. The redistribution of components between the phases participating in reaction (6) is portrayed in Fig. 4. The simultaneous formation of staurolite and garnet in the matrix at the expense of chloritoid, chlorite, and muscovite is consistent with the mineral reactions proposed by Whitney *et al.* (1996) for Fe-rich metapelites in Dutchess County in the United States.

A generalized scheme of mass transfer in the rocks with the participation of all minerals (which sums up all local reactions) during the early development of the pseudomorphs (4) and matrix transformations (6) can be written in the following form (without regard for the phase rule):



This is one of the calculation variants. The values of the coefficients of phases may slightly vary, but the quantitative proportions of minerals observed in the rocks (Table 2) generally justify the generalized form of reaction (7). New minerals were formed at the expense of the original minerals of metapelites (I), which reacted in stoichiometric proportions ($Ilm : Chl : Cld : Ms : And = 1 : 3 : 3.5 : 9 : 16$) that are nearly identical to the coefficients in reaction (7): $Ilm : Chl : Cld :$

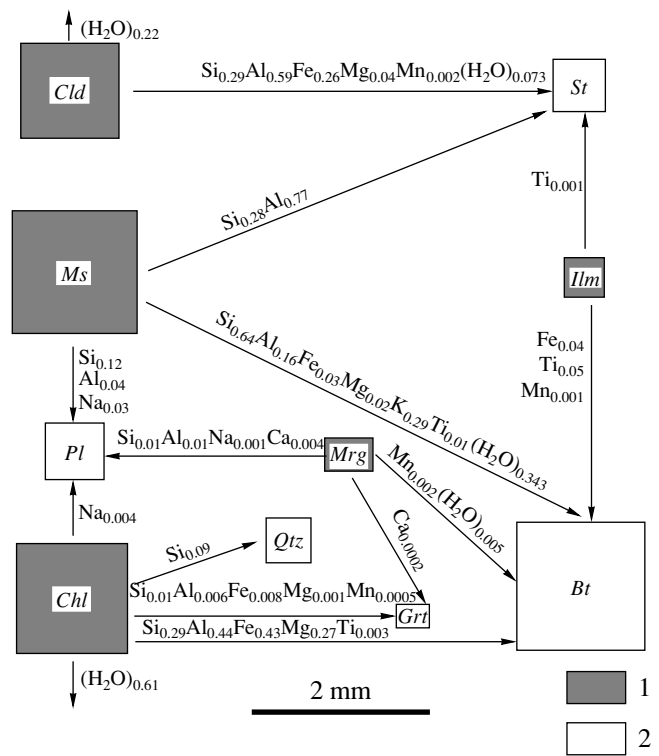


Fig. 4. Redistribution of components between reacting phases in the rock matrix. (1) Original phases; (2) reaction products. The volumes of all minerals are shown to scale.

$Ms : And = 1 : 3 : 5 : 8 : 17$. The comparison between the volumetric proportions of the newly formed minerals ($Grt < St < Pl < Bt < Ky < Qtz$) and those observed in the rocks and of the quantitative proportions between the original and newly formed minerals ($Ky : And = 1 : 1.5$ and $Ms : Bt = 1 : 1$) exhibits a satisfactory consistency, with the difference not exceeding 20%. This and some other deviations (for example, for quartz and plagioclase) can be explained by the lack of an absolute identity between the bulk-rock compositions, errors in the calculations of the mole volumes of minerals of variable composition, and analytical errors in microprobe analyses of minerals. A variant of the generalized scheme of redistribution of elements between phases is shown in Fig. 5. The calculated scheme (5) is in good agreement with the mass-balance results obtained by Whitney *et al.*, 1995) for metamorphic rocks in British Columbia, Canada, in which garnet, staurolite, and biotite were formed due to the decomposition of chloritoid, muscovite, and ilmenite at analogous $P-T$ parameters.

