Fed'kin V.V., Kotova L.S. Are P-T paths caprices of experiment or peculiar features of the metamorphic evolution?

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Methods of the mineralogical geothermobarometry deduced on the basis of experimental calibration of exchange and net-transfer equilibria and microprobe data give a possibility to determine the character of physicochemical evolution of metamorphism during the formation and an evolution of the complex. However, in some cases, different mineral assemblages show P-T conditions, which significantly differ from each other both in absolute values and the tendency of evolution. The difficulties in P-T determination arise owing to different reasons. They could be both experimental data, which is a basis for calibration of the P-T tools, and natural data on the mineral assemblages.

First of all, it concerns the estimation of the equilibrium in assemblages. That is important not only for coexisting phases, but the equilibrium for all the components of a system as well. A practice of the study of the phase consistency in natural and experimental systems shows that the efficiency of mineral sensors (thermometers, barometers, etc.) drastically depends on the presence and influence of the third, forth components and even impurities, controlling the distribution of major isomorphic components. Examples are Ca in garnet, Zn in staurolite, Al and Ti in biotite, Al and K in pyroxenes, etc. As usual, because of technical, kinetic, and analytical difficulties, experimental studies are performed in simple model systems using the mixtures of starting compounds, or synthetic phases of simplified composition of end-members. That results in the data, which sometimes are far enough from the natural relations.

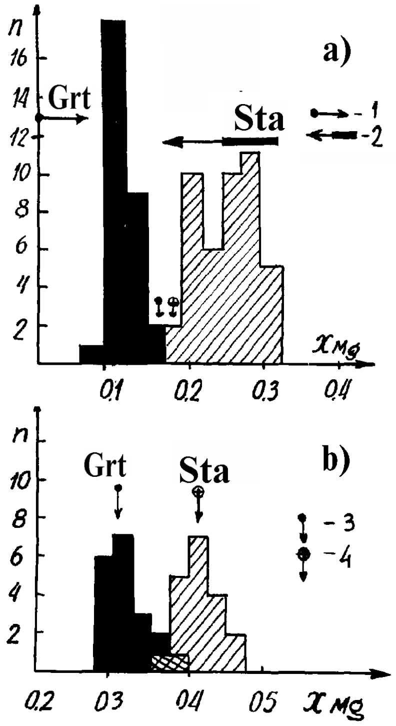

Fig. 1. Histograms of variations of staurolite (Sta) and garnet (Gr) compositions in the experiments on Fe-Mg exchange: (a) – runs on decomposition of natural staurolite with quartz; (b) – runs on simultaneous synthesis of Sta and Gr. 1, 2 – starting compositions of Gr (1) and Sta (2); 3, 4 – compositions (3 – Gr, 4 – Sta) accepted to be equilibrated.

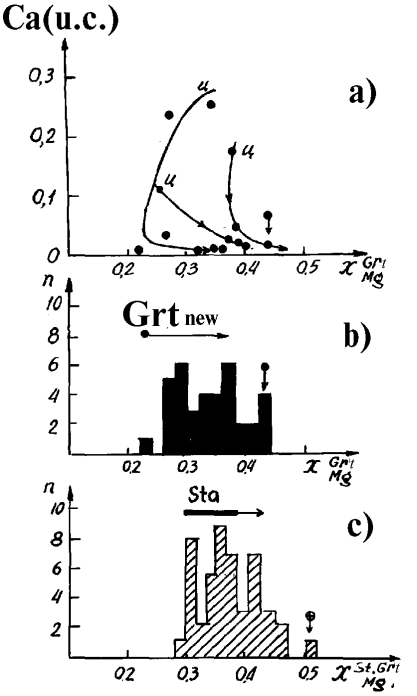

Fig. 2. Changes in Sta and Gr compositions during the experiment: decrease of Ca in Gr (a); histograms of changes in Mg-numbers of Gr (b) and Sta (c).

For example, the study of the Sta-Gr exchange equilibrium as a geothermometer (Fed'kin, Yakovleva, 1993, 1994) showed that during the experiments, Zn in staurolite and Ca and Mn in garnet had different kinetic characteristics of dissolution and composition equilibration. The similar feature concerns Fe and Mg, the major components. Therefore, depending on the experimental procedure, the equilibrium compositions were determined by different ways. In the experiments on the decomposition of staurolite and quartz to Gr+Al_2SiO_5, equilibrium compositions were determined by Gr and Sta compositions maximally shifted from the initial compositions (Fig. 1a). Either in the simultaneous synthesis of Sta and Gr, or in the synthesis of one phase (e.g. Gr) in the presence of another (Sta), the equilibrium was determined by the statistical maximum of composition (Fig. 1b). In the experiments on the exchange with natural grains, the content of minor elements, Ca in Gr and Zn in Sta, was controlled. Figures 2 and 3 show that, during the experiments, these components were dissolved in the solution, and their concentration decreased down to the phonic concentration. The dissolution of Zn from Sta occurred independently on the direction of the approach to the equilibrium, either from the Mg-rich portion or from the Mg-poor portion (Fig. 3a, 4a). As a result, the starting system was simplified to the binary system with respect to the exchanging components and practically did not differ from the model system.

