

A REAPPRAISAL OF THE P – T EVOLUTION OF HIGH-PRESSURE TECTONIC BLOCKS FROM THE LEAOTA MASSIF, SOUTH CARPATHIANS

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Abstract. The P - T metamorphic evolution of several high-pressure blocks (eclogites, metagabbro-norites, Mg-rich chloritoid-bearing micaschists) from the Bughea Complex (Leaota Massif) were re-evaluated based on calculated pseudosections in the NCFMMnASTH and KNCFMMnASTH system, and the multi-equilibria intersection method. Extensive to moderate inconsistency between the two sets of PT -data resulted, and moderate differences between measured and calculated mineral isopleths have been recorded. However, the data are convergent as they correctly predict critical assemblages and indicate a geothermal gradient ranging between 7–11°C/km, in agreement with the thermal structure of subduction zones.

Key words: Leaota Massif, Bughea Complex, eclogites, PT conditions, multi-equilibria intersections, pseudosections, isopleths, subduction mélange, geotherms.

Résumé. L'évolution thermobarique metamorphique des plusieurs blocs de haute pression (éclogites, metagabbro-norites, micaschistes à chloritoïde magnésien) du Complexe de Bughea (Massif de Leaota) a été réévalué en partant des pseudosections calculées dans les systèmes chimiques NCFMMnASTH et KNCFMMnASTH, aussi bien que par la méthode des intersections multi-équilibre. Les résultats ont entraîné une incompatibilité étendue à modérée entre les deux ensembles de données PT , pendant que les différences enregistrées entre isoplètes minérales mesurées et calculées ont été modérées. Cependant, les données sont convergentes en prédisant correctement les associations critiques et en indiquant un gradient géothermique compris entre 7–11°C/km, en accord avec la structure thermique des zones de subduction.

Mots-clés: Massif de Leaota, Complexe de Bughea, éclogites, conditions thermobariques, intersections multi-équilibre, pseudosections, isoplèthes, mélange de subduction, géothermes.

INTRODUCTION

The Leaota Massif, building the metamorphic basement units of the Leaota and Iezer-Păpușa Mountains, is one of the most extensively studied basement unit of the South Carpathians. The rock units and geological structure were detailed and accurately described by Gherasi & Dimitrescu (1964), Gheuca & Dinică (1984, 1986, 1996), but the metamorphic and tectonostructural history was a topic of debate. Interpretations variably supported by facts ranged from differential retrogression of a coherent sequence (Gheuca & Dinică, 1986) to tectonic stacking of several units (*e.g.* Medaris *et al.*, 2003). Recent studies (*e.g.* Negulescu *et al.*, 2009; Negulescu, 2013) documented that the metamorphic basement of the Leaota Massif (named in the following Leaota Metamorphic Suite, LMS) comprises several complexes displaying internal lithologic and metamorphic contrasts.

The Bughea Complex (BC) of the LMS is one of the most extensively studied complexes by reason of its diverse lithologic assemblages and PT conditions recorded, representing a critical segment for understanding the formation and evolution of the LMS. The estimation of the PT -conditions was mostly focused on the part of the pile containing and neighbouring the BC (*e.g.* Săbău, 2000; Medaris *et al.*, 2003; Negulescu *et al.*, 2007).

The BC was well documented as a mélange of semipelitic (micaceous gneisses, amphibole-garnet schists and chloritoid-bearing micaschists) and basic (amphibolites) rocks, containing high-pressure (HP) lenses of metagabbro-norites and different eclogite types (*e.g.* Săbău, 2000; Negulescu *et al.*, 2009).

The eclogites from the BC, first mentioned by Gherasi (1956, 1961), Gherasi *et al.* (1971), are by far the most investigated lithologies and a topic tackled with by several papers providing a large array of often conflicting data and interpretations. For example, the Bughița Albeștilor outcrop was analysed by Iancu *et al.* (1995), Mărunțiu *et al.* (1997), Săbău (2000), Medaris *et al.* (2003) reporting PT-conditions ranging from slightly above 600°C up to 860°C, grouped along an interpreted PT-path or spread over a large PT-field. The Bughea Complex on the whole was construed as a HP blastomylonitic shear zone by Iancu *et al.* (1995), a subduction-accretion complex containing eclogite knockers (Săbău, 2000) or a post-eclogitic tectonic melange containing HP boudins (Medaris *et al.*, 2003). The results presented by Negulescu *et al.* (2007) place the metamorphic peak temperatures between 600°–650°C for most of the eclogite bodies.

The available geochemical data together with mineralogical features and calculated PT conditions (Negulescu *et al.* 2009, 2013; Negulescu *et al.* 2014) are discriminating for several HP-rock types:

– continental pelitic fragments: (1) very-high pressure (VHP) eclogites (Săbău, 2000), characterized by unusual mineral compositions (jadeite-rich clinopyroxene, Al-rich glaucophane) and very-high pressure conditions, and (2) Mg-rich chloritoid-bearing micaschists (Negulescu *et al.*, 2014) characterized by Mg-rich chloritoid (up to 0.42 X_{Mg}) preserved in garnet porphyroblasts;

– normal eclogites (Săbău, 2000) or common eclogites consisting of simple – to complex mineral assemblages, representing N-MORB – derived eclogites;

– Cr-bearing eclogites (Costin & Luffi, 2001) containing of Cr-rich silicates (Mg-staurolite, kyanite, clinopyroxene and mica) aside usual eclogitic phases, and probably representing MARID-type nodules carried by arc picritic magmas, which were subducted together with the host MORB-type crust (Negulescu & Săbău, 2013);

– (meta)gabbro-norites (first reported by Gheuca, unpublished data) characterized by a whole-rock compositions indicating SSZ-type EMORB with a distinctive LILE enrichment and HFSE depletion (Negulescu *et al.*, 2007).

In this article we re-evaluate the metamorphic evolution of several HP-blocks using the calculated pseudosections in the KNCFMnASTH system and multi-equilibria intersection methods in order to: (1) compare the mineral parageneses predicted *versus* the assemblages identified and their textural relationships, (2) verify the consistency of calculated and measured chemical compositions of minerals, and (3) better understand the mineral assemblages stability fields in the P-T-X space. Four representative common eclogite samples (phengite-free – kyanite-bearing eclogite, phengite-bearing eclogite, phengite-rich atoll-garnet-bearing eclogite, and talc-bearing eclogite) were selected and investigated. The metamorphic P-T conditions of other HP-blocks from literature (Săbău, 2000; Negulescu *et al.*, 2007; Negulescu, 2013; Negulescu *et al.*, 2014) were updated and presented together in the following.

METHODS

THE MULTI-EQUILIBRIA METHOD

One of the methods adopted for thermodynamic processing of mineral composition data in order to derive P-T and activity values is that of multi-equilibria calculations according to Brown *et al.* (1988) and Berman (1991). The method allows the calculation of mineral equilibria and graphical display of the results, making use of an internally consistent dataset with the thermodynamic properties of the pure end-members, a Schreinemaker's analysis of the chemical system for identifying possible reactions among phases, and the possibility of complex formulation of excess mixing parameters for the calculated solid solutions. However, the Ge0-Calc program of Brown *et al.* (1988) itself or its successor PTAX were not used because of some limitations, namely failure to generate all equilibria in systems with the number of phases exceeding the number of effective components by 4,

and errors in activity-composition formulations for equilibria which involve more than two non-ideal solid solutions. Instead we used the PTGIBBS routine of Brandelik & Massonne (2004), which behaves correctly in treatment of the complex solutions, but has so far no module to generate the mineral reactions to be calculated. However, it contains a module with a built in listing of mineral reactions that can be augmented by the user. For augmenting the built-in list of reactions when needed, we used Excel macro modules which generate all stoichiometric reactions in chemical systems, so far for a number of phases up to the number of components plus 5, as the practical needs, however, do not go much beyond investigating a system with $N_{\text{ph}} = N_{\text{c}} + 5$.

The thermodynamic properties of pure phases used for calculations were those of Berman (1991) augmented according to Brandelik & Massonne (2004) and references therein. Activity-composition model adopted were: for garnet a two-site ionic mixing model where ideal mixing is considered to occur in octahedral and non-ideal mixing in eight-fold coordinated sites, slightly modified by Massonne (1992) after Berman (1990), for clinopyroxene and white mica the molecular non-ideal models of Massonne (1992), and for Ti-bearing white mica the molecular model of Massonne *et al.* (1993). For other phases ionic ideal mixing on sites was considered for 1 or 2 non-equivalent crystallographic sites.

PT-conditions are defined by the position of the invariant point involving the phases of interest in the investigated systems. The position of an invariant point can be determined in an internally consistent dataset using only two of the intersecting univariant equilibria, irrespective of their mutual orientation. However, consistent datasets derived by linear programming (as is the case of the dataset of Berman, 1998) allow no error estimates on the accuracy of the resulting point. An estimate of the error can be obtained only if the number of phases present allows several invariant points, which must superpose if the mixing models are realistic and the phases at equilibrium. The spread of several equivalent invariant points thus obtained is an inverse measure of the confidence that can be conferred to the results.