From the viewpoint of thermodynamics (Zharikov, 1976), calculated reactions (3)–(6) with the ratios of stoichiometric coefficients as cited above are characterized by large volume differences and small entropy differences (without regard for water). Using the standard volumes of minerals from the thermodynamic database

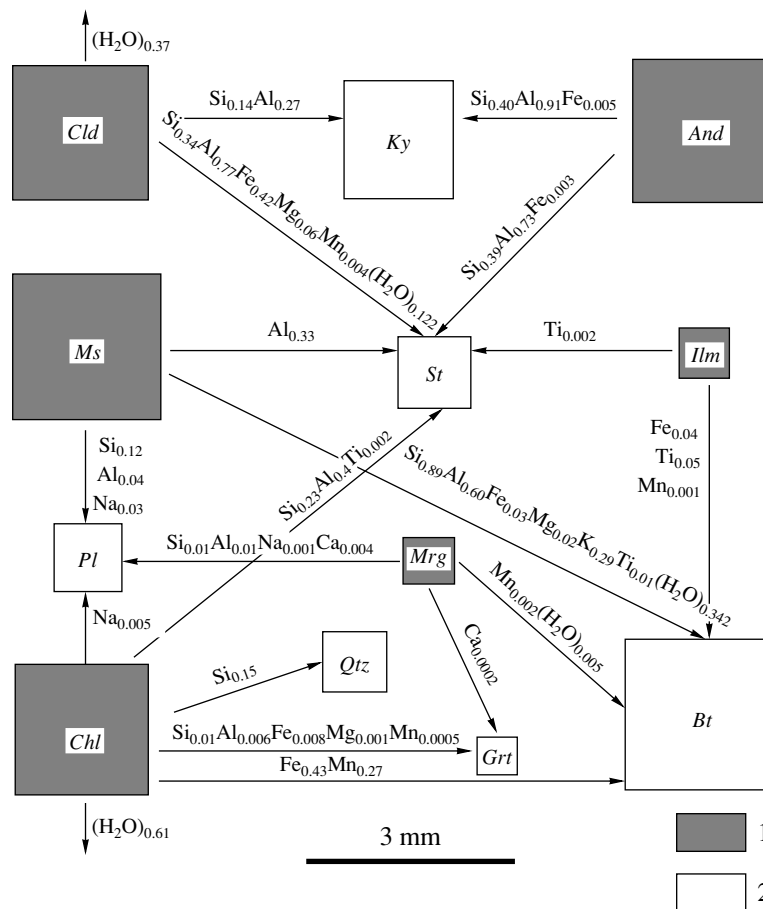


Fig. 5. Generalized scheme of material redistribution resulting from reactions (4) and (6). (1) Original phases; (2) reaction products. The volumes of all minerals are shown to scale.

(Holland and Powell, 1998), it is possible to quantify the overall volume differences of the solid phases ($-\Delta V$). It is equal to 49% for the initial development of pseudomorphs according to reactions (3)–(4) and 42–39% for reactions (5)–(6) in the matrix. This implies that the main driving force of these reactions was a pressure increase, which is in agreement with geothermobarometric data (Likhanov *et al.*, 2001).

DISCUSSION

Our results concerning the nature and characteristics of the initial andalusite pseudomorphing by kyanite in the matrix allowed us to evaluate the minimum volumes within which material could be redistributed with the preservation of its balance. Grains of each mineral in a metamorphic rock are situated at different distances from one another, which average ~ 2 – 3 mm. The maximum distance between mineral grains determines the minimum volume within which a balance is maintained between mineral reactants and products. To quantify this minimum volume for reactions (3) and (4), we examined a selection of thin sections oriented in the plane of the rock schistosity and perpendicular to it.

Within each thin section, a square region was chosen with a side equal to 20 ± 2 mm within which we counted the cross section areas of andalusite crystals and *Ky*–*St*–*Ms*–*Qtz* pseudomorphs. The shapes and sizes of these sections remained unchanging with the transition from the rocks of zone I to those of zone II. Proceeding from the thickness of the *Ky*–*St*–*Ms*–*Qtz* reaction rims around andalusite crystals (2 mm on average) and the estimated distances between the grains of mineral reactants and products of reactions (3) and (4), we calculated the minimum volume of material redistribution, which appeared to be no greater than $\sim 1.2 \pm 0.4$ cm³. It is generally thought (see, for example, Ridley, 1985) that this volume depends on the rates of diffusive transfer of components, temperature, the duration of the metamorphic processes, and the intensity of deformations. The latter increases the rate of diffusion-controlled mass transfer by enhancing the rock permeability and creating pressure gradients on the grain-size scale (these gradients appear during the opening and closure of submicron-sized fractures and direct local fluid flows along networks of grain boundaries; Brodie and Rutter, 1985). Because of this, the minimum volume in inner zone IV (where andalusite crystals are

fully pseudomorphed due to intensification of deformations and a pressure increase at a constant temperature) increases to $\sim 1.7 \pm 0.7 \text{ cm}^3$.

