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P-T pseudosections in KFMASH, KMnFMASH, NCKFMASH and NCKMnFMASH systems: a case study from garnet-staurolite mica schist from the Alpine metamorphic basement of the Pannonian Basin (Hungary)

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Abstract: *P-T* pseudosections (quantitative phase diagrams) in the KFMASH, KMnFMASH, NCKFMASH and NCKMnFMASH systems were calculated with PERPLEX and THERMOCALC from garnet-staurolite mica schist originating from the basement of the Pannonian Basin (Hungary) in the *P-T* range 0.2–1.2 GPa and 450–700 °C with quartz and H_2O in excess. The previously published peak *P-T* conditions (650 ± 30 °C and 0.9 ± 0.1 GPa) are confirmed by the resultant pseudosections in all systems with garnet-biotite-kyanite-muscovite-plagioclase-quartz as the stable parageneses. Mineral composition isopleths mostly model the mineral chemical changes. The *P-T* path outlined in the NCKFMASH system shows that biotite and quartz inclusions in host staurolite with matrix muscovite and plagioclase are stable at 560–650 °C and 0.35–0.6 GPa. During simultaneous *P-T* increase garnet started to form at about 0.6 GPa in the garnet-biotite-staurolite-muscovite-plagioclase-quartz field, and then kyanite appeared at the expense of staurolite near the *P-T* peak. The cooling path passed the garnet-biotite-staurolite-muscovite-plagioclase-quartz field again and ended in chlorite-bearing assemblages. The presented *P-T* pseudosections in combination with the published Ar-Ar age data on muscovite (85.5 ± 1.2 Ma) support the Eo-Alpine age of amphibolite facies metamorphism in the basement of the Tisza Unit (southwestern part of the Pannonian Basin), but do not exclude the possibility of a polymetamorphic origin (Variscan-Alpine).

Key words: Pannonian Basin, Alpine metamorphism, metamorphic petrology, pseudosection calculations, PERPLEX and THERMOCALC, mica schist.

Introduction

The model system KFMASH (K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O) has been studied intensively in order to develop petrogenetic grids for the range of common mineral assemblages in metapelitic rocks. Early qualitative grids were based on natural mineral parageneses (e.g. Albee 1965; Pattison & Tracy 1991; Droop & Harte 1995); later quantitative grids were based on internally-consistent thermodynamic data sets (e.g. Spear & Cheney 1989; Powell & Holland 1990). In recent years a number of studies have been carried out to augment the system with additional components such as Na_2O, CaO, TiO_2, Fe_2O_3 and MnO (e.g. Mahar et al. 1997; Worley & Powell 1998; White et al. 2001). From these components MnO has the most important role in stabilizing ferromagnesian minerals, mostly garnet. Mahar et al. (1997) calculated a quantitative grid for the KMnFMASH system in the range 450–700 °C and 0–2 GPa based on the Holland & Powell (1990) thermodynamic dataset to determine the effect of Mn on mineral stabilities. Wei et al. (2004) presented a new calculation of the petrogenetic grid in the KMnFMASH system for low- and medium-pressure conditions using THERMOCALC 3.1 with the internally-consistent thermodynamic data set of Holland & Powell (1998 and upgrades) and updated models of activity-composition relationships. Their main conclusions are that the addition of Mn to the KFMASH system: enhances the stability field of garnet, extends the medium-P stability of muscovite and reduces the stability of staurolite and cordierite. Vance & Mahar (1998), Tinkham & Stowell (2000) and Stowell et al. (2001) used the NCKMnFMASH system to derive garnet growth *P-T* paths from medium-grade metapelites. Stowell et al. (2001) concluded that the NCKMnFMASH is the minimum system required to apply quantitatively pseudosections to natural metapelites containing garnets and Na- and Ca-bearing phases (e.g. plagioclase, zoisite).

There are three main focuses of this paper. First, a comparison between pseudosections (quantitative phase diagrams) calculated with PERPLEX (Connolly 1990; Connolly & Petrini 2002) and THERMOCALC (Powell et al. 1998) are performed in the KFMASH and KMnFMASH systems on a representative garnet-staurolite mica schist sample from the basement of the Pannonian Basin, Hungary (Újszentiván Uszi-2 borehole). THERMOCALC phase diagrams involving solid solutions are calculated by solving sets of non-linear equations, while PERPLEX uses the minimization of Gibbs energy. A similar type of comparison was performed by Hoschek (2004) who compared the programs THERMOCALC, PERPLEX and DOMINO on a kyanite eclogite from the Tauern Window (Eastern Alps, Austria). Then, we present NCKFMASH and NCKMnF-MASH pseudosections with mineral compositional isopleths to model mineral stability and mineral compositional changes in the studied sample. Finally, we present a *P-T* path for the studied mica schist sample in the NCKF-MASH system.

Geology and previous data on metamorphism

The basement of the southwestern part of the Pannonian Basin (Tisza or Tisia Unit) covered by several thousand meter-thick sedimentary sequences consists of polymetamorphic formations. The Tisza Unit (Fig. 1a) originated from the northern, European margin of Tethys by mostly Meso-Alpine horizontal displacements of microplates (Géczy 1973; Kovács 1982; Kázmér & Kovács 1985; Kovács et al. 2000). It forms the basement of the southern part of Hungary, and is bounded by the Mid Hungarian (or Zagreb-Zemplín) Line to the north, while it can be followed over the state boundary to Northern Croatia and Serbia-Montenegro, and to Western Transylvania (Romania) in the southern and eastern directions, respectively. Szederkényi (1984) divided the pre-Alpine (mostly Variscan) basement complexes of the Tisza Unit into two major parts: the Parautochthon Unit and the South Hungarian Nappe. Fülöp (1994) distinguished three tectonic units on the basis of Mesozoic sedimentary facies zones: the Mecsek, Villány-Bihar (VBU), and Békés-Codru Units (BCU). The first two represent the Parautochthon Unit, whereas the latter is equivalent to the South Hungarian Nappe. These tectonic units are of Late Cretaceous age, so their presence in pre-Alpine tectonic reconstructions is not unambiguous. The prevailing rocks are paragneisses, mica schists and granitoids with minor amphibolites and — in some areas — marble intercalations.

In general, the first metamorphic event recorded in the Tisza Unit in Hungary is characterized by Barrow-type amphibolite facies regional metamorphism (330–350 Ma). Árkai (1984) and Árkai et al. (1985) calculated peak conditions of 500–600 °C and 0.5–0.9 GPa for gneisses, mica schists and intercalated amphibolites. This event was overprinted by a low-pressure Variscan event in the BCU (270–330 Ma). No reliable isotopic ages older than Variscan are available for the metamorphic basement of the Hungarian part of the Tisza Unit (Lelkes-Felvári et al. 1996; 2003). Recently, Balen et al. (2006) reported pre-Variscan (428 ± 25 and 444 ± 19 Ma) monazite U-Pb ages for the medium-grade metamorphism of garnet-bearing mica schists from the Slavonian Mts (NE Croatia). Eo-Alpine tectonism caused a very low- to low-grade prograde metamorphism in the Permian-Mesozoic rocks beneath the overthrusted Variscan basement which shows strong Alpine retrogression (Árkai et al. 2000). Some parts of the Variscan basement in the BCU were affected by Eo-Alpine amphibolite facies metamorphism (Algyő basement-high, Horváth & Árkai 2002). Non-metamorphic Late Paleozoic overstep sequences were deposited on different parts of the Tisza Unit (Kovács et al. 2000). Lower Permian and Mesozoic formations occur in the entire area; however they do not form a continuous cover above the basement. Lower-Middle Miocene conglomerates contain the basement rocks as pebbles. In these clastic sediments exotic rock types such as eclogites and garnetiferous amphibolites occur (Horváth et al. 2003).