Calculations were performed on mineral compositions of the identifiable stages in the rock evolution according the following general scheme: derivation of PT-conditions using water-absent equilibria, when possible also with accuracy estimates, followed by iterative calculation of water activity by employing dehydration reactions anchored on the result of the previous determinations. If the first option was inoperative, systems were chosen with at least two theoretical invariant points involving water, allowing iterative estimation of the $PT_{\text{H}_2\text{O}}$ variables in order to find a graphic solution. Only if the previous two situations led to misfits or in case of insufficient compositional data, invariant systems or mere curve intersections were used. The extent at which the procedure could be applied depended in particular cases on the options allowed by the assemblages; in case of results affected by unknown errors, they were inspected for consistency with more precise determinations or evaluated using independent criteria.

Mineral compositions were analysed using a Cameca SX100 WDS electron microprobe with 5 spectrometers at the Institut für Mineralogie und Kristallchemie, Stuttgart. Operating conditions were: 15 kV accelerating voltage, 15 nA beam current, focussed beam for anhydrous minerals, and 10 nA, beam spot of 6 μm for hydrous or volatile-bearing minerals. Compositional maps were obtained using the same EMP. Measurement conditions were 15kV and 30nA; $K\alpha$ radiations of Fe, Mn, Ca and Mg were simultaneously detected. EPM analyses were recalculated as structural formulae and ideal end-member concentrations.

THE PT-PSEUDOSECTION METHOD

Four common eclogite samples were modelled in the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MnO}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2-\text{H}_2\text{O}$ system. P_2O_5 was neglected in the input data for simplification purposes, also considering that this component occurs only in apatite which is not involved in the calculations. PT-pseudosections were computed for the whole-rock compositions using the PERPLE_X computer package (Connolly, 1990), Perplex 6.6.8 version available at http://www.perplex.ethz.ch/perplex/ibm_and_mac_archives/WINDOWS/, using an updated internally consistent thermodynamic data set

of Holland & Powell (1998). The solid-solution models used are those identified by the following abbreviations in the 'solution_model.dat' file of the above-mentioned package, modified from Holland & Powell (1998) according to the references therein: Chl(HP) for chlorite, Gt(HP) for garnet, Pheng(HP) for phengite, Omph(HP) for omphacite, Amph(DPW) for amphiboles, T for talc, the pure phases lawsonite, rutile, kyanite, zoisite and the compensated Redlich-Kwong fluid equation of state from Holland & Powell (1998). Plagioclase end members (albite only stable under the investigated conditions) and paragonite were considered as ideal terms for simplification reasons. Quartz and water were considered as excess phases.

Mineral isopleths were computed using the Verami routine included in the Perplex package combined with Matlab functions for plotting line graphs.

Bulk rock chemical analyses were performed by RFA (major and trace elements) and ICPAES (trace elements) performed at the Institut für Mineralogie und Kristallchemie, Stuttgart.

SAMPLE DESCRIPTION

VALEA LUI DĂNIȘ COMMON ECLOGITES (SAMPLE 1059)

The common eclogites from the Valea lui Dăniș were first mentioned by Gherasi (1961). Gherasi *et al.* (1971) described an eclogite lens close to the Albești Granite, characterized by an inner fresh zone made up by $Jd_{30}(EnDi)_{43}Hd_{17}Ts_7Acm_3$ clinopyroxene + $Prp_{32}Alm_{36}Grs_{23}And_8Sps_1$ garnet + titanite + rutile and an outer retrogressed rim rich in amphiboles and diablastic structures. The data were updated by Săbău *et al.* (1986), Iancu *et al.* (*e.g.* 1994; 1995), and Medaris *et al.* (2003).

Based on mineral assemblages of the Valea lui Dăniș common eclogites of two types can be distinguished: zoisite-phengite-bearing eclogites (Medaris *et al.*, 2003; Negulescu *et al.*, 2007) and kyanite-bearing eclogites (Negulescu *et al.*, 2007).

The *zoisite-phengite-bearing eclogites* from the Valea lui Dăniș are composed by garnet, clinopyroxene, phengite, amphibole, quartz, rutile, and minor zoisite and apatite.

Garnet occurs as millimeters-sized crystals rich in clusters of small rutile inclusions, outlining the contour of former magmatic clinopyroxene; they are also rich in clinopyroxene, amphibole, zoisite, and quartz inclusions; anhedral poikiloblastic crystals inside clinopyroxene + phengite + quartz aggregates.

Garnet crystals display a slight chemical zoning. However, several compositional zones correlated with the distribution of mineral inclusions can be defined: (1) garnet cores, characterized by the highest Mn and Ca identified in zones rich in epidote and quartz inclusions. The core compositions are $Prp_{27-25.19}Alm_{37.08-37.35}Grs_{22.66-23.05}Sps_{0.92-0.77}$ mol%, $X_{Mg}=0.29-0.30$; (2) intermediate zones with clinopyroxene inclusions and $Prp_{27.32-28.89}Alm_{38.48-42.51}Grs_{18.11-20.98}Sps_{0.58-0.83}$ mol% compositions, $X_{Mg}=0.30-0.31$; (3) overgrown rims characterized by the highest Mg and lowest Mn, of $Prp_{28.73-28.92}Alm_{39.85-38.38}Grs_{20.06-19.77}Sps_{0.62-0.69}$ mol% compositions, $X_{Mg}=0.31-0.33$; (4) retrograde fringes with compositions close to the intermediate zones.

Clinopyroxenes of omphacite composition are abundant in the rock matrix or included in garnet, zoisite and phengite. Quartz and phengite inclusions in clinopyroxene are common. The chemical compositions fluctuate from the highest jadeite components (39.46 – 45.34 mol%) of the omphacite in the matrix, and included in phengite and zoisite to 31.38–33.68 mol% jadeite component of the omphacite included in garnets.

White mica is phengite with 3.26–3.39 Si p.f.u. and is abundant in the matrix.

Amphiboles are calcic – to sodic-calcic amphiboles and grew in three textural sites: (1) pargasites, magnesiotalcites și aluminomagnesiotalcites included in garnet; (2) large crystals of aluminobarroisite și pargasite in the rock matrix, in equilibrium with the eclogitic paragenesis; and (3) secondary pargasite at garnet rims.

Clinzoisite occurs (1) in the rock matrix ($a_{zo}=0.85-0.68$), rich in clinopyroxene, quartz and rutile inclusions, interpreted as a secondary phase, and (2) zoisite inclusions in garnet cores ($a_{zo}=0.79$).

VALEA LUI RUS COMMON ECLOGITES (SAMPLE 1057)

The common eclogites from the Valea lui Rus are very low-potassium rocks ($K_2O = 0.04$ wt%) made-up by garnet, clinopyroxene, kyanite, quartz, rutile, and minor amphibole, zoisite, paragonite and apatite. Rare phengite inclusions were identified only in a garnet porphyroblast.

Garnet porphyroblasts are rich in quartz, rutile, amphibole, clinopyroxene, kyanite, and minor epidote and apatite. The outline of fine rutile inclusions suggest idiomorphic shapes of former Ti-rich clinopyroxene replaced by garnet and omphacite (Fig. 1A – mineral abbreviations are after Kretz, 1983), readily apparent in the compositional map of Ti (Fig. 1B). Abundant quartz inclusions also outline regular contours, probably of former idiomorphic plagioclase crystals. Other zones are rich in kyanite (\pm epidote) needles. Large amphiboles and clinopyroxenes inclusions are usually disposed towards the rims of garnet crystals.

The interpretation of garnet zoning is difficult due to the large number of mineral inclusions. However, four compositional zones were identified by following the Mn time-line (Săbău *et al.*, 2006), also related with the nature, size and abundance of inclusions: (1) the oldest garnet cores characterized by the highest Mn and $Prp_{25.47-31.6}Alm_{47.23-40.76}Grs_{19.13-19.16}Sps_{1.94-1.16}$ mol% composition, $X_{Mg}=0.27-0.34$ were identified in the kyanite (\pm epidote) needles and abundant quartz inclusions zones; (2) envelope of the cores, delineated by clinopyroxene inclusions, displaying a Mn-, Fe-decreasing and Mg-increasing trend; (3) rims characterized by low Mn, Fe and Ca and the high Mg, of $Prp_{32.26-35.89}Alm_{41.01-39.01}Grs_{18.9-17.46.5}Sps_{0.79-0.56}$ mol% compositions, $X_{Mg}=0.34-0.38$; (4) high-Mn retrograde fringes at crystal rims.

Clinopyroxenes of omphacite composition occur in the rock matrix or as inclusions in garnet porphyroblasts, as also occasionally in kyanite. The omphacites in the matrix are richer in jadeite component (jd_{39-42} mol%) than those included in garnet (jd_{33-37} mol%).

Kyanite is common in the rock matrix and as inclusions in garnet and omphacites. Omphacite inclusions were rarely identified in large kyanite crystals.

Amphiboles occur as inclusions in garnet or as secondary phase near garnet rims. The amphiboles included in garnet are Cl-richer (up to 0.2425 p.f.u.), Mg-poorer amphiboles of barroisite and pargasite compositions comparing with the secondary ones, which are mostly alumino-magneziotaramites.

Clinzoisite was occasionally found in the rock matrix ($a_{zo}=0.56-0.58$); minor epidote ($a_{zo}=0.39$) inclusions associated with kyanite in garnet porphyroblasts may be regarded as relics of a pre-eclogitic stage.

White mica is represented by secondary paragonite associated with secondary amphiboles at the garnet rims or along minor cracks in garnet.