Owing to these circumstances, the experimental data on the Fe-Mg exchange between Gr and Sta differ from the results of the study of natural assemblages. It is reflected in different values of free energy for this equilibrium for experimental and natural systems (Fig. 5). After the combined thermodynamic treatment of both experimental and natural data accounting for the influence and character of behaviour of additional components, an accuracy of the Sta-Gr thermometer became more acceptable in the wide range of compositions (Fig. 6) and in the complete temperature range of stability of the Sta-Gr pair (Fed'kin, Yakovleva, 1994):

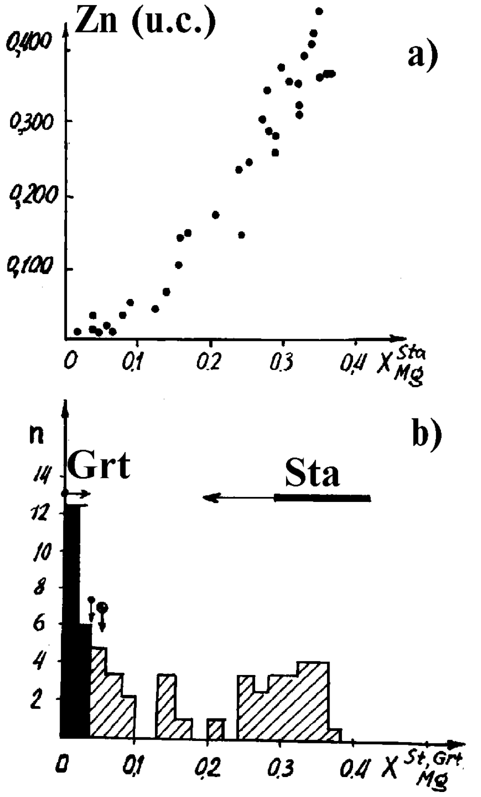

Fig. 3. Changes in Zn content in Sta during the experiment (a) and changes in Mg-numbers of Gr and Sta (b).

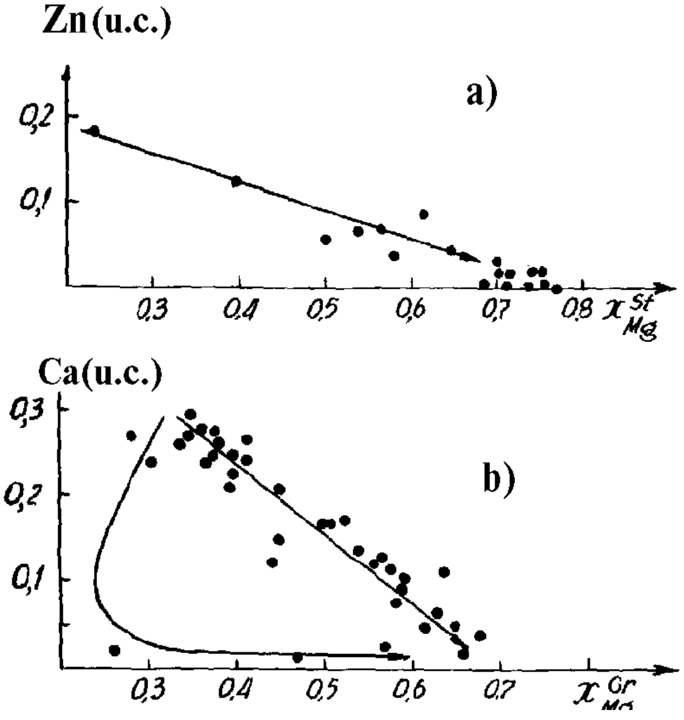

Fig. 4. Issue of Zn in Sta (a) and Ca in Gr (b) in the experiments with high-Mg phases.

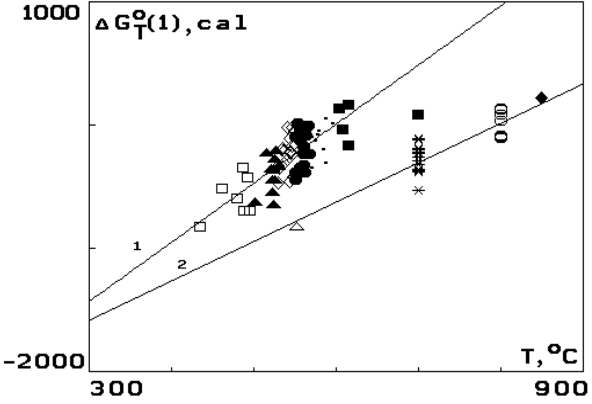

Fig. 5. Free Gibbs energy of the exchange Fe-Mg equilibrium for natural (1) and experimental (2) systems Sta-Gr.