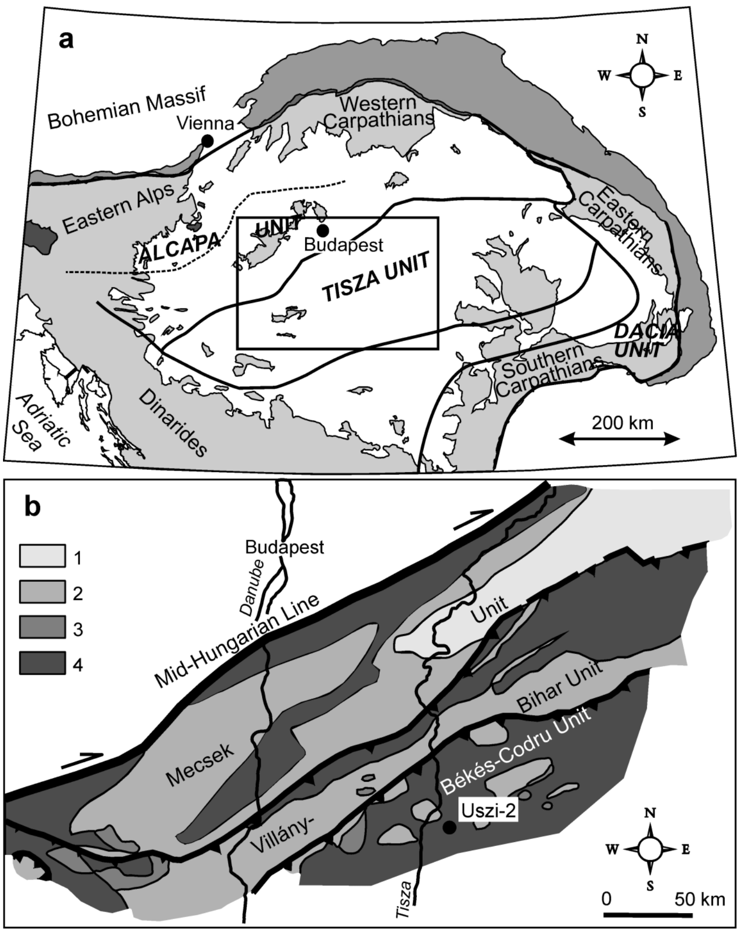

Fig. 1. a — Main tectono-stratigraphic units of the Pannonian Basin and neighbouring areas. Box indicates area enlarged in Fig. 1b; **b** — Pre-Tertiary geological map of the Tisza Unit. 1 — Cretaceous-Paleogene flysch deposits, 2 — Mesozoic rocks, 3 — Permian and Carboniferous molasse-type rocks, 4 — metamorphic and igneous basement rocks.

The metamorphic basement near the Algyő basement-high is built up mainly by Variscan andalusite-bearing metapelites (Ar-Ar cooling ages of muscovite are in the range of 318–321 Ma, Lelkes-Felvári et al. 2003). Sm-Nd analyses of a garnet concentrate yielded a Permian age of 273 ± 7 Ma (Lelkes-Felvári et al. 2002, 2003). According to Lelkes-Felvári et al.

(2003) the garnet, together with K-feldspar and crystal-shape relics of andalusite formed during a high-T/low-P event. Kyanite aggregates (sometimes with staurolite) replaced andalusite, and the rock pile suffered intense mylonitic deformation during the Eo-Alpine tectono-metamorphic event. An Ar-Ar age dating on muscovite (85.5±1.2 Ma) from the Uszi-2 sample proved the Eo-Alpine age of metamorphism (Lelkes-Felvári et al. 2003). Slightly younger Ar-Ar plateau ages (68.4–84.3 Ma) were published by Balogh & Pécskay (2001). Horváth & Árkai (2002) studied the mica schist samples from the Algyő basement-high in detail and found several garnet generations distinguished by petrographic studies and compositional features as well: 1. complex zoned garnet porphyroblasts with 3 growth stages; 2. zoned garnets with S-shaped inclusion trails; 3. small, homogeneous garnets with compositions similar to the rim of the large porphyroblasts. Having applied various thermobarometric methods and calibrations (TWEEQU of Berman 1991 and THERMOBAROMETRY by Kohn & Spear 1995) combined with *P-T* calculations from garnet zoning profiles (GIBBS program of Spear & Menard 1989) a *P-T* path with increasing P and T conditions was established. Peak conditions of 650±30 °C and 0.9±0.1 GPa were reached and followed by subsequent cooling (Fig. 9 in Horváth & Árkai 2002).

Petrography and mineral chemistry

Chemical analyses of minerals were carried out by a JEOL JXCA-733 electron microprobe equipped with 3 WDS in the Institute for Geochemical Research, Hungarian Academy of Sciences, Budapest. The measuring conditions were: 15 kV acceleration voltage; 40 nA sample current; electron beam with a diameter of 5 μm; 5 s counting time. Matrix effects were corrected by using the ZAF method. The following standards were used for quantitative analysis: orthoclase (K, Al, Si), synthetic glass (Fe, Mg, Ca), spessartine (Mn), rutile (Ti) and albite (Na).

The garnet-staurolite mica schist sample (Uszi-2) chosen for this study contains garnet porphyroblasts that are nearly homogeneous and have idioblastic staurolite inclusions (Fig. 2a). The garnets are $Alm_{78-80}Prp_{12-15}Grs_{3-4}Sps_{1-3}$, whereas some small areas (< 10 μm) have lower Alm and

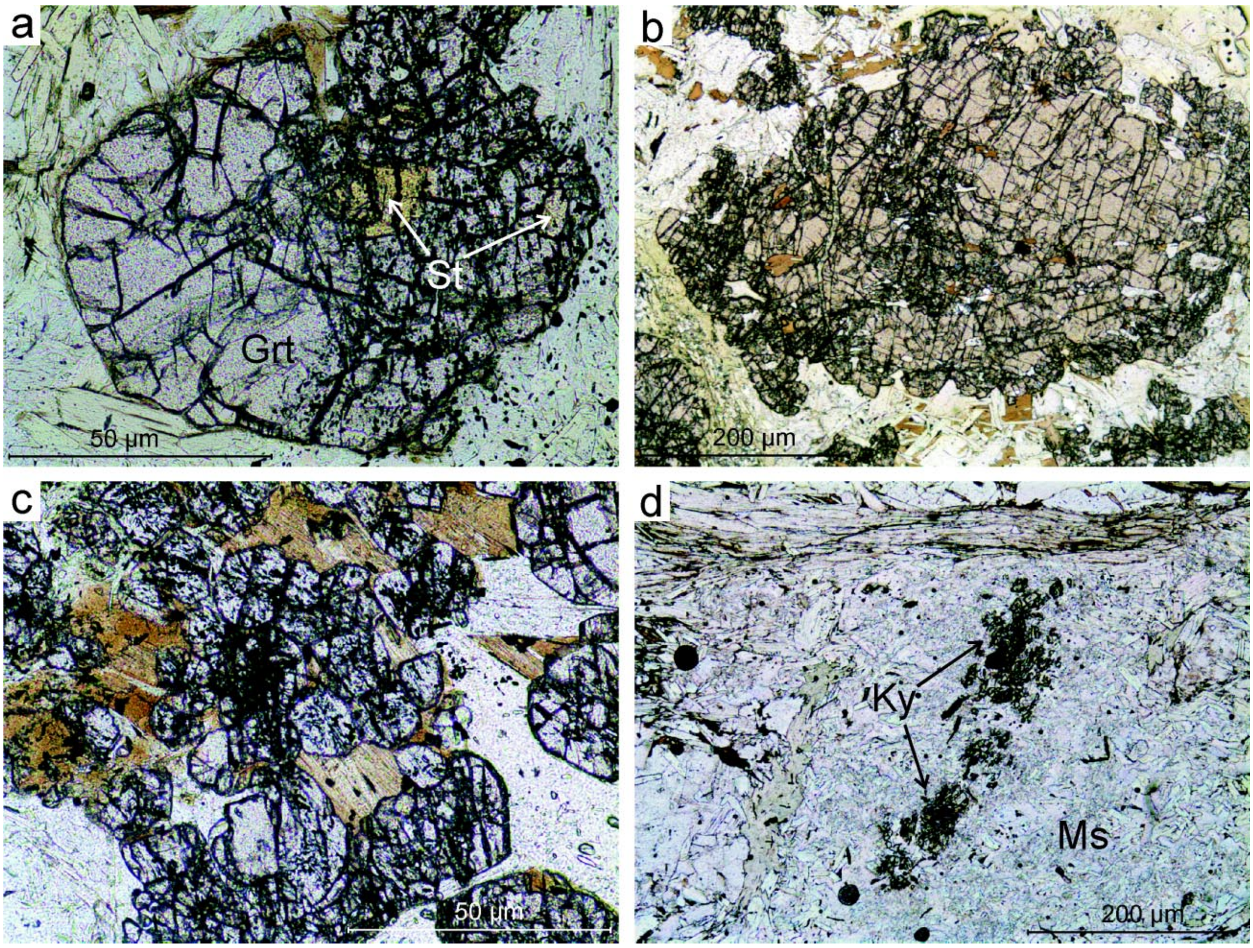

Fig. 2. Petrographic images from the Uszi-2 sample. **a** — Hypidioblastic staurolite (St) inclusions in garnet (Grt); **b** — Corona of small garnets on larger garnet porphyroblasts; **c** — idioblastic garnet aggregate in biotite-muscovite-quartz matrix; **d** — Ky aggregate (pseudomorphs after andalusite?) in muscovite-rich matrix. Note the discordant orientation of the aggregate in relation to the main foliation of the rock represented by biotites (horizontal in the thin section).