VALEA POPII COMMON ECLOGITES (SAMPLE 989B)

The Valea Popii common eclogites are very-fresh massive eclogites made-up by garnet + omphacite, and minor amphiboles, phengites, rutile, quartz.

Garnets are: (1) idiomorphic crystals rich in mineral inclusions, and (2) atoll-shaped garnets of open or closed rings enclosing phengite + quartz \pm amphiboles (Fig. 2). Garnet porphyroblasts display a wide compositional range, from $Prp_{7.78-15.49}Alm_{53.03-48.08}Grs_{34.12-32.27}Sps_{0.8-1.03}$ mol%, $X_{Mg}=0.08-0.16$ core compositions to $Prp_{27.53-28.21}Alm_{45.6-43.97}Grs_{23.61-22.70}Sps_{0.06-0.05}$ mol%, $X_{Mg}=0.28-0.30$ of intermediate zones, and $Prp_{23.35-27.50}Alm_{48.70-53.41}Grs_{21.82-15.02}Sps_{0.94-1.13}$ mol%, $X_{Mg}=0.25-0.28$ of outer rims. The

garnet cores are characterized by the lowest Mg, highest Mn compositions, being often corroded as atoll shapes appear by crystallization of large amphiboles and quartz. The atoll-shaped garnet composition is nearly homogenous, about $\text{Prp}_{21}\text{Alm}_{48.6}\text{Grs}_{25}\text{Sps}_{1.14}$ mol%, $X_{\text{Mg}}=0.28\text{--}30$, close to the outer rim crystal compositions.

Clinopyroxenes are widely distributed in the matrix (Fig. 2A), and very rich in fine rutile inclusions. They are homogenous omphacites of 36.69 – 38.07 mol% jadeite component. Omphacites were only occasionally found as inclusions in garnet porphyroblasts.

White mica of phengite compositions (3.33–3.54 Si p.f.u.) is present in the matrix and inside the atoll-shaped garnets.

Amphibole compositions are close to (1) barroisite, included in atoll-shaped garnets; (2) taramite, aluminotaramite and ferropargasite, included in garnet porphyroblasts. Insignificant amount of amphiboles were noticed in the matrix.

VALEA CĂLUGĂRULUI COMMON ECLOGITES (SAMPLE X9A)

The common eclogites from the Valea Călugărului – Podu Runcu were first mentioned by Chirică (1982) and analysed in detail by Săbău *et al.* (1986) and Săbău (2000). They represent one of the rare talc-bearing eclogites from the BC, characterized by large poikiloblastic amphiboles of tremolite composition and clinopyroxenes; small idiomorphic garnet crystals are included both in amphiboles and clinopyroxenes (Fig. 3). The peak metamorphic mineral assemblage is garnet – omphacite – phengite – talc – zoisite – amphibole – rutile – quartz.

Garnet porphyroblasts are strongly zoned and include taramite amphiboles. Compositions of garnet vary significantly between 7–32 mol% pyrope component; the highest pyrope concentrations occurring at garnet rims.

Jadeite component in *clinopyroxenes* ranges between 36–44 mol%.

White mica (talc, phengite) together with zoisite occur as inclusions in amphiboles and in the rock matrix. The highest content of Si in phengite is 3.32 p.f.u.

RESULTS

VALEA LUI DĂNIȘ COMMON ECLOGITES (SAMPLE 1059)

The equilibrium garnet (of overgrown rim composition) – omphacite (matrix) – phengite (matrix) – quartz mineral assemblage was investigated in CaSiO_3 , MgSiO_3 , FeSiO_3 , Al_2O_3 , $\text{KSi}_3\text{O}_7 \cdot 5\text{H}_2\text{O}$ five components system using the multi-equilibria intersection method. The mineral compositions are indicated in Fig. 4. The nine calculated equilibria intersect within $\pm 25^\circ\text{C}$ and ± 1.5 kbar limits, indicating 21 kbar and 670°C metamorphic peak conditions (Fig. 4). The estimated temperature is close to 686°C value reported by Medaris *et al.* (2003), but poorly consistent with the estimated pressure (15.5 kbar).

The calculated pseudosection in the Na_2O – K_2O – CaO – MnO – FeO – MgO – Al_2O_3 – SiO_2 – TiO_2 – H_2O system predicts the equilibrium conditions of the garnet – omphacite – phengite – amphibole – rutile – quartz metamorphic peak assemblage at $T > 575^\circ\text{C}$ and $P > 12$ kbar (Fig. 5). The X_{Mg} isopleths of garnet, jadeite isopleths of clinopyroxenes, and Si isopleths of phengite constrain 670°C and 18 kbar PT-conditions. Zoisite in equilibrium with garnet-clinopyroxene-phengite-rutile-quartz mineral assemblage occurs in a narrow field (labeled 5 in Fig. 5) probably representing pre-peak metamorphic conditions recorded by garnet core – epidote inclusion zones.

VALEA LUI RUS COMMON ECLOGITES (SAMPLE 1057)

The equilibrium garnet (of rim composition) – omphacite (inclusion in garnet rim) – kyanite – quartz mineral assemblage was investigated in the CFMAS system using multi-equilibria intersection method; mineral compositions are given in Fig. 6. The eight calculated equilibria define a poor intersection around 670–680°C and 19–21 kbar (Fig. 6). The primary source of these errors is probably the inaccuracy of Si measurements, as we noticed a systematic underestimation and applied a correction of factor of 1.015 to garnets in order to compensate the results. Another possible error source could be the inappropriate garnet-pyroxene pair selected for inputs, as large pyroxene grains are included in zoned garnets. The temperature appears to be overestimated, but a tighter constraint is not possible because of the simple mineralogy of this eclogite. Yet, comparable temperatures resulted also for the previous sample 1059.

The calculated pseudosection in the Na₂O–CaO–MnO–FeO–MgO–Al₂O₃–SiO₂–TiO₂–H₂O system predicts the equilibrium conditions of the garnet – omphacite – rutile – quartz metamorphic peak assemblage at *T*>590°C and *P*>18.4 kbar (Fig. 7). The amphiboles in equilibrium with garnet, omphacite and kyanite constrain a range of 19–22kbar, 590–630°C for the equilibrium of the investigated metamorphic peak assemblage. Considering the possibility of an overestimated temperature output of multi-equilibria intersection method, the *P*–*T* conditions predicted by the calculated pseudosection seem to better documented. However, significant differences between measured and calculated mineral compositions can be noticed.

VALEA POPII COMMON ECLOGITES (SAMPLE 989B)

The equilibrium garnet (atoll composition) – omphacite (matrix) – phengite (from atoll-shaped garnet core) – quartz mineral assemblage was investigated in CaSiO₃, MgSiO₃, FeSiO₃, Al₂O₃, KSi₃O_{7.5}H₂ five components system; mineral compositions are given in Fig. 8. The nine calculated equilibria intersect in a single point placed at 550°C and 23.5 kbar. However, phengites directly corroding garnet might be in equilibrium rather with a K, Si-rich fluid than with the solid phases in the rock, and truly equilibrium compositions are approached in the corrosion-recrystallization domains near the margin of pre-existing garnet and pyroxene.

The calculated pseudosection in the Na₂O–K₂O–CaO–MnO–FeO–MgO–Al₂O₃–SiO₂–TiO₂–H₂O system predicts the equilibrium conditions of garnet – omphacite – phengite – amphibole – rutile – quartz metamorphic peak assemblage at *T*>600°C and *P*>12 kbar (Fig. 9). The X_{Mg} isopleths of garnet, jadeite isopleths of clinopyroxenes, and Si isopleths of phengite constrain a range of 670–690°C and 16–17 kbar. The large differences between the two *PT*-data set are probably due to the uncertainties induced by effective-bulk composition, together with uncertainties in selection of equilibrium mineral pairs in the first case.

VALEA CĂLUGĂRULUI ECLOGITES (SAMPLE X9A)

The *PT* conditions of the talc-bearing eclogites (X9A) from the Valea Călugărului were estimated using the Berman (1991) routine by Săbău (2000). Garnet cores and amphibole inclusions coexisting with rutile, titanite and zoisite in the system NCMASHTH gave well-defined equilibrium conditions at around 520°C, 15 kbar at very low water activities of 0.22, and garnet rims and coexisting pyroxene, zoisite and talc indicated a very steep prograde path going above 22.5 kbar, under increasing water activity and peak temperatures of 630°C (Fig. 10). A similar case is well documented by the calculated *P*–*T* metamorphic conditions for metagabbroites (Negulescu *et al.*, 2007), illustrating a constant increase of water activity during prograde eclogitization of gabbroites, from 0.26 at 15 kbar and 540°C, to 0.92 at 22.8 kbar and 625°C (Fig. 10).

The calculated pseudosection in the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MnO}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2-\text{H}_2\text{O}$ system predicts the equilibrium conditions of garnet – omphacite – phengite – talc – zoisite – amphibole – rutile – quartz metamorphic peak assemblage ranging between 590–665°C and 17–18.5 Kbar (Fig. 11). The highest $\text{Si} = 3.32$ isopleth recorded in phengites from the peak metamorphic assemblage together with the jadeite isopleths of clinopyroxenes and X_{Mg} isopleths of garnets constrain a point placed 600°C and 18.3 kbar, close to the PT-path calculated by Săbău (2000).