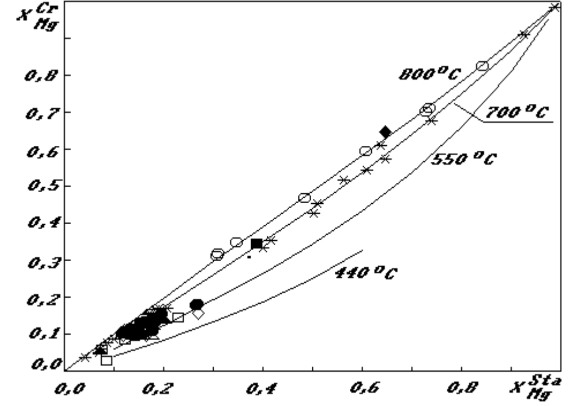

Fig. 6. Relations between Mg-numbers of Sta and Gr within 440-800°C (Sta-Gr geothermometer) according to the natural and experimental data.

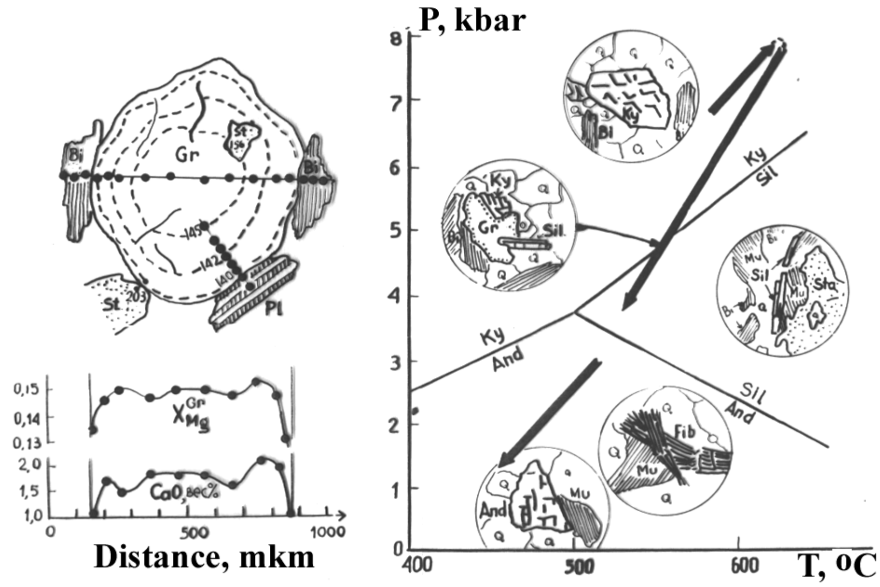

Fig. 7. A scheme of reconstruction of the P-T path by the data of microprobing and geothermobarometry. Left – a profile across garnet and contacting phases, right – P-T path of formation of this paragenesis (Fed'kin, 1982).

$-3851 + 3.639T - 7.8P - (253 - 1.38T)(X_{Fe}^{Sta} - X_{Mg}^{Sta}) - (1741 - 3.702T)X_{Zn}^{Sta} - (5704 - 1.242T)X_{Ca}^{Gr} + 1.987T\ln K_D = 0;$

$K = 0.956;\ \sigma = \pm 116$ cal ($\pm 27^{o}$C)

Similar difficulties appear in the study of natural assemblages, when neglecting additional components can result in significant errors in P-T estimations. It is known, for example, that the Al content in Opx is "chilled" at high parameters, while Fe-Mg exchange continues down to the lowest temperatures during the retrogression (Perchuk, Gerya, 1998). Appreciable difficulties appear in choosing the necessary thermometer or barometer in the study of polymetamorphic complexes, when several mineral assemblages of different metamorphic stages are present in rocks. In this case, an amount of possible pseudo-univariant reactions in the system drastically increases, and determination of P-T parameters by means of a random choosing of several tools without the detailed paragenetic analysis becomes impossible.

The first problem is choosing equilibrium phases. Unfortunately, despite the significant progress, the only and the simplest idea of such choosing is based on an assumption, that the most probable equilibrium portions of grains at the moment of their nucleation are centres, then middle portions, and, finally, rims and contacts. A scheme of such approach is shown in Figure 7. It shows that the garnet composition along the profile reflects a variation of P-T parameters. A distinct petrographic control, the presence of an additional controlling phase (aluminum silicate), similar morphological features of the contacts should unambiguously determine the P-T path. Nevertheless, the P-T data and the slope of P-T paths obtained from different geothermobarometers are different. Possibly, the reason for such deviations is the method of P-T estimations including many uncertainties, questions, and tentative approaches:

- is a crystallization of phases, used for thermobarometry, simultaneous or not?
- were the newly formed phases in the thermodynamic equilibrium with the previous phases?
- was the equilibrium with respect of all necessary components?
- how were the temporal and spatial equilibrium phase relations changing?

Nevertheless, there is no any other method of choosing the equilibrium mineral pairs (Perchuk et al., 1985). In any case, we can suppose, that direct contacts of coexisting phases or inclusions of one phase in another without any reaction relations or decomposition provide the most reliable information on P-T conditions of formation.