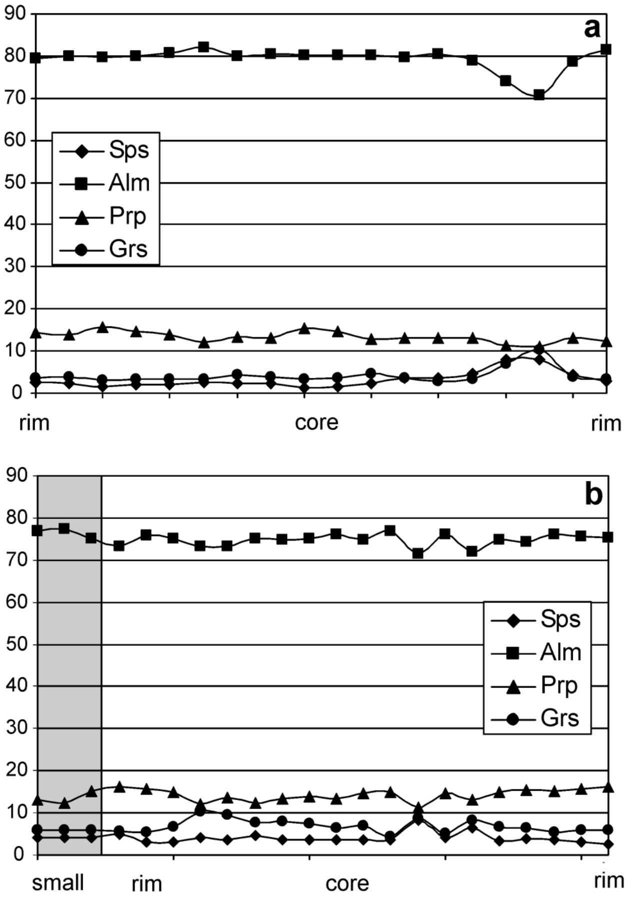

Fig. 3. Zoning profiles of garnets from Uszi-2 mica schist: **a** — large porphyroblast; **b** — small garnet corona (shaded) on large porphyroblast.

Prp, and higher Grs and Sps contents ($Alm_{70}Prp_{11}Grs_{10}Sps_8$). These areas occur inside the garnets near the rims (Fig. 3a), but they are not related to any specific microtextural positions (e.g. cracks, grain-edges), so tentatively they are interpreted as relics of an earlier lower-T event. The absence of growth zonation in garnet either results from fast garnet growth near the metamorphic peak or from diffusive smoothing out of an initial growth zonation (Zeh 2001). Small garnets with compositions similar to the rims of the large porphyroblasts form overgrowths on them (Figs. 2b and 3b) or occur as aggregates in the matrix (Fig. 2c). XFe [$Fe^{2+}/(Fe^{2+}+Mg)$] varies between 0.84 and 0.87. Staurolites occur either in garnet, or they are present in the matrix as large (up to 5–7 mm) porphyroblasts. These porphyroblasts are rimmed or cross-cut by kyanite aggregates. Staurolites have quite uniform XFe values ranging from 0.77 to 0.82. There is no zonation found inside the analysed samples or differences in chemical composition regardless of their textural position (i.e. inclusion in a garnet core or relic porphyroblast in the matrix). The matrix assemblage consists of muscovite, biotite, kyanite, quartz, plagioclase and accessory minerals such as zircon, tourmaline, ilmenite and magnetite. Fine-grained aggregates of kyanite appear in the muscovite-rich matrix (Fig. 2d); they were interpreted as pseudomorphs after andalusite by Szederkényi (1984). The orientation of the kyanite aggregates is sometimes discordant to the main foliation of the matrix. Matrix biotites are chemically homogeneous with XFe values of 0.44–0.52 and 1.5–1.9 wt. % TiO_2. Biotite inclusions in staurolite have lower XFe values (0.38–0.41). Muscovites have 6.2–6.3 Si atoms p.f.u., and plagioclases are An_{10-15}. Retrograde chlorite replaces biotite and garnet; it occurs in larger quantities in some of the Újszentiván samples than in

Table 1: Representative mineral chemical analyses from the Uszi-2 garnet-staurolite mica schist.

Mineral position	Grt rim	Grt Ca-rich	Bt matrix	Bt incl. in St	St matrix	Ms matrix	Pl matrix
SiO_2	36.55	36.60	36.09	35.80	27.72	46.62	68.02
TiO_2	0.00	0.00	1.92	2.51	0.71	0.85	0.00
Al_2O_3	21.53	21.41	20.88	19.06	53.77	35.72	21.59
FeO_{total}	35.59	32.85	18.47	14.59	12.35	0.99	0.00
MnO	1.08	3.44	0.01	–	0.02	0.01	0.00
MgO	3.56	2.80	9.78	12.36	1.70	0.77	0.00
CaO	1.26	2.36	0.03	0.05	0.00	0.02	1.57
Na_2O	0.00	0.00	0.19	0.28	0.00	0.95	8.00
K_2O	0.00	0.00	8.53	8.42	0.00	9.20	0.11
Total	99.57	99.46	95.90	93.07	96.27	95.13	99.29
Si	2.934	2.962	5.377	5.417	2.022	6.161	2.960
Ti	0.000	0.000	0.215	0.286	0.039	0.084	0.000
Al	2.037	2.042	3.666	3.399	4.622	5.564	1.107
Fe^{2+}	2.389	2.223	2.301	1.846	0.753	0.109	0.000
Mn	0.073	0.236	0.001	–	0.001	0.001	0.000
Mg	0.426	0.338	2.172	2.788	0.185	0.152	0.000
Ca	0.108	0.205	0.005	0.008	0.000	0.003	0.073
Na	0.000	0.000	0.055	0.082	0.000	0.243	0.675
K	0.000	0.000	1.621	1.625	0.000	1.551	0.060
Sum cat	7.967	8.021	15.413	15.451	7.622	13.869	4.875
Alm/An	79.44	74.08	–	–	–	–	9.69
Prp/Ab	14.41	11.25	–	–	–	–	89.50
Sps/Or	2.48	7.85	–	–	–	–	0.81
Grs	3.66	6.82	–	–	–	–	–
XFe	0.85	0.87	0.51	0.40	0.80	–	–

the others from different part of the basement (e.g. Ferencszállás or Algyő samples). Representative mineral chemical analyses are listed in Table 1.

Pseudosections

Phase relations are best illustrated and understood using pseudosections (quantitative phase diagrams) where the bulk composition of a rock is incorporated into the calculations. The PERPLEX calculations (Connolly 1990; Connolly & Petrini 2002) were performed with an updated (2002) version of the internally-consistent thermodynamic data set of Holland & Powell (1998), and the solid solution models incorporated in the software package. The THERMOCALC pseudosection modelling (Powell et al. 1998) was undertaken with the 3.25 version of the software and the internally-consistent thermodynamic dataset 5.5 (August 2004 upgrade). The datafile coding of the activity-composition relationships of the minerals used in the MnNCKFMASH calculations is that of Stowell & Tinkham (2003). For the KFMASH and KMnFMASH systems we used the coding of Wei et al. (2004), and for NCKFMASH the coding of White et al. (2001). All the constructed pseudosections are in the *P-T* range 0.2–1.2 GPa and 450–700 °C with quartz and H_2O in excess.

The bulk composition in the system NCKMnFMASH is (SiO_2:Al_2O_3:MgO:FeO:K_2O:CaO:Na_2O:MnO) 77.07:27.55:4.94:9.01:5.58:0.57:2.29:0.27 in molar amounts, with the corresponding KFMASH, KMnFMASH and NCKFMASH compositions involving the omission of MnO, CaO or Na_2O if necessary. Major element composition of the bulk rock sample was determined using a Perkin Elmer 5000 atomic absorption spectrophotometer (AAS), after digestion with lithium metaborate. In addition to the AAS technique, permanganometric (FeO), gravimetric (SiO_2, TiO_2, H_2O and P_2O_5) and volumetric (CO_2) methods were applied.

KFMASH and KMnFMASH pseudosections using PERPLEX

The KFMASH pseudosection is scarcely consistent with the 650±30 °C and 0.9±0.1 GPa peak *P-T* range (Fig. 4a). The largest field in the peak *P-T* range is occupied by garnet-biotite-staurolite-muscovite without kyanite which is not in accordance with the petrographic observation that the sample has abundant kyanite. Moreover, garnet-free assemblages such as biotite-staurolite-muscovite, biotite-kyanite-muscovite or biotite-staurolite-kyanite-muscovite form parts of the *P-T* range. Chlorite is stable up to about 570 °C at 0.9 GPa. The lower stability of biotite is at 520 °C at low pressures. Garnet is not stable below 0.9 GPa. In the KMnFMASH pseudosection (Fig. 4b) only three assemblages are stable at the above-mentioned *P-T* conditions: garnet-biotite-staurolite-muscovite, garnet-biotite-staurolite-kyanite-muscovite and garnet-biotite-kyanite-muscovite. The biotite-staurolite-muscovite assemblage disappears when MnO is added to the calculations.