CONCLUSIONS

The attempt to derive coherent PT-arrays for the same sample met with limited success, as it is to be expected for kinetic reasons, namely compositional shifts of the earlier assemblages along the prograde path; also for kinetic reasons peak conditions are more likely to be preserved along the retrograde path rather than retrograde equilibrium assemblages.

For PT-values determination first water-absent and water independent equilibria were applied in order to check the consistency of the multiple equilibria; in case of favourable assemblages water-dependent equilibria were anchored on the previous invariant points and iteratively set for best fit by varying the input water activity.

Samples displaying low chemical variability, especially limited zoning of garnet made impossible to establish a PT-trend, while samples with higher variability made possible to retrieve a wider span of PT conditions.

The general PT-trend in individual samples, in connection with the chemical shift from older to younger zones supports Ca and Mg enrichment of garnet during the prograde path, followed by further increase in Mg and decrease in Ca as amphibole is consumed and replaced by pyroxene with higher Ca/Mg ratio. PT-estimates indicate a very sharp pressure increase from garnet core to rim, also obtained by Săbău (2000) for the talc-bearing eclogite sample X9A containing sharply zoned garnet. It is, however, possible that between the inner zones of garnet and the inclusions contained within, diffusional exchange may have taken place along the prograde path, resulting in temperature overestimates for the early stages. However, such compositional readjustments around inclusions were not found on the compositional maps.

The inconsistency between the PT-data attained on the base of multi-equilibria intersections and calculated pseudosections, and the differences recorded between measured and calculated mineral isopleths are generally connected with a) the accuracy of considering the effective bulk composition; b) the consistency of thermodynamic data; c) the solid solution models employed; d) the simplification operated, as all iron is considered as bivalent in the pseudosection method.

Though the consistency between the values obtained by using two different methods (pseudosections and mineral-equilibria intersections) is not always fair, the data are consistent in predicting critical mineral assemblages such as the garnet-kyanite-chloritoid association at high pressures and moderate temperatures in pelitic rocks, as well as the presence of talc at higher pressures in magnesian eclogites, both actually identified in the studied rocks. The calculated PT-conditions are consistent, indicating a geothermal gradient ranging between 7–11°C/km (fig. 10), comparable to geotherms of subduction zones and in concordance with other literature data like the Alpine-type HP to UHP-LT metamorphic rocks from peri-Pacific and peri-Mediterranean fold belts of Paleozoic to Tertiary ages which are characterized by geothermal gradients of 4–10°/km (*e.g.* Maruyama *et al.*, 1996).

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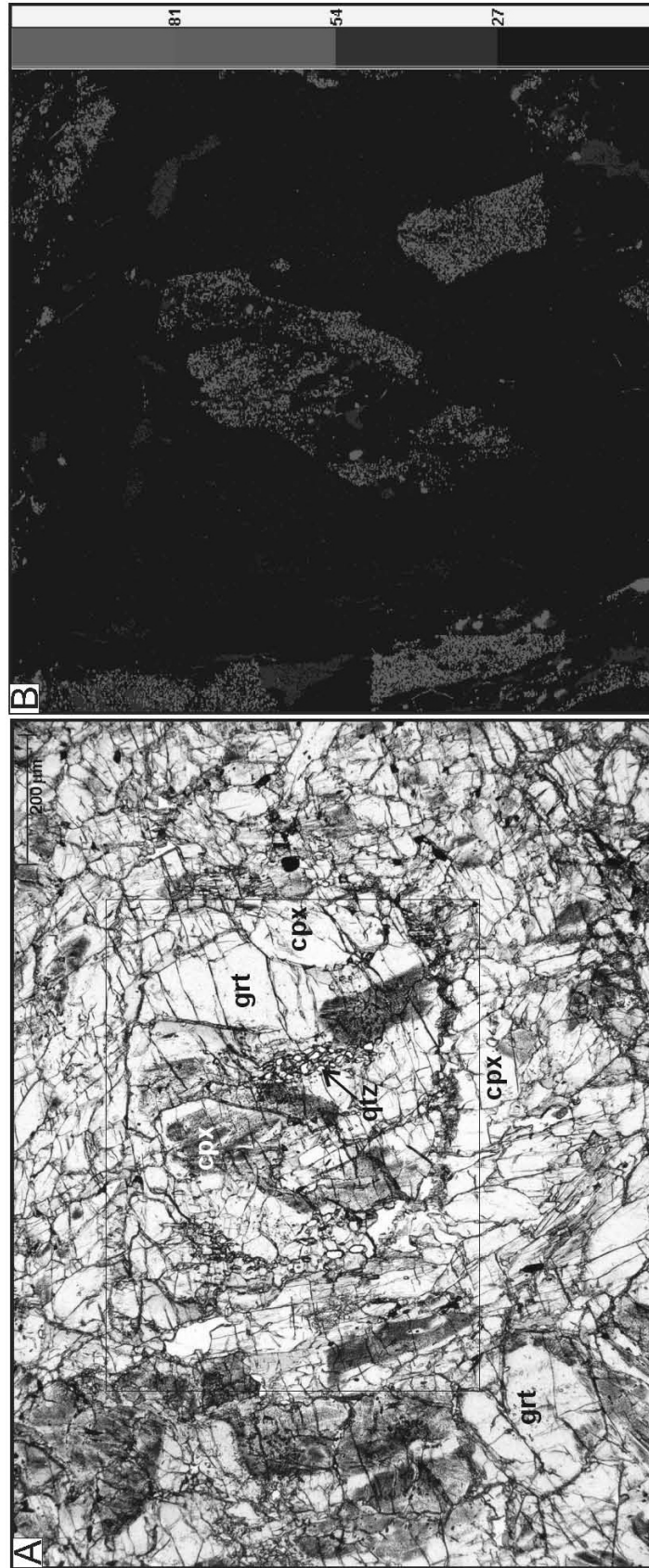


Fig. 1A – Photomicrograph showing garnet and clinopyroxene rich in fine rutile inclusions delineating idiomorphic shapes of former Ti-rich clinopyroxene replaced by garnet and omphacite, N//. B. Ti distribution map in the area marked on A, well illustrating the former Ti-rich zones.

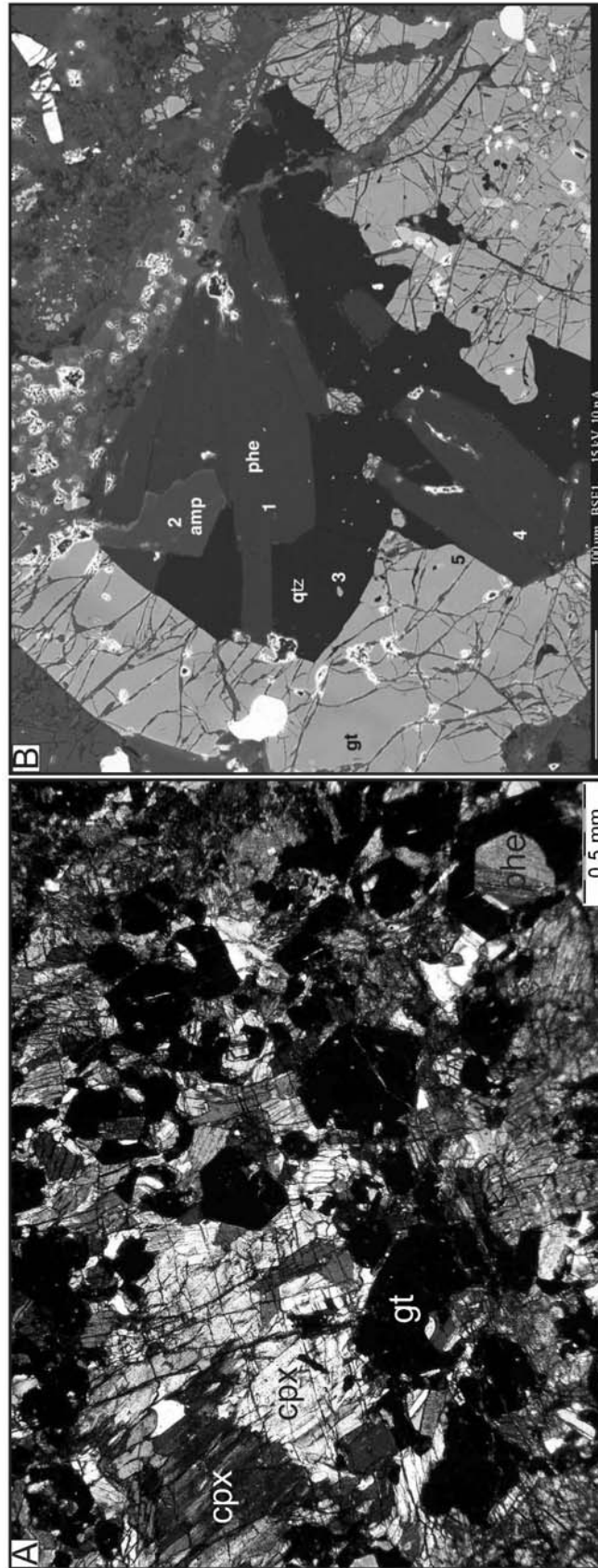


Fig. 2A – Photomicrograph showing idiomorphic garnets and atoll-shaped garnets enclosing phengite ± quartz cores, N+.