The most demonstrative are the results of numerous P-T estimations for intercalating rocks of different composition in one separate complex. The detailed study of the metamorphic Batocina Complex (Balkans) showed that basic rocks (amphibole and biotite-amphibole schists, amphibolites, and garnet amphibolites) showed the prograde tendency of metamorphism on the earliest stage, while Al-rich rocks (staurolite, staurolite-garnet-biotite, two-mica schists) demonstrated the decrease of P-T parameters (Fed'kin et al., 1998). The final conditions of the prograde stage strongly correspond to the beginning of the retrograde stage (Fig. 8).

The following example is the eclogite-glaucophane Atbashi Complex, Southern Tien-Shan. The Atbashi Complex is involved into the system of the intracontinental Ural-Tien-Shan Hercynian fold belt and is attached to the major tectonic boundary between the Northern and Southern Tien-Shan. A metamorphic age of the Atbashi Complex is 320-360 Ma (Dobretsov, 1974), although there are some older data, 1100 and 520-550 Ma. There is a hypothesis that the glaucophane belts are the ancient analogies of "Binioff zones", marking the ancient oceanic crust, or show a boundary of relatively narrow troughs with the oceanic crust (the type of the Red Sea) on a stage of their collapse ("subduction") (Dobretsov, Sobolev, 1977).

In any case, the attachment of the glaucophane-schist complexes to some active crustal structure specifies their metamorphism. The prograde high-pressure trends are relatively steep and coincide with the line of geothermal gradient, ~10°/km. The whole subsequent evolution of the complex reflects a gradual increase of P-T trends on the latest stages of metamorphism.

The Atbashi Complex is composed of diaphthorized eclogites, diverse Gr-Gl, chlorite-carbonate, and zoisite rocks, quartzite-schists, quartzites, and green-schists (Kotova, 1989). Complex petrographic relations of diverse rocks and reaction relations between minerals correspond to the multi-stage evolution of the non-isochemical metamorphism, complicated with the Ca-Mg metasomatism and quarzitization (the stage of acid leaching). Figure 9 shows a sketch (Kotova, 1989) of an exposure, which shows complex transformations of almost unaltered eclogites and pyroxenites to quartzites, quartzite-schists, and diaphthorites.

Complex and diverse petrographic relations of rock-forming minerals, sequence of their crystallization, and reaction replacement (Fig. 10) correspond to rapid metamorphic processes. They also show that mineral equilibria were "chilled" on different stages of mineral formation and not always reached an equilibrium.

In this situation, it is clear, why different mineral parageneses show different P-T parameters. They reflect the stage, on which they evidenced any tectonic or other event, which interrupted the gentle evolution. Nevertheless, admitting, that compositions of contacting coexisting minerals reflect their equilibrium, we attempted to reconstruct all process from these fragments of the metamorphic evolution.

The subsequent transition from eclogites to Gr-Gl rocks, quartzite-schists, and chlorite diaphthorites is shown in the scheme of Figure 11. It is reflected in P-T paths of formation of corresponding mineral assemblages (Fig. 12). The most high-temperature and high-pressure parameters are detected for Gr-Cpx rocks and eclogites, while intermediate parameters are found for Gr-Gl parageneses. The most low-pressure and relatively low-temperature parameters are estimated for Gr-Chl-Mu assemblages and carbonate equilibria (down to 250-300^{o}C and 0.3-1.8 kbar). Such difference in P-T conditions of formation of the contrast parageneses (those, where garnet is present) is characteristic, in some extend, for all studied samples from the Atbashi Complex. The extensive Mg-metasomatism notably changed composition of coexisting minerals, and in the conditions of low temperature during the retrograde stage, the equilibrium was not attained. As a result, most of silicates preserved the evidence of the earlier prograde stage. Nevertheless, in samples with evident petrographic features of equilibrium, a good correspondence of P-T parameters for different mineral assemblages could be observed. The continuity of P-T paths from one assemblage to another can be identified for such samples as well (Fig. 12, Samples. At-052, At-054). That implies a reliable application of mineralogical thermometers. However, it also illustrates a different sensitivity of the mineral assemblages to variation of P-T parameters of metamorphism (Fed'kin, 2000). Just a complex study of prograde tendencies in mineral compositions, displacement of P-T paths for different mineral assemblages, and retrograde paths allows reconstruction of the whole metamorphic evolution of the complex. Generalization and comparison of the data on mineralogical geothermobarometry and petrographic observations can, finally, result in the construction of a general scheme of evolution of the complex and P-T parameters during its metamorphism.