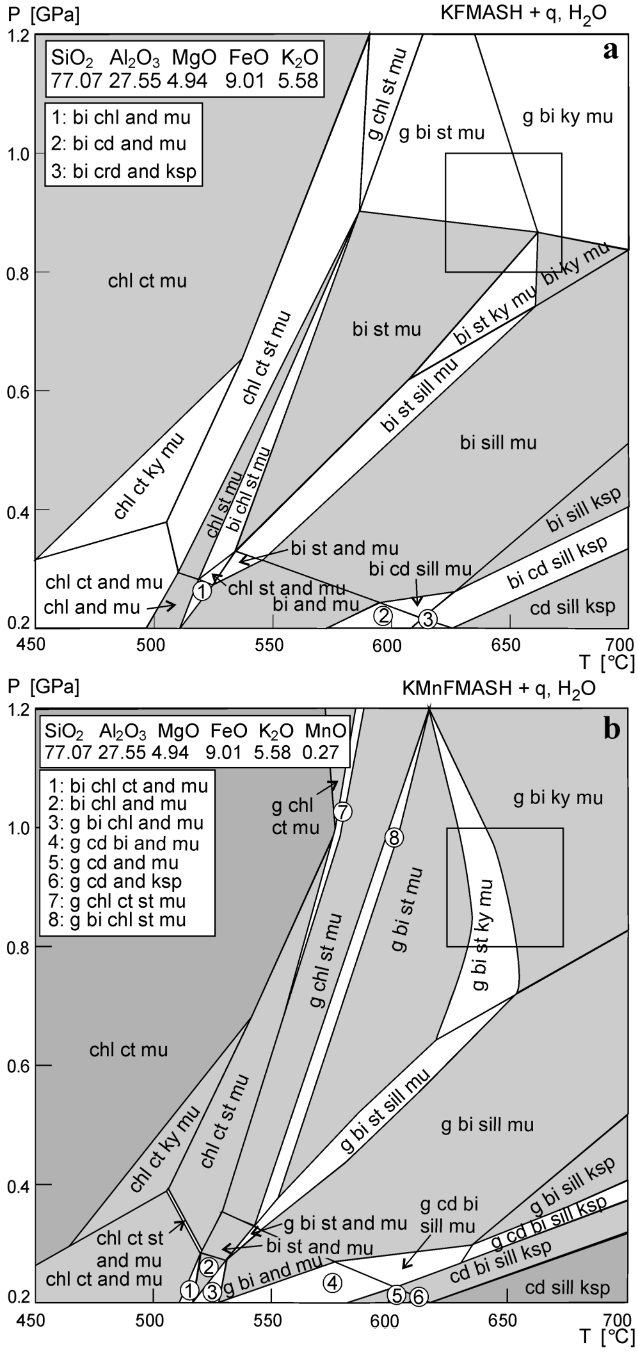

Fig. 4. *P-T* pseudosections (**a** — KFMASH, **b** — KMnFMASH) of Uszi-2 mica schist sample calculated with PERPLEX. Box indicates calculated peak *P-T* conditions after Horváth & Árkai (2002).

KFMASH and KMnFMASH pseudosections using THERMOCALC

The main feature of the KFMASH pseudosection (Fig. 5a) is that garnet is stable only above 0.8 GPa at 570–650 °C. The lower stability of biotite is at about 550 °C. The lower stability of the peak assemblage of garnet-biotite-muscovite-quartz is at 620–650 °C and 0.7–1.2 GPa, partly covering the calculated peak *P-T* range of 650±30 °C and 0.9±0.1 GPa. Staurolite is stable in the P

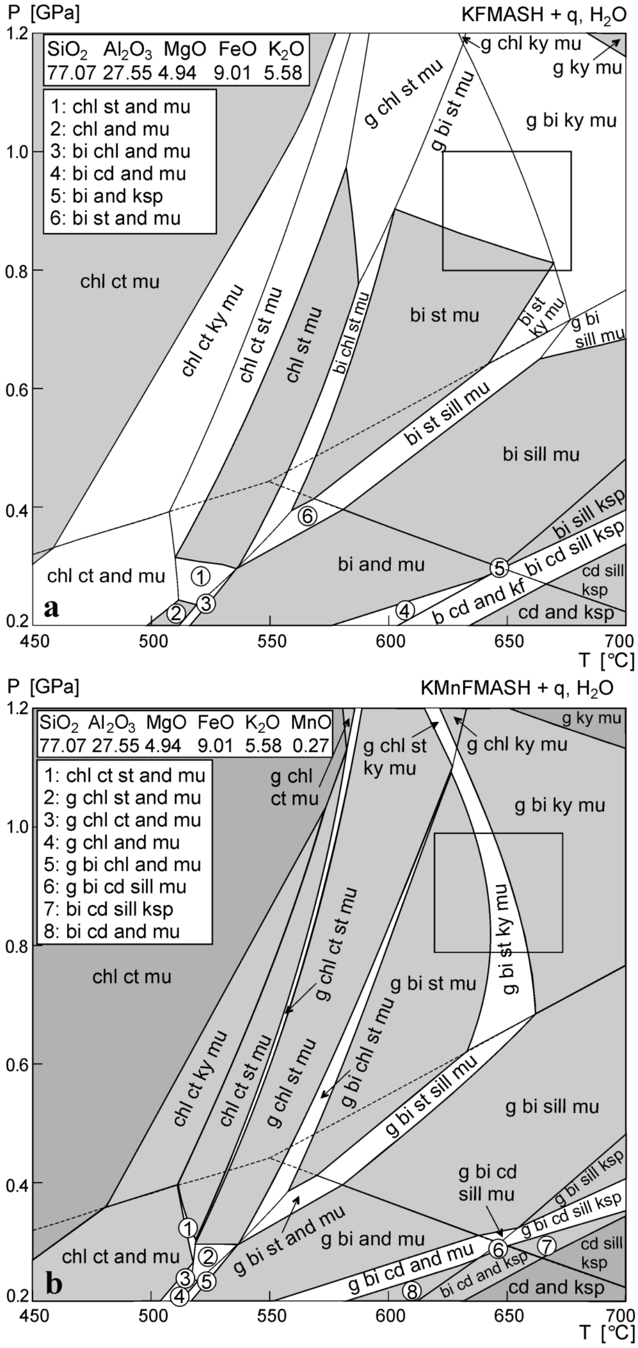

Fig. 5. *P-T* pseudosections (**a** — KFMASH, **b** — KMnFMASH) of Uszi-2 mica schist sample calculated with THERMOCALC. Box indicates calculated peak *P-T* conditions after Horváth & Árkai (2002).