B. Back-scattered electron (BSE) image of an open garnet ring; phengite + quartz + amphibole inner fill.

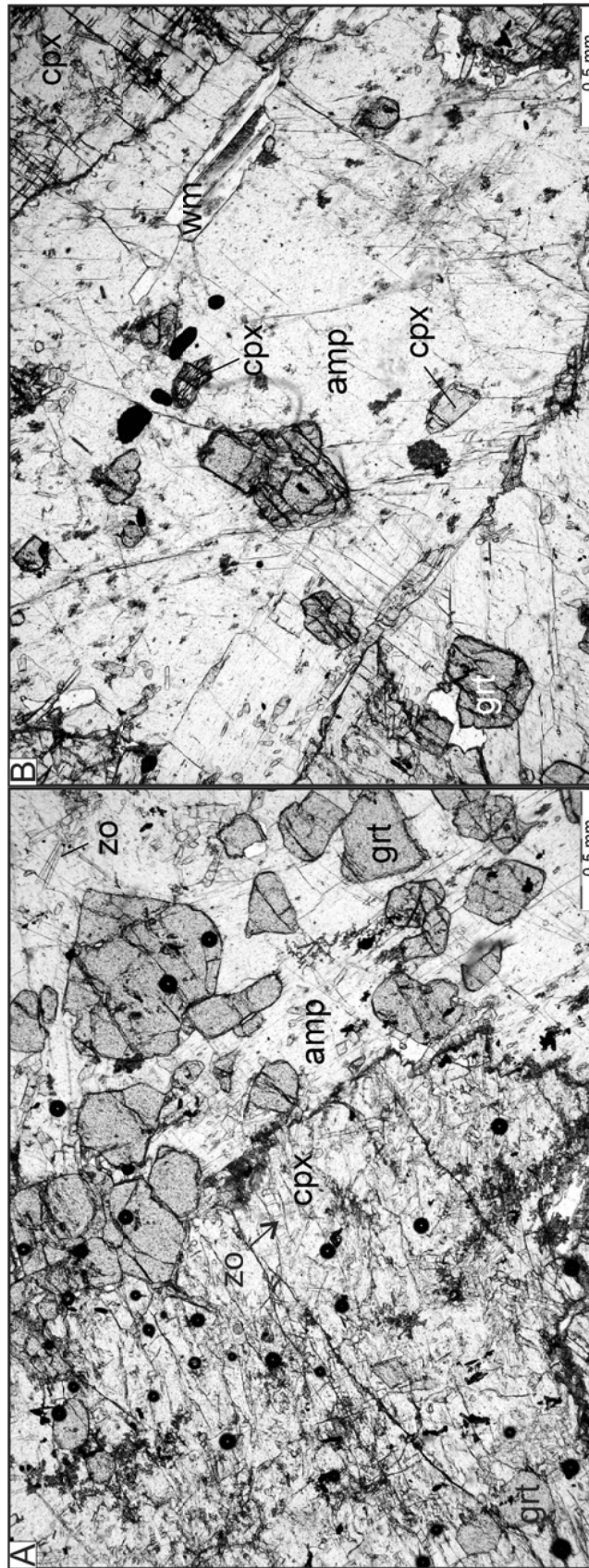


Fig. 3 – Photomicrographs showing A. poikiloblastic clinopyroxene substituted by amphibole; zoisite and idiomorphic garnets formerly included in pyroxene are preserved in amphiboles, 4X, N//. B. Relics of clinopyroxene from the replaced crystal and white mica inclusions in poikiloblastic amphibole, 4X, N//.

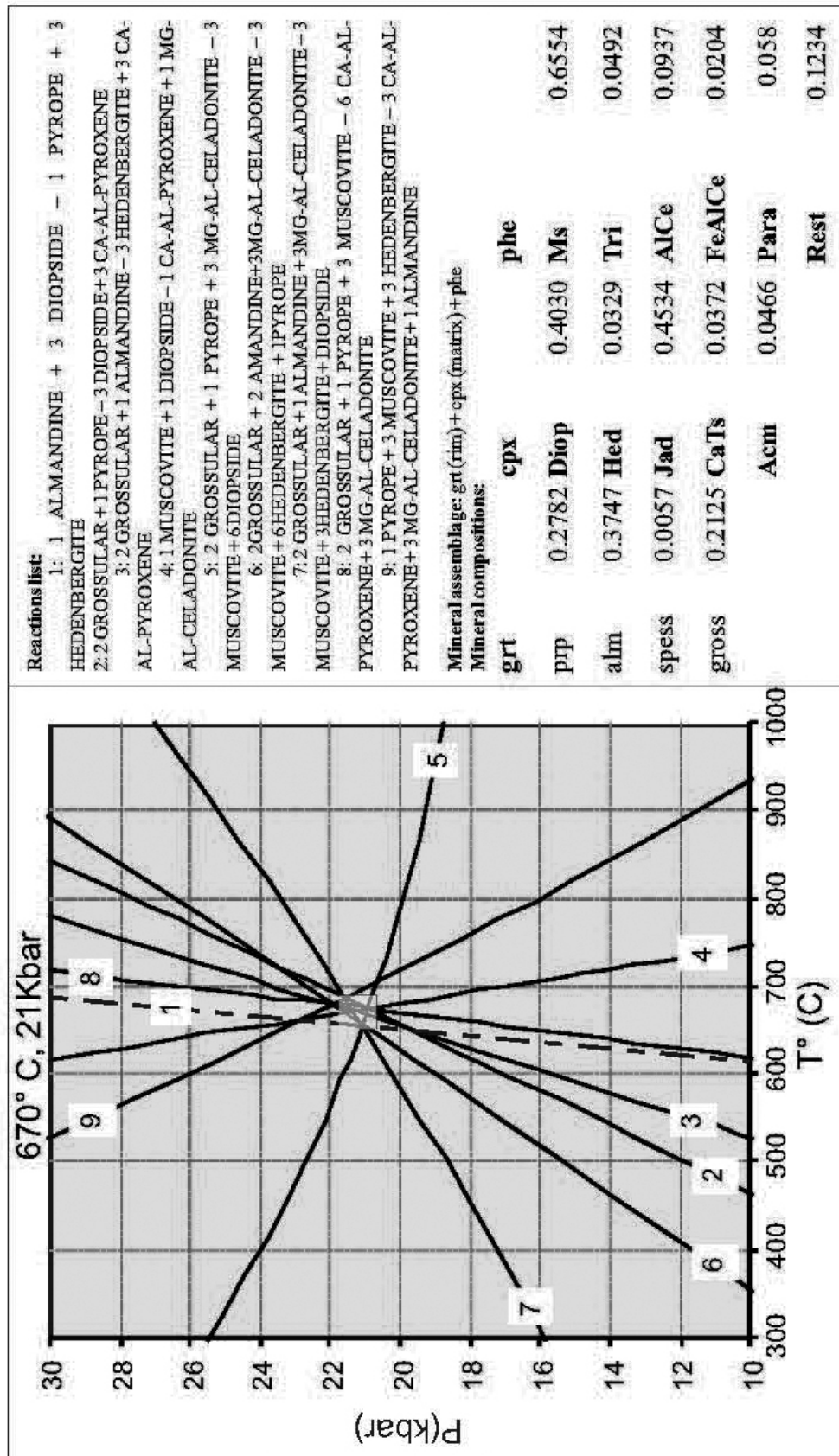


Fig. 4 – Calculated mineral equilibria for sample 1059B (Valea lui Dăniș zoisite-phengite-bearing common eclogites), reactions list and mineral compositions employed for computations.