As a result, a "clockwise" P-T path is identified for the Atbashi Complex. Such trend is peculiar for the regions of intracontinental suture zones. The trend in characterized by low (~10 ^{o}/km) geothermal gradient on the initial stage and maximum t = 650-700^{o}C at P = 14-15 kbar for eclogites and Gr-Cpx rocks. The minimal parameters of mineral formation in the Atbashi Complex are estimated for chlorite-carbonate rocks, chlorite-muscovite quartzite-schists, chlorite schists, and quartzites, corresponding to the lower green-schist facies. The retrograde path begins at 550-570^{o}C and 3.5-5.0 kbar and continues down to 350-400OC at 0.5-1.8 kbar (Fig. 13). Garnet-glaucophane assemblages were formed in the wide range of temperatures (from 250-300^{o}C to 500-550^{o}C) and pressures (from 2-4 to 8-10 kbar). This range encompasses almost the whole P-T interval, excluding the highest-pressure Gr-Cpx assemblages. The trends for individual Gr-Gl pairs are, as a rule, prograde, that corresponds to the petrographic features. A reason for it is the strongest Mg-metasomatism, which changed garnet composition at the latest (retrograde) stage of the formation of the complex. Similar feature can explain a prograde tendency for some Gr-Chl pairs, although the general "clockwise" trend of metamorphic transformation has no doubt (Fig. 13).

Thus, a complexity of the experimental study, calibration of mineralogical tools (thermometers, barometers, etc.), difficulties in choosing of natural assemblages, and deciphering of complexity of petrographic relations of coexisting phases in rocks show, that only the detailed approach to the study of metamorphic processes allows estimation of physico-chemical paragenetic assemblages and tracing the evolution of the complex as a whole.

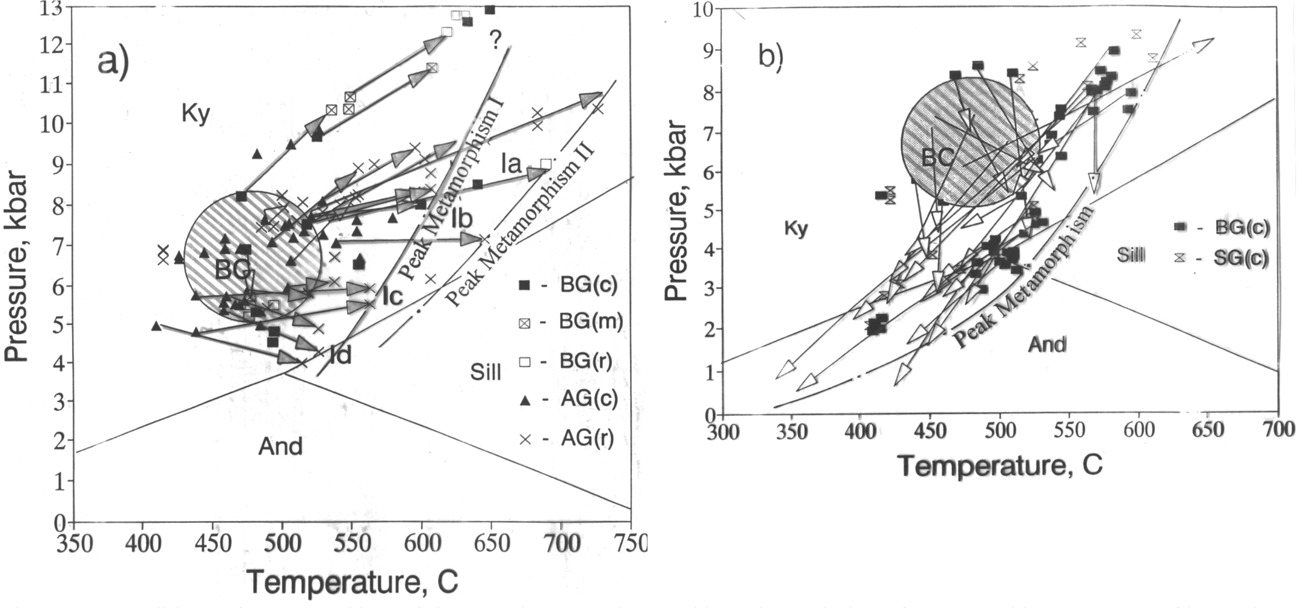

Fig. 8. P-T conditions of metamorphism of the Batocina Complex (Serbia). The evolution of metamorphic parameters of intercalating garnet amphibolites (a) and metapelites (b) according to the mineral geothermonarometry: BG – Bt-Gr, AG – Amph-Gr, SG – Sta-Gr geothermobarometers. Different portions of grains are shown in parentheses: cores (c), middle portions (m), rims (r).