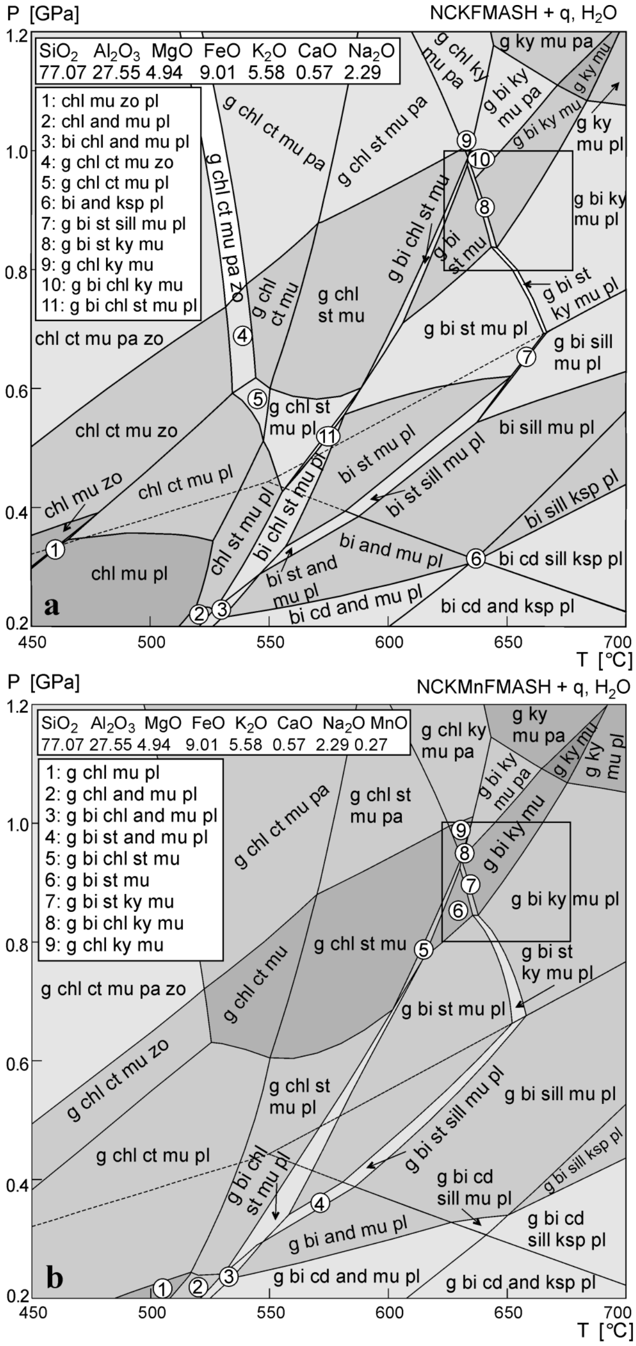

Fig. 6. *P-T* pseudosections (**a** — NCKFMASH, **b** — NCKMnFMASH) of Uszi-2 mica schist sample calculated with THERMOCALC. Box indicates calculated peak *P-T* conditions after Horváth & Árkai (2002).

range of 0.3–1.2 GPa. The upper stability of chlorite is at 600 °C at medium pressures. When MnO is added to the pseudosection (KMnFMASH system) the garnet is stable to lower pressures, it is present in all assemblages over 500 °C (Fig. 5b). Biotite and chlorite stability are not changed drastically, the same is seen in the case of staurolite. The lower stability of the peak assemblage is at around 650 °C. The assemblages of garnet-biotite-staurolite-muscovite and garnet-biotite-staurolite-kyanite-muscovite are expanded at the expense of biotite-staurolite-muscovite and biotite-staurolite-kyanite-muscovite, respectively. A new feature in the KMnFMASH pseudosection compared to the KFMASH one is the presence of the divariant assemblage garnet-biotite-staurolite-kyanite-muscovite.

NCKFMASH and NCKMnFMASH pseudosections using THERMOCALC

The KFMASH and KMnFMASH pseudosections are widely used in metapelites, in spite of the fact that they

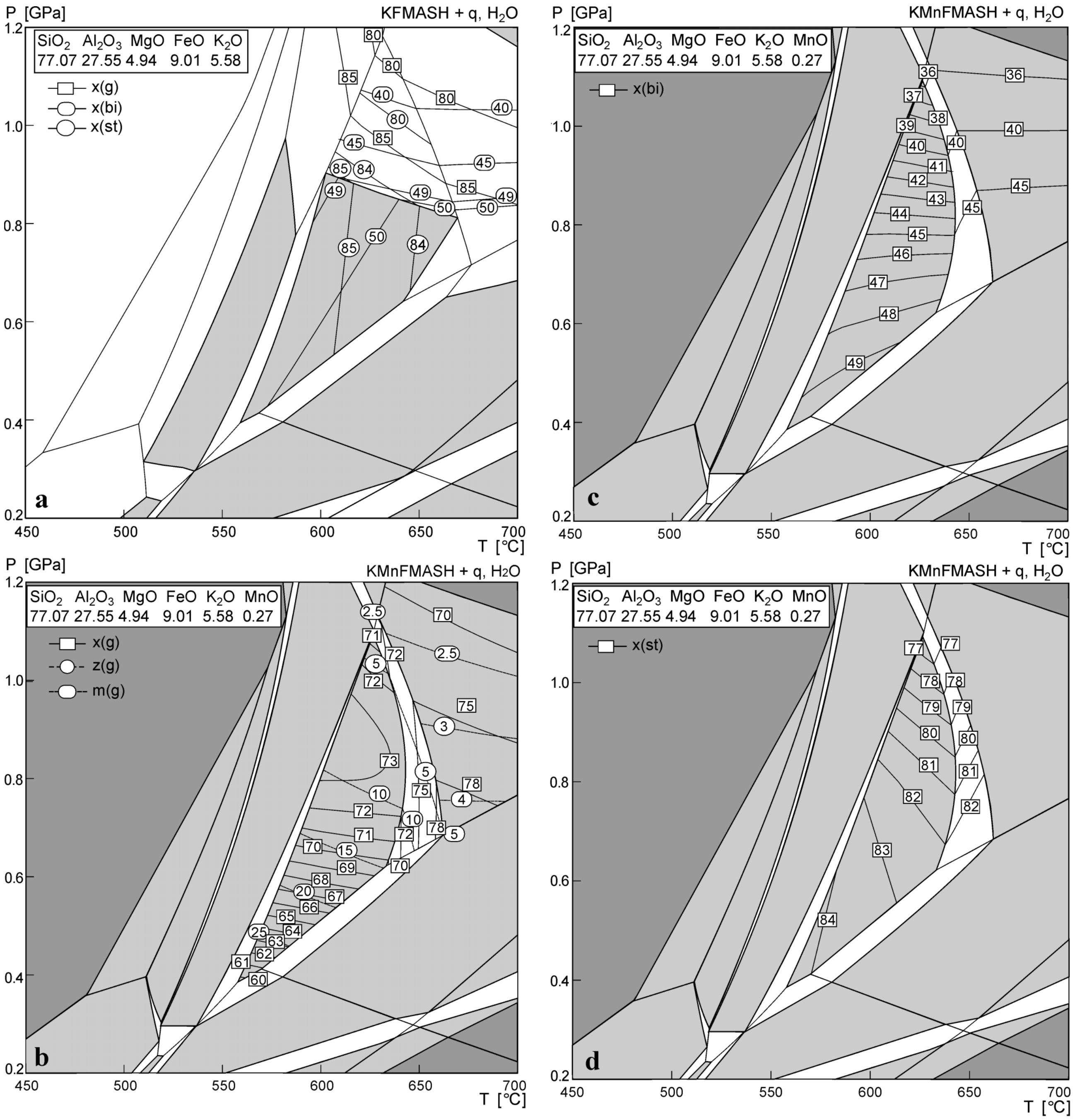

Fig. 7. Mineral composition isopleths in KFMASH (**a**) and KMnFMASH systems for garnet (**b**), biotite (**c**) and staurolite (**d**). X(i) is Fe^{2+}/(Fe^{2+} + Mg) in phase(i) in Fig. 7a, and Fe^{2+}/(Fe^{2+} + Mg + Mn) in Fig. 7b,c and d.

cannot incorporate important Na-Ca phases such as plagioclase, or zoisite, and cannot model garnet and white mica chemical compositions properly. To model the real mineralogical features of the studied sample, we constructed NCKFMASH and NCKMnFMASH pseudosections using THERMOCALC. The main feature of NCKFMASH pseudosection (Fig. 6a) is the appearance of plagioclase at about 450 °C and 0.3 GPa. It is stable up to 1.1 GPa at 670–700 °C. Paragonite is stable at the high-pressure part of the *P-T* pseudosection; at lower pressures white mica ('muscovite') has an increased paragonite component instead. Biotite lower stability is shifted to somewhat higher temperatures. The staurolite stability field is not changed. The calculated peak *P-T* range is mainly covered by garnet-biotite-kyanite-muscovite-plagioclase and garnet-biotite-kyanite-muscovite in strong accordance with petrographic data. The addition of MnO to the system (KMnFMASH) has the same effect such as in the case of KFMASH–KMnFMASH. Garnet stability expands to lower pressures at the expense of biotite and chlorite (Fig. 6b), with the result that all assemblages in the studied *P-T* range contain garnet.