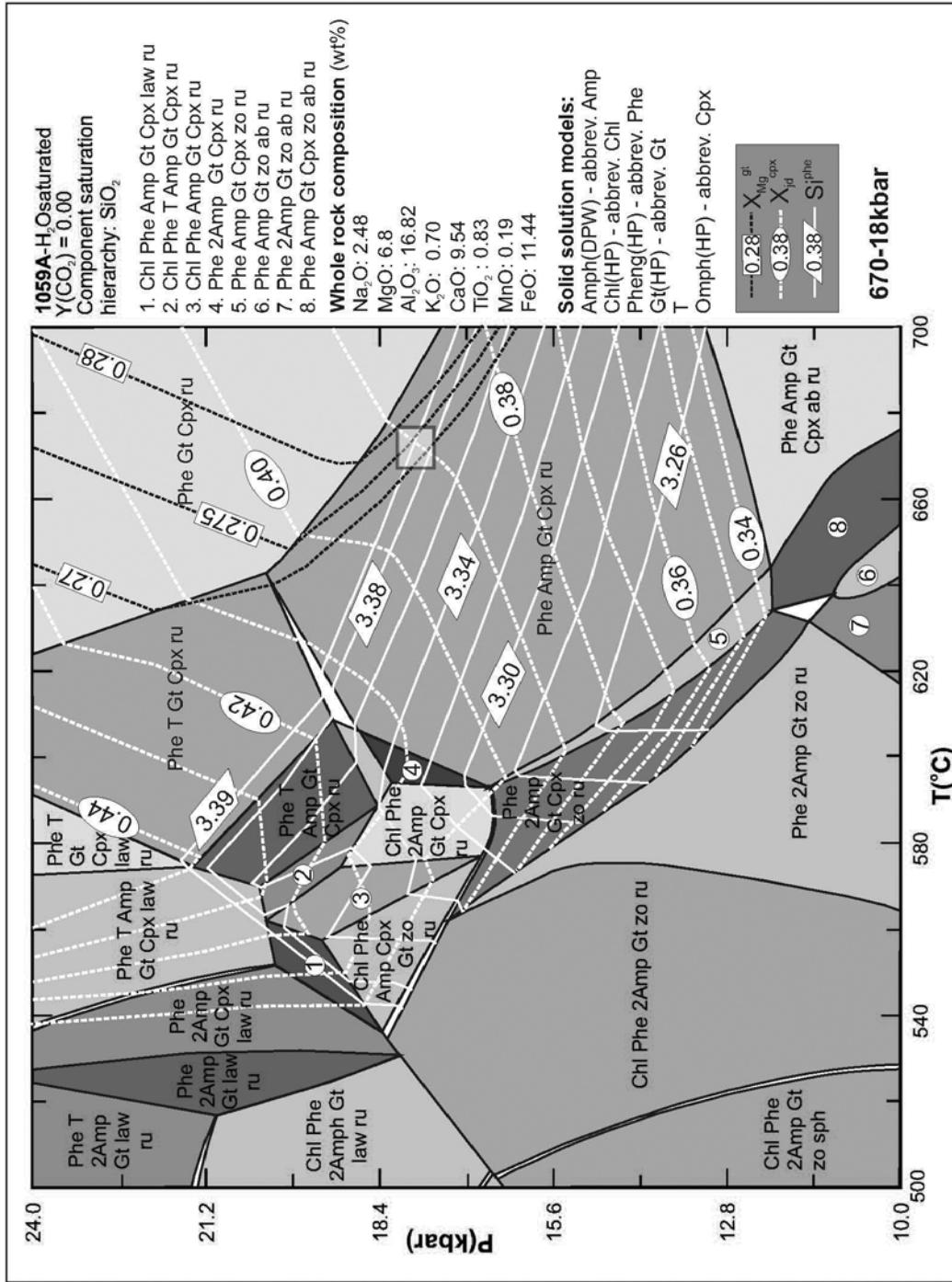


Fig. 5 – *P-T* pseudosection calculated for sample 1059B in the Na₂O–K₂O–CaO–MnO–FeO–MgO–Al₂O₃–SiO₂–TiO₂–H₂O system (+ quartz) using the XRF-derived bulk-rock composition. Isotherms for X_{Mg} in garnet (numbers in rectangles), jadeite in clinopyroxene (numbers in ellipses), and Si p.f.u. in phengite (numbers in parallelograms) are also shown. Translucent rectangle indicates the *PT* conditions constrained by mineral assemblage.

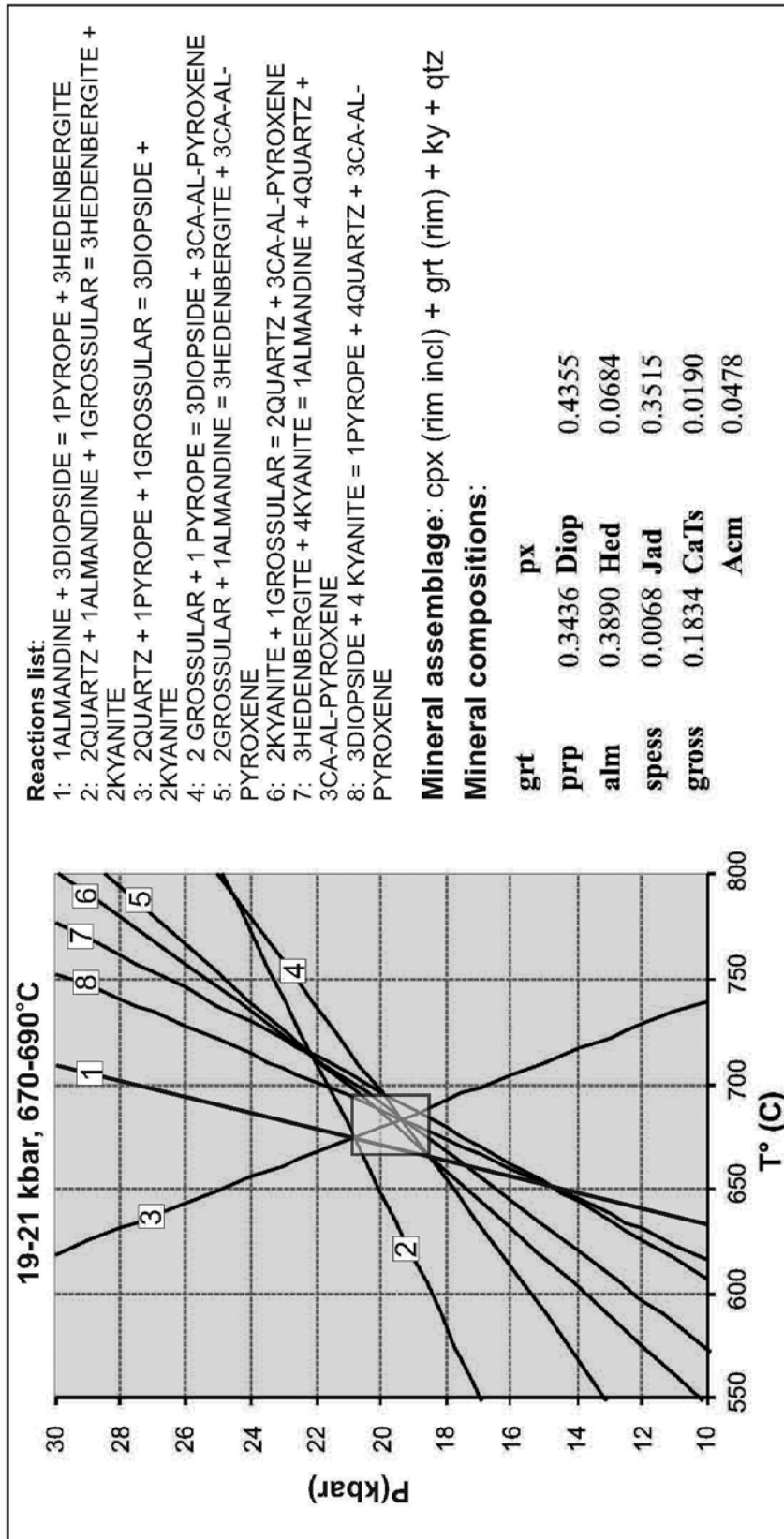


Fig. 6 – Calculated mineral equilibria for sample 1057 (Valea lui Rus phengite-free kyanite-bearing common eclogite), reactions list and mineral compositions employed for computations.