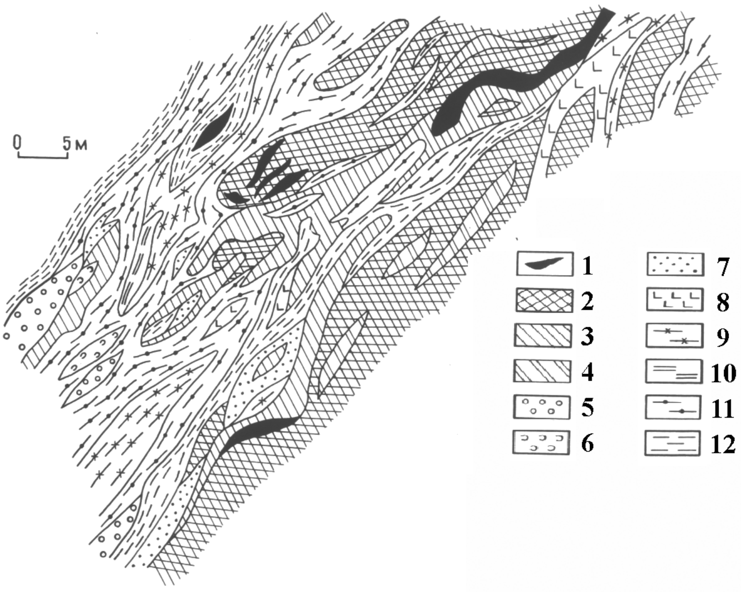

Fig. 9. Relationships of different rocks within the Atbashi eclogite-glaucophane-schist Complex (sketch by L.S. Kotova (1989)). *1 Eclogites 2 Eclogitic schist 3 Gl rocks 4 Zo rocks 5 Garnetites 6 Tc schist 7 Carbonat rocks 8 Chl-Carbonat-Ab rocks 9 Chl-Carbonat-Qzt rocks 10 Px-Gl-Qzt rocks 11 Quartzites and Quartzitic schists 12 Interbanded rocks different composition*

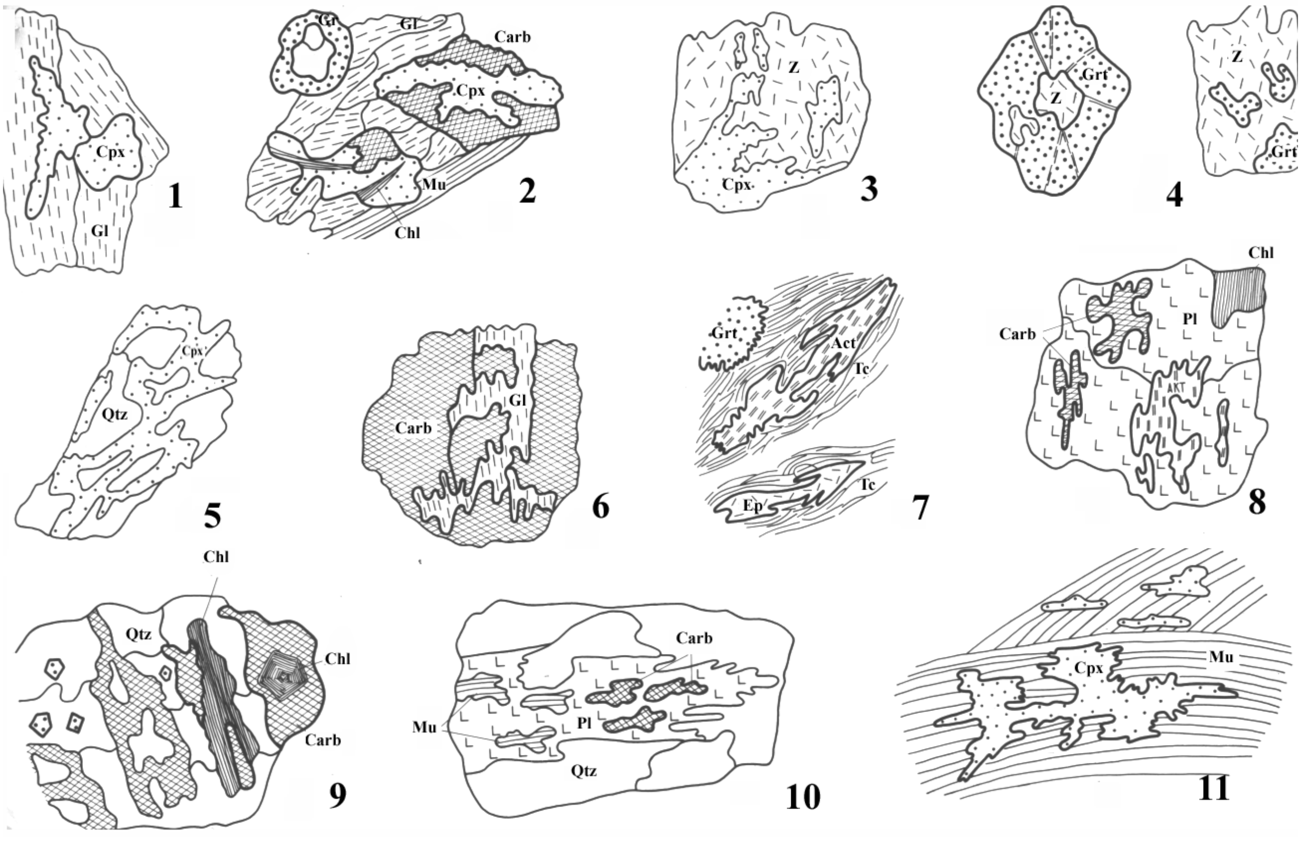

Fig. 10. Complex petrographic relations of rock-forming minerals in the rocks of the Atbashi Complex (Kotova, 1989*)*. 1 – Cpx, replaced by Gl, 2 – Changed relicts of Cpx in aggregate of new Gl gains, 3 – Cpx, replaced by Zo, 4 – Successive stages of Gr replacement by Zo, 5 – Cpx, replaced by Qtz, 6 – Carbonatization of Gl, 7 – Act, Ep, Gr, replaced by Tc, 8 – Act and Carb, replaced by Ab, 9 – Silicification of Chl-Carb rocks, 10 – Ab rock fragments in quartzitic schist, 11 – Cpx, replaced by Mu.