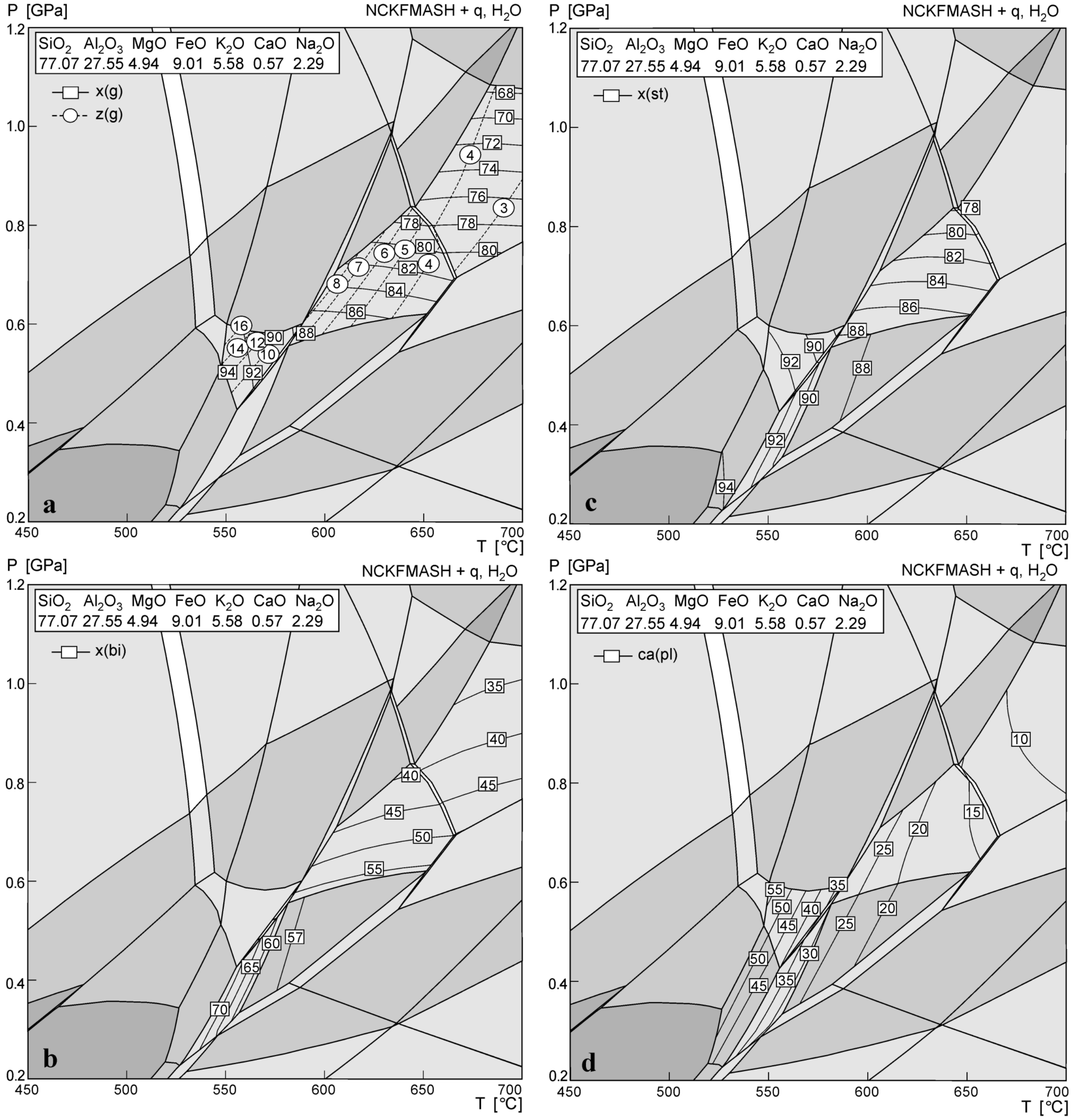

Fig. 8. Mineral composition isopleths in NCKFMASH for garnet (**a**), biotite (**b**), staurolite (**c**) and plagioclase (**d**). X(i) is $Fe^{2+}/(Fe^{2+}+Mg)$ in phase(i), z(g) is $Ca/(Ca+Fe^{2+}+Mg)$ in garnet, ca(pl) is the An content in plagioclase.

Mineral composition isopleths calculated with THERMOCALC

Quantitative phase diagram calculations (pseudosections) are powerful tools as the mineral compositions of various phases in question can be calculated at any P and T and compared with 'real' compositions measured, for example, with electron microprobe (EMP). In this chapter the composition isopleths of garnet, biotite, staurolite and plagioclase are presented using THERMOCALC in the systems KFMASH, KMnFMASH, NCKFMASH and NCKMnFMASH, respectively. The KFMASH system is appropriate for modelling the Fe-Mg partitioning relationships in Fe-Mg phases (i.e. biotite, staurolite), but cannot quantitatively model garnet composition or the effect of Al-rich Na- and Ca-bearing phases (i.e. plagioclase, zoisite) on mineral stability.

KFMASH system

The x(st) [$=Fe^{2+}/(Fe^{2+}+Mg)$] isopleths in the biotite-staurolite-muscovite field are strongly T dependent, similarly to x(bi). When garnet is introduced, namely in garnet-biotite-staurolite-muscovite, the isopleths change dramatically, they show slightly negative slope (Fig. 7a). The same holds true for garnet and biotite isopleths in garnet-biotite-muscovite field. Isopleths for measured garnet and biotite compositions intersect at around 670–690 °C and 0.8–0.95 GPa matching fairly well with peak conditions calculated (650±30 °C and 0.9±0.1 GPa). Biotite inclusions in staurolite have x(bi)=0.38–0.41 presuming higher-P conditions. Staurolite x(st) isopleths yield *P-T* conditions at around 650 °C and 0.9 GPa.

KMnFMASH system

X(g) [$=Fe^{2+}/(Fe^{2+}$+Mg+Mn)] isopleths in garnet-biotite-staurolite-muscovite field show an interesting feature (Fig. 7b). They have a very gentle negative slope with increasing x(g) until 0.8 GPa. Then the x(g)=0.73 isopleth has a turned U-shape and x(g) starts to decrease with a steep negative slope. The m(g) [=Mn/(Mn+Fe^{2+}+Mg)] isopleths do not show this effect. Garnet isopleths in the narrow garnet-biotite-staurolite-kyanite-muscovite field are nearly vertical, while in garnet-biotite-kyanite-muscovite they have a gentle negative slope with decreasing values. X(bi) [$=Fe^{2+}/(Fe^{2+}$+Mg+Mn)] isopleths are strongly P-dependent aside from the garnet-biotite-staurolite-kyanite-muscovite field (Fig. 7c). X(st) [$=Fe^{2+}/(Fe^{2+}$+Mg+Mn)] isopleths have a steep positive slope in garnet-biotite-staurolite-kyanite-muscovite field, while in the upper part of the garnet-biotite-staurolite-muscovite field they feature a steep negative slope (Fig. 7d). This steepness becomes almost vertical then turns into a positive slope near the area where the x(g) isopleths change their slope. The x(g) isopleths are lower in the pseudosections than those measured, while m(g) isopleths are higher. Calculated biotite and staurolite isopleths weakly match the measured ones.

NCKFMASH system

The z(g) [=Ca/(Ca+Fe^{2+}+Mg)] isopleths are nearly vertical and decrease with increasing T from 16 to 3 in the T range of 550–680 °C (Fig. 8a). They closely match the measured ones in garnet-biotite-kyanite-muscovite (3–4). The areas with higher Ca content in garnet (10) probably formed at lower T. On the other hand, the x(g) [$=Fe^{2+}/(Fe^{2+}$+Mg)] isopleths are lower than the measured ones similarly to the KMnFMASH system. This is assigned to diffusional re-equilibration. The x(bi) isopleths are strongly P-dependent in garnet-biotite-staurolite-muscovite-plagioclase and garnet-biotite-kyanite-muscovite-plagioclase, but change drastically in biotite-staurolite-plagioclase (Fig. 8b). They are nearly uniform with x(bi)=0–57–0.58. The x(bi) isopleths in biotite-chlorite-staurolite-muscovite-plagioclase are subvertical showing strong T-dependence. The x(st) isopleths have a similar behaviour to biotite ones (Fig. 8c). The ca(pl) [=Ca/(Ca+Na)] isopleths decrease intensively with increasing T (Fig. 8d). The calculated isopleths in the peak assemblage closely match the measured ones (10–15).

NCKMnFMASH system

The x(g) isopleths are lower than the measured ones in the peak assemblage. The m(g) [=Mn/(Mn+Fe^{2+}+Mg+Ca] and z(g) [=Ca/(Ca+Fe^{2+}+Mg+Mn)] isopleths fairly match the measured ones. They yield *P-T* conditions at around 630–660 °C and 0.9–1.0 GPa (Fig. 9a). The slopes of the m(g) isopleths are positive in the pseudosection with values decreasing with T. The z(g) isopleths have a gentle positive slope in the garnet-biotite-kyanite-muscovite-plagioclase and garnet-biotite-staurolite-muscovite-plagioclase fields, but become steeper in garnet-biotite-chlorite-staurolite-muscovite-plagioclase. The slopes turn negative in garnet-chlorite-staurolite-muscovite-plagioclase. The x(g) isopleths are subvertical in this field and become gently negative in the biotite-bearing fields. The biotite and staurolite isopleths are similar to the ones in NCKFMASH in chlorite-free assemblages (Fig. 9b and c). They turn nearly vertical when chlorite becomes part of the mineral assemblage. They fairly match the measured compositions in the peak assemblage. The ca(pl) isopleths have a similar slope to the NCKFMASH ones but plagioclase is Ca-poorer in this system at the same *P-T* conditions (Fig. 9d). Ca(pl) is between 10 and 16 in the peak assemblage fitting well with the measured plagioclase compositions.