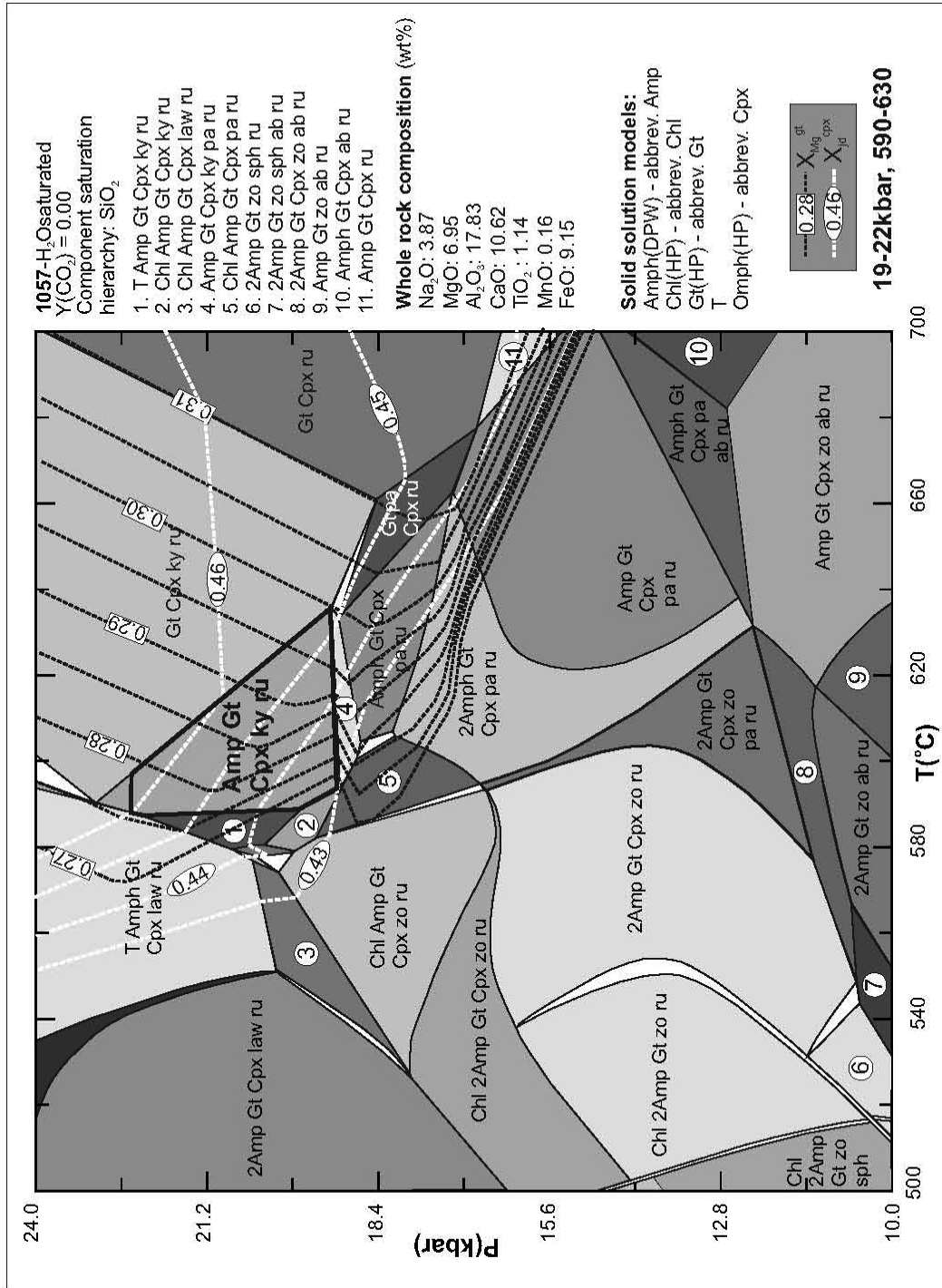


Fig. 7 – *P-T* pseudosection calculated for sample 1057B in the Na₂O–CaO–MnO–FeO–MgO–Al₂O₃–SiO₂–H₂O system (+ quartz) using the XRF-derived bulk-rock composition. Isotherms for X_{Mg}^{gt} in garnet (numbers in rectangles) and clinopyroxene (numbers in ellipses), and Si p.f.u. in phengite (numbers in parallelograms) are also shown. Thicker contour indicates the *PT* conditions constrained by mineral assemblage – cyanite and amphiboles in equilibrium with garnet and omphacite, and X_{Mg}^{cpx}

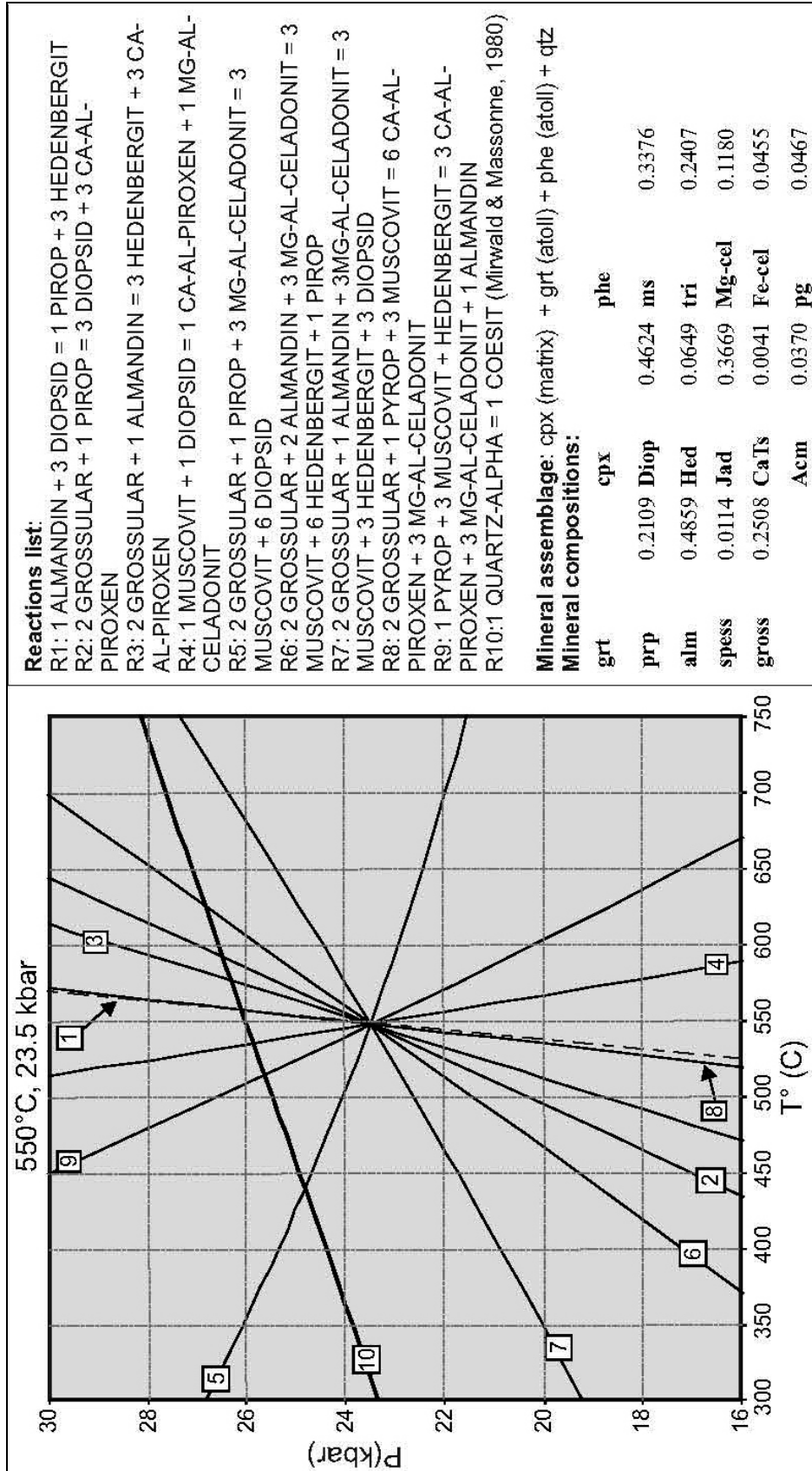


Fig. 8 – Calculated mineral equilibria for example 989B (Valea Plopilor phengite-bearing common eclogite), reactions list and mineral compositions employed for computations.

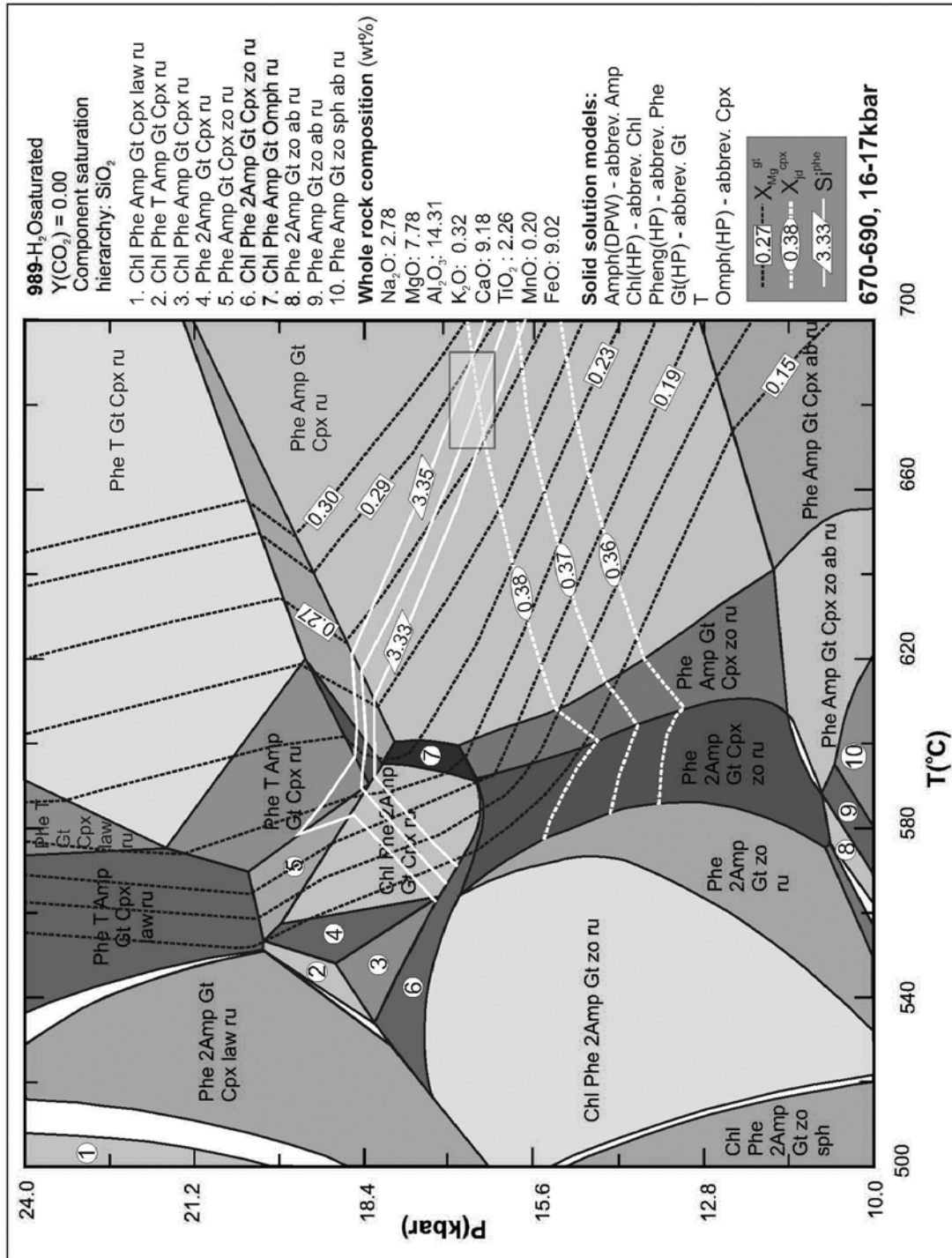


Fig. 9 – *P-T* pseudosection calculated for sample 989B in the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MnO}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2-\text{H}_2\text{O}$ system (+ quartz) using the XRF-derived bulk – rock composition. Isoleths for X_{Mg} in garnet (numbers in rectangles), jadeite in clinopyroxene (numbers in ellipses), and Si p.f.u. in phengite (numbers in parallelograms) are also shown. Translucent rectangle indicates the *PT* conditions constrained by mineral isopleths and amphiboles in equilibrium with the eclogitic mineral assemblage.