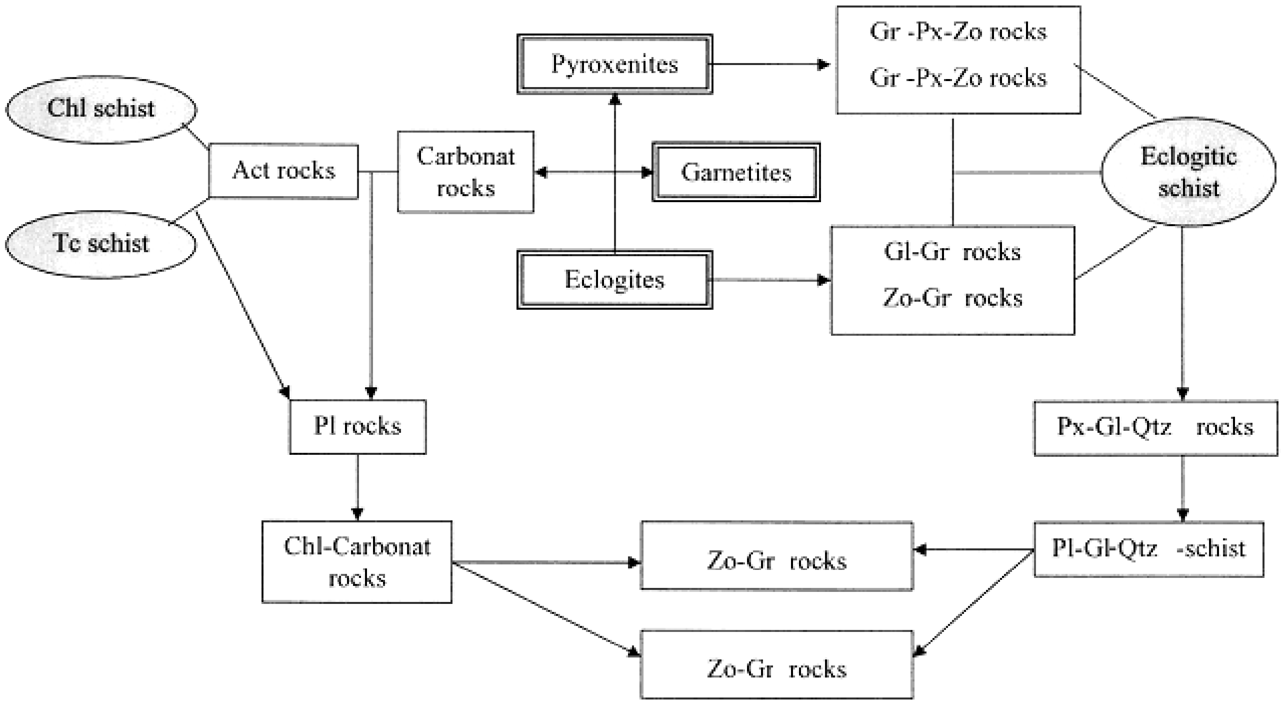

Fig. 11. The scheme of gradual transformation of the rocks of the Albashi Complex (Kotova, 1989).