Discussion

PERPLEX vs. THERMOCALC pseudosections in KFMASH and KMnFMASH systems

Quantitative phase diagrams (pseudosections) were calculated in the *P-T* range 0.2–1.2 GPa and 450–700 °C in the systems KFMASH and KMnFMASH for a representative garnet-staurolite mica schist sample from the basement of the southwestern part of the Pannonian Basin (Figs. 4 and 5) with PERPLEX and THERMOCALC computer programs. Despite the fact that the two programs use different ways of approaching the calculation of mineral equilibria involving solid solutions, one should expect the same results with the two calculation methods, especially when the same mineral solution models are used. Hoschek (2004) pointed out several differences in the resulting *P-T* pseudosections when he compared PERPLEX, DOMINO and THERMOCALC for a kyanite eclogite. Our results have similar conclusions. The KFMASH pseudosections show similarities in the medium-pressure range (0.5–0.8 GPa). Both are dominated by the assemblages biotite-staurolite-muscovite, biotite-staurolite-sillimanite-muscovite, biotite-sillimanite-muscovite and biotite-staurolite-kyanite-muscovite (all assemblages have quartz in excess). The same holds true for the high-pressure part. There are some differences in the low-pressure region. This could be due to the different Al_2SiO_5 triple point calibrations used by the two software packages, but additional, currently unknown causes can be assumed. In the KMnFMASH system the medium- and high-pressure parts of the *P-T* diagrams match each other closely. The differences in the low-pressure regions are probably due to

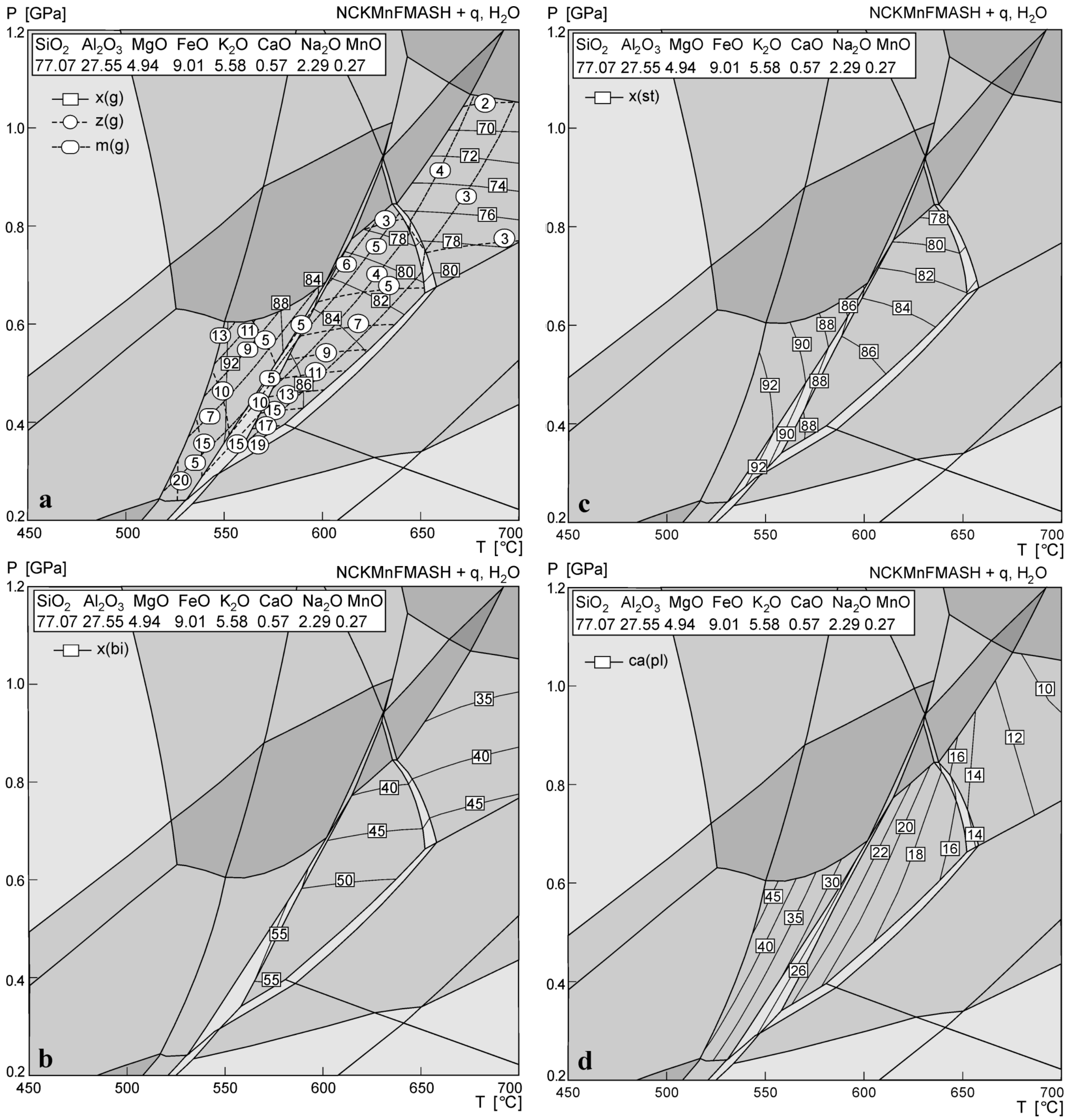

Fig. 9. Mineral composition isopleths in NCKMnFMASH for garnet (**a**), biotite (**b**), staurolite (**c**) and plagioclase (**d**). X(i) is Fe^{2+}/(Fe^{2+} + Mg) in phase(i), z(g) is Ca/(Ca + Fe^{2+} + Mg) in garnet m(g) is Mn/(Mn + Fe^{2+} + Mg + Ca) in garnet, ca(pl) is the An content in plagioclase.

the above-mentioned facts and the different garnet solid solution models used. Garnet is stable from 520 °C in the whole THERMOCALC diagram, while in the PERPLEX calculations garnet-free assemblages are present at 520–540 °C at 0.3 GPa. Overall, the *P-T* pseudosections calculated with both methods yield the same information on the evolution of the studied sample. The peak *P-T* conditions calculated with thermobarometric methods (650±30 °C and 0.9±0.1 GPa, Horváth & Árkai 2002) are confirmed by the mineral assemblage garnet-biotite-kyanite-muscovite in both systems, the stability field covered is larger in the Mn-bearing systems.

P-T path of the Uszi-2 mica schist

Since garnets contain staurolite inclusions, and these staurolites have biotite and quartz included in them, a *P-T* path can be established. This will be discussed in this chapter with the critical investigation of the long-standing debate whether these mica schists had stable andalusite during their *P-T* history (Szederkényi 1984; Horváth & Árkai 2002; Lelkes-Felvári et al. 2003). The *P-T* pseudosection calculated in the NCKFMASH system is used, because it can model garnet composition and the effect of Na- and Ca-bearing phases (plagioclase, paragonite, and zoisite) commonly found in metapelites (Fig. 10). The main difference between NCKFMASH and NCKMnFMASH systems is the presence of garnet at low-pressure (< 0.4 GPa) in the latter. Since the Sps content in our garnets are generally low (1–3) and the other rock-forming minerals (biotite, staurolite) have MnO contents near the detection limit of EMP, the system NCKFMASH is enough to quantitatively model the mineralogical and mineral compositional changes in our sample during the *P-T* evolution. Within the framework of the NCKMnFMASH system the outlined *P-T* path (see below) would be similar to the NCKFMASH system, only the garnet-free assemblages would be garnet-bearing.