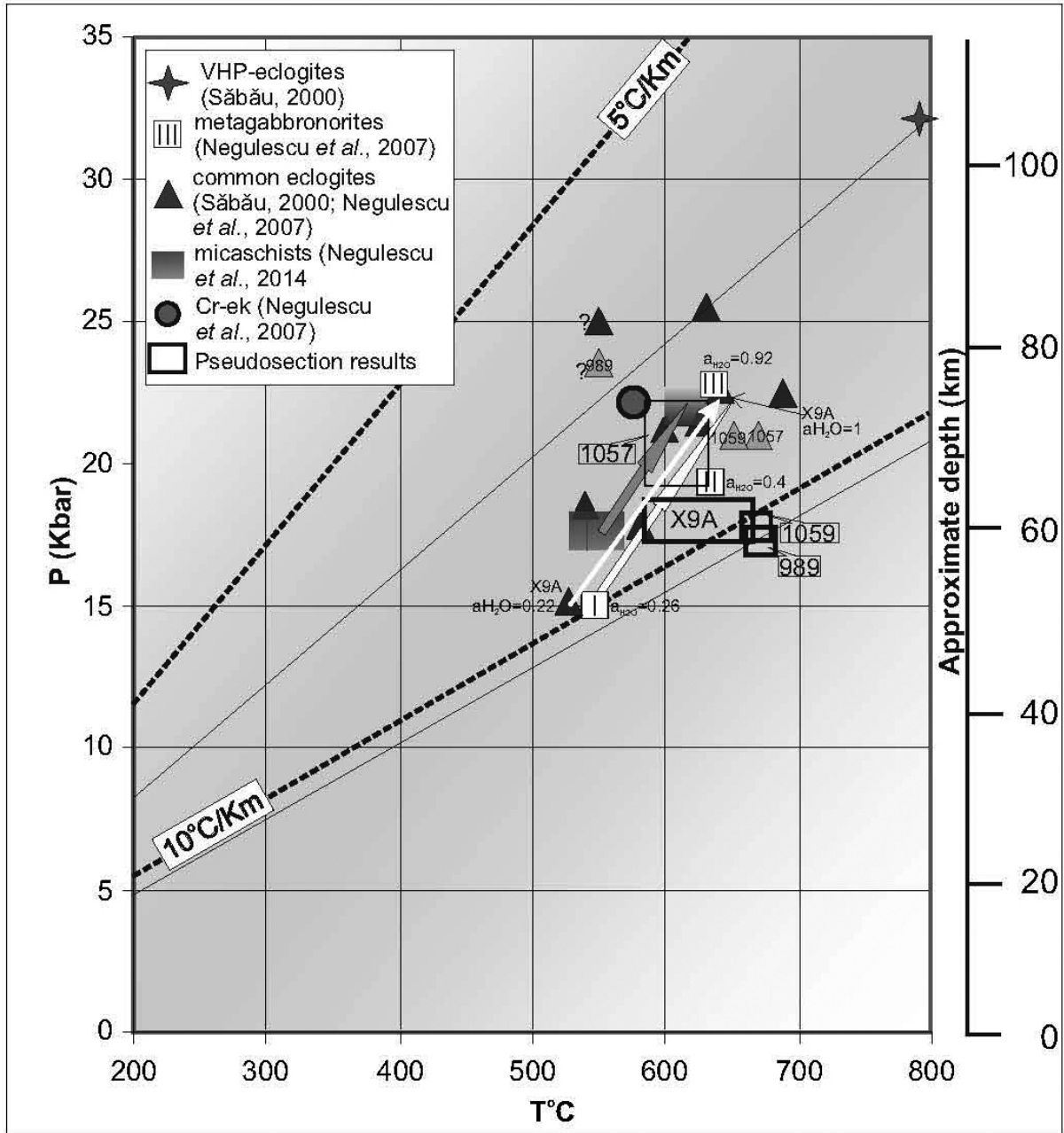


Fig. 10 – PT-metamorphic peak conditions and PT-paths for HP-blocks from the Bughea Complex (Leaota Massif); input data from this study and from literature as cited.

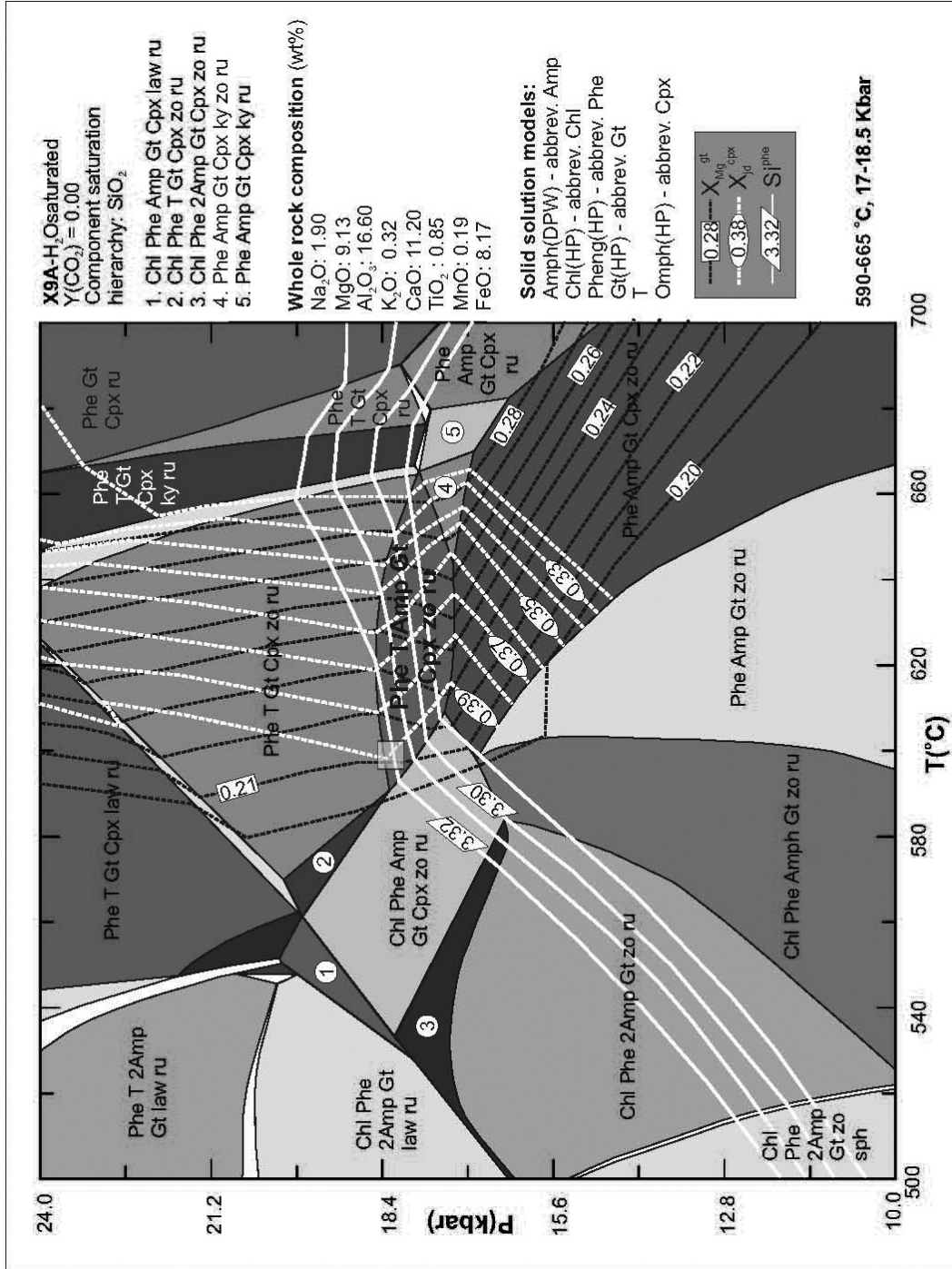


Fig. 11 – *P-T* pseudosection calculated for sample X9A (Valea Călugărului common talc-bearing eclogites) in the Na₂O-K₂O-CaO-MnO-TiO₂-FeO-MgO-Al₂O₃-SiO₂-H₂O system (+quartz) using the XRF-derived bulk-rock composition. Isopleths for X_{Mg} in garnet (numbers in rectangles), jadeite in clinopyroxene (numbers in ellipses), and Si p.f.u. in phengite (numbers in parallelograms) are also shown. Translucent rectangles indicates the *P-T* conditions constrained by mineral isopleths.

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