In order to evaluate the minimum volume within which local reactions (5) and (6) in the matrix operated and a material balance was maintained, we determined (in thin sections) the sizes of grains of coexisting minerals that participated in the reactions and measured distances between them. At an average grain size of approximately 0.5–1 mm, all minerals are present in the thin section plain within a square region with a size of $\sim 7.5 \text{ mm}$. Based on these estimates and the assumption that minerals are equally distributed over the rock, we estimated the minimum volume at $\sim 0.4 \text{ cm}^3$. Taking into account textural features of the rocks, it can be hypothesized that the overall mass transfer between local volumes during andalusite replacement by kyanite occurred within a minimum volume equal to the sum of the volumes of local reactions (4) and (6), i.e., no more than 1.6 cm^3 . Table 4 indicates that material was redistributed in accordance with this mass transfer scheme with the preservation of a mass balance and could be restricted to this volume. This estimate seems to be realistic, because the discrepancies for all components except CaO and Na₂O are no higher than 20% (they could be caused by one of the aforementioned factors). Some deficit of the initial CaO and Na₂O concentrations compared with the final concentrations of these components is explained by the unequal distribution of plagioclase and accessory minerals (calcite and margarite) in the rocks. Given an error of 20%, the overall volume of balanced mass transfer should be no larger than 2 cm^3 .

The reactions were controlled by the congruent and incongruent dissolution of primary minerals, the full or partial passage of matter into the interstitial fluid (Foster, 1977, 1986; Likhanov *et al.*, 1994, 1995, 1999), and diffusion of components in the interstitial space. The nucleation of newly formed minerals in pseudomorphs is usually restricted to grain boundaries and defects in the andalusite structure, which are high-energy sites favorable for nucleation (Vernon, 1976). With the origin of crystallization centers at grain boundaries, the lengths of these boundaries decrease. Deformations associated with metamorphism facilitate nucleation and mass transfer. Similarities between crystal structures of nesosubsilicates (andalusite, kyanite, and staurolite), whose fundamental elements are chains of AlO₆ octahedrons, allow for the epitaxial origin of crystallization centers, i.e., the inheritance of some structural elements of a newly formed mineral from the preexisting atomic structure (Vernon, 1976). The further growth of the grains and the mutual readjustment of their boundaries in the course of deformations is coupled with changes in the phase composition and mineral replacements.

CONCLUSIONS

Our calculations of reaction equations, material balance, and characteristic changes in the mineralogical composition during dislocation metamorphism of Al- and Fe-rich metapelites in the Yenisei Range indicate that the general scheme of mass transfer during andalusite replacement by kyanite is the sum of two local reactions responsible for the development of Ky–St–Ms–Qtz pseudomorphs and mineral transformations in the rock matrix with the origin of staurolite and garnet. Each of the local reactions is isochemical and does not require any external source of material outside the two local systems to maintain a balance of mass transfer. The minimum volume of the joint system within which a component exchange proceeded and a balance of major components was attained between the reacting phases did not exceed $\sim 1.6 \pm 0.4 \text{ cm}^3$. Deformation intensification was associated with an increase in this minimum volume (by $\sim 0.5 \pm 0.7 \text{ cm}^3$ on average) due to the full pseudomorphic replacement of andalusite crystals. These values are consistent with the estimates, made by other researchers, of the scale of mass transfer in the course of metamorphic reactions in metapelites under similar *P–T* conditions.

The literature offers examples of mineral replacements without changes in the bulk chemical composition on the scale of a few grains related to cyclic reactions of kyanite–sillimanite polymorphic transitions (Carmichael, 1969), staurolite decomposition (Kwak, 1974), the growth of reaction coronas in metabasic rocks (Miller, 1974), and others. Foster (1977, 1981, 1986) also explored this problem. Based on the detailed examination of crystalline schists in Maine, United States, he arrived at the conclusion that the generalized reaction in the metapelites is the sum of a series of local reactions that are not isochemical and involve the exchange components between staurolite and sillimanite segregations, garnet porphyroblasts, and the matrix. Foster's analysis of mass balance within a rock volume of $\sim 1 \text{ cm}^3$ indicates that the system as a whole was isochemical and remained closed with respect to all major components except water. Reverdatto and Kolobov (1987), Avchenko (1988), and Likhanov *et al.* (1994, 1995, 2001a, 2001b) used a series of examples of contact and regional metamorphism to demonstrate that the minimum volumes within which material is redistributed may vary from a few cubic millimeters to a few cubic centimeters depending on the temperature and duration of metamorphic processes. In this paper, we demonstrate that another important factor controlling mass transfer is deformations, which increase the permeability of the rocks and the velocities of component transport during metamorphic reactions.

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