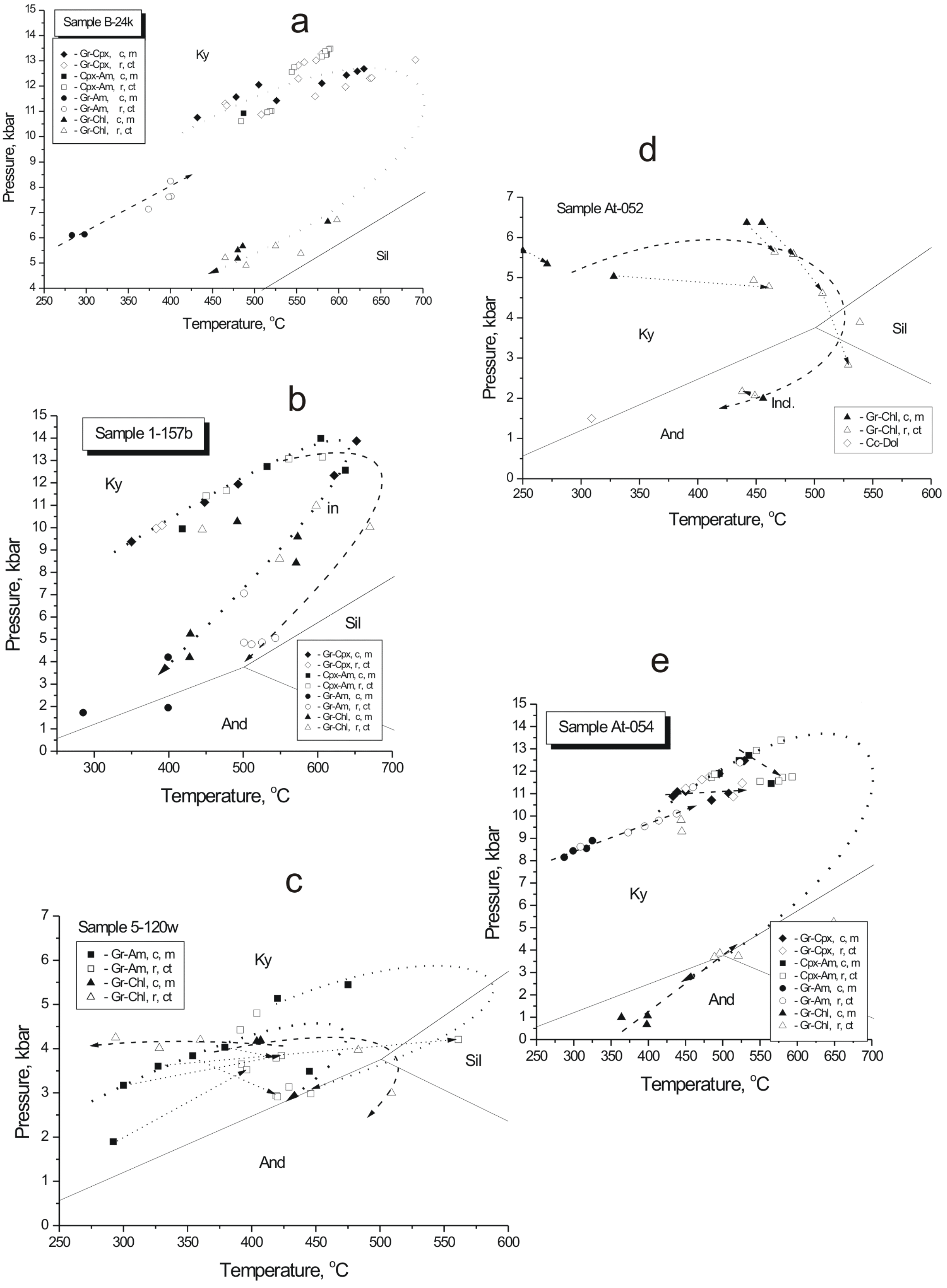

Fig. 12. P-T conditions of formation of diverse mineral assemblages of the Albashi Complex according to the mineral geothermobarometry: (a) – Gr-Cpx-Gl rock (Sample B-24k) with different P-T parameters of formation of Gr-Cpx, Gr-Gl, and Gr-Chl assemblages; (b, c) – displacement of the P-T path toward lower pressure following to the rims (Samples 1-157b, 5-120w); (d, e) – inheritance of the direction of P-T paths for different assemblages and the tendency to their clock-wise rotation. c – core, m – middle, r – rims, ct – contacts.

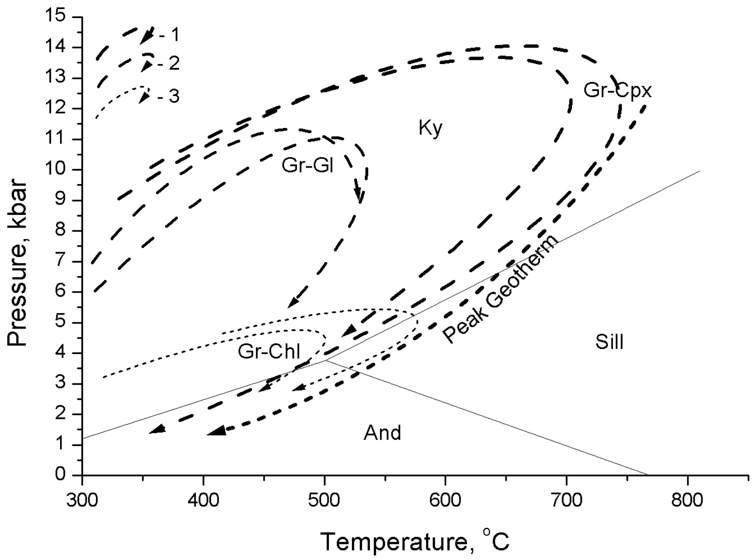

Fig. 13. The P-T evolution of the Atbashi Complex (Southern Tien-Shan) according to the mineral geothermobarometry (generalized data) for eclogites and Gr-Cpx crystalline schists (1), Gr-Gl assemblages (2), and Gr-Chl diaphtorites (3).

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