Szederkényi (1984) described the fine-grained kyanite aggregates as pseudomorphs after andalusite. If this holds true then the prograde *P-T* path starts from biotite-staurolite-andalusite-muscovite-plagioclase or biotite-andalusite-muscovite-plagioclase (point I in Fig. 10). There are several boreholes in the BCU near to the study area with Variscan andalusite-bearing mica schists and gneisses. Ar-Ar muscovite age data are 305–322 Ma in these rock types (Lelkes-Felvári et al. 2003). The pseudomorphs could also represent former sillimanite according to Lelkes-Felvári et al. (2003). The *P-T* path barely touches the biotite-staurolite-sillimanite-muscovite-plagioclase field, so this assumption is questionable. Horváth & Árkai (2002) described sillimanite-bearing mica schist from the Algyő-54 borehole located about 3 km north of the Uszi-2 borehole. Garnet zoning patterns and thermobarometric data indicate growth during prograde conditions from 610 °C and 0.4 GPa to peak *P-T* conditions at 650–680 °C and 0.5–0.6 GPa. Another possibility is that the pseudomorphs were staurolites (point II). Petrographic evidence shows that staurolite porphyroblasts occurring in the matrix are replaced by kyanite. In this case, the *P-T* path starts from chlorite-staurolite-muscovite-plagioclase or biotite-chlorite-staurolite-muscovite-plagioclase and passes the same fields. No chlorite inclusions were found in staurolite beside biotite and quartz. So far there is no conclusive evidence to decide between the two possibilities. The assemblage biotite-staurolite-quartz with matrix muscovite and plagioclase is stable at 560–650 °C and 0.35–0.6 GPa in NCKFMASH. This is the earliest detectable mineral assemblage in the sample. The chemical compositions of the inclusion biotites and the host staurolites do not match with the calculated ones in the biotite-staurolite-muscovite-plagioclase field. Instead, they reflect compositions in the garnet-biotite-staurolite-muscovite-plagioclase field suggesting chemical re-equilibration during the prograde evolution of the rock at about 620–640 °C and 0.7–0.8 GPa. Lelkes-Felvári et al. (2003) also mentioned K-feldspar porphyroclasts with relic staurolite, andalusite (now pseudomorphed by kyanite) and garnet as a pre-tectonic assemblage with respect to their S_2 defined by fine-grained biotite, muscovite, plagioclase and quartz. We were unable to find K-feldspar in our sample, so this assumption could not be confirmed by our study. In the calculated pseudosections there is no joint stability field for staurolite, andalusite and K-feldspar with or without garnet which is in accordance with other published grids (e.g. White et al. 2001; Wei et al. 2004). The lowest T where K-feldspar enters the parageneses is about 630 °C at low-pressure conditions, and even higher at high-pressure. The K-feldspar is most probably a relic of an earlier high-T metamorphic event. Continuous T increase in the garnet-biotite-staurolite-muscovite-plagioclase field followed, and then kyanite appeared at the expense of staurolite. The peak conditions represented by garnet-biotite-kyanite-muscovite-plagioclase were reached at about 650–670 °C and 0.7–0.8 GPa. The observed prograde path is similar to the one in Horváth & Árkai (2002); they used the Gibbs method on zoned garnets (Spear & Menard 1989) on mica schist samples from Ferencszállás (4 km east from the present study). After the thermal peak the cooling path passed the garnet-biotite-staurolite-muscovite-plagioclase field again and ended in chlorite-bearing assemblages. Since no plagioclase breakdown was observed, the cooling path was below 0.6 GPa at 600 °C, and was above 0.4 GPa due to the absence of sillimanite. The *P-T* path presented here is outlined in Fig. 10, the dashed line indicates parts of the *P-T* path which are not constrained by mineral chemical data.

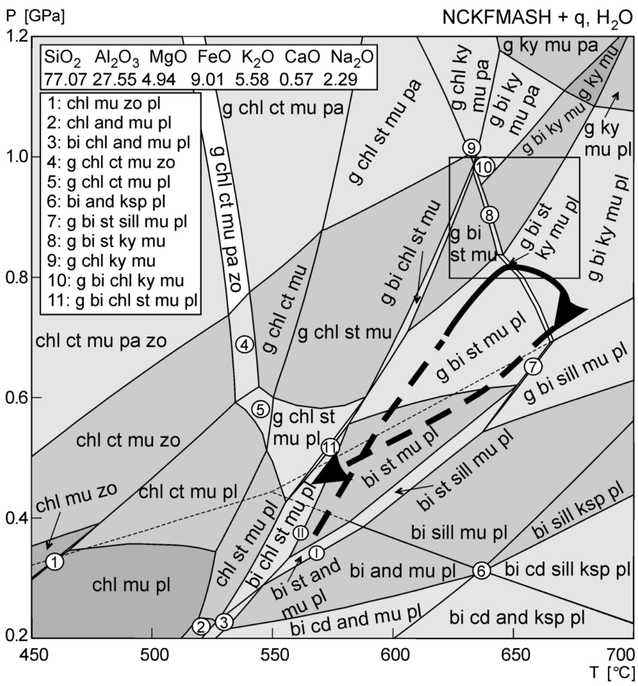

Fig. 10. *P-T* path of the Uszi-2 mica schist sample. Bold arrow indicates the outlined *P-T* path, the dashed line indicates the uncertain parts (see text for explanation). Box indicates calculated peak *P-T* conditions after Horváth & Árkai (2002). Roman numbers (I and II) are described in the text.

Several authors published Eo-Alpine Ar-Ar ages on muscovites from the Algyő basement-high (85.5±1.2 Ma in Lelkes-Felvári et al. 2003; 68.4–84.3 Ma in Balogh &

Pécskay 2001). These data are interpreted as cooling ages. The oldest ages from this tectonic unit were determined by Sm-Nd analyses from garnet- and kyanite-bearing mylonitic rocks (Lelkes-Felvári et al. 2002, 2003). The isochron calculated from a garnet concentrate yielded a Permian age of 273±7 Ma. Unfortunately, no chemical data from garnet are presented in these papers. Taking into consideration these features the Permian ages obtained by the above-mentioned authors could be mixed Variscan and Alpine ages or represent a separate thermal event. Horváth & Árkai (2002) showed strongly zoned garnets from the Algyő basement-high. They evaluated the core of the zoned garnets as possible relics of a Variscan metamorphic event, and calculated 520–560 °C and 0.8–1.0 GPa for the Ca-rich outer core using inclusions of muscovite, plagioclase and quartz. In the calculated NCKFMASH pseudosection (and in NCKMnFMASH as well) garnet-chlorite-chloritoid-muscovite-paragonite would be the stable assemblage in the studied sample which is not confirmed in this study. A polymetamorphic evolution with garnet-staurolite (±andalusite/sillimanite) in the first (Variscan) cycle, and garnet-kyanite in the second (Eo-Alpine) is evaluated here. The Variscan cooling ages from andalusite-bearing mica schists outside the Algyő basement-high support this idea. On the other hand, there is no conclusive evidence for the Variscan age of the andalusites in the studied sample, and within the framework of the presented *P-T* pseudosections both andalusite and kyanite (and even sillimanite) can be the products of a single (Eo-Alpine) tectono-metamorphic event.

Conclusions

1 — *P-T* pseudosections (quantitative phase diagrams) in the KFMASH and KMnFMASH systems were calculated with PERPLEX and THERMOCALC from garnet-staurolite mica schist originating from the basement of the Pannonian Basin (Hungary). The resultant pseudosections are similar to each other highlighting the effectiveness of both software packages. Differences only occur in the low-pressure regions. The peak *P-T* conditions calculated with thermobarometric methods (650±30 °C and 0.9±0.1 GPa, Horváth & Árkai 2002) are confirmed by the mineral assemblage garnet-biotite-kyanite-muscovite in both systems. The mineral composition isopleths in the KFMASH, KMnFMASH, NCKFMASH and NCKMnFMASH systems mostly model the mineral chemical changes.

2 — The *P-T* path of the Uszi-2 mica schist was outlined in the NCKFMASH system. The biotite- and quartz inclusions in host staurolite with matrix muscovite and plagioclase are stable at 560–650 °C and 0.35–0.6 GPa. The mineral compositions reflect chemical re-equilibration in the garnet-biotite-staurolite-muscovite-plagioclase field during the prograde evolution of the rock at about 620–640 °C and 0.7–0.8 GPa. During simultaneous *P-T* increase garnet started to form at about 0.6 GPa in the garnet-biotite-staurolite-muscovite-plagioclase field, and then kyanite appeared at the expense of staurolite. The peak conditions in garnet-biotite-kyanite-muscovite-plagioclase-quartz were reached at about 650–670 °C and 0.7–0.8 GPa. After the T peak the cooling path passed the garnet-biotite-staurolite-muscovite-plagioclase-quartz field again and ended in chlorite-bearing assemblages. Since no plagioclase breakdown was observed, the cooling path was under 0.6 GPa at 600 °C, and was over 0.4 GPa due to the absence of sillimanite. The observed *P-T* path is similar to the one published by Horváth & Árkai (2002).

3 — From the study area andalusite and sillimanite as possible Variscan phases were speculated by Szederkényi (1984) and Lelkes-Felvári et al. (2003). No petrographic evidence was found for the existence of these phases in the studied sample. All three Al_2SiO_5 polymorphs are present in the study area; so the possibility of their formations during one single *P-T* path could not be excluded. Together with published Ar-Ar age data on matrix muscovite (85.5±1.2 Ma) from the Uszi-2 sample, the presented *P-T* pseudosections also support the Eo-Alpine age of amphibolite facies metamorphism in the basement of the Tisza Unit (southwestern Pannonian Basin).

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