Implications of micro-compositions of garnet and biotite from high-grade meta-pelites*

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Abstract Based on detailed studies on the compositional zoning of garnet and biotite in pelitic rocks from the Jingshan group of granulite facies in north Jiaodong, P-T pseudosections with isopleths of Fe/(Fe + Mg) in garnet and biotite were calculated in the KFMASH system for two representative rocks of sillimanite-garnet-cordierite-biotite gneiss ($V_{bi}/V_g > 1$) and sillimanite-garnet gneiss ($V_{bi}/V_g < 0.2$) using the software THERMOCALC and the internally consistent thermodynamic dataset. With a comparison of the calculated Fe/(Fe + Mg) values in garnet and biotite in the peak P-T fields constrained by peak mineral assemblages with the measured ones, it is concluded that the coarse garnet crystals with diffusion zoning from high grade meta-pelites can preserve their peak compositions even when they have experienced a cooling event, and that biotite crystals surrounded by felsic minerals in biotite-rich rocks with $V_{bi}/V_g > 1$ can nearly preserve their peak compositions, and biotites in garnet-rich rocks with $V_{bi}/V_g < 0.2$ cannot preserve their peak compositions due to the influence of grain-boundary fluid.

Keywords: high-grade meta-pelites, THERMOCALC, P-T pseudosection, peak compositions of garnet and biotite.

Metamorphic *PTt* path has been a main point in recent metamorphic geology, and determination of reliable PT conditions for each metamorphic stage is the key to construct a reliable *PTt* path. At present, the most commonly-used method to get metamorphic PT conditions is geothermo-barometry. For example, the garnet-biotite thermometry is widely used for meta-pelites. However, garnet in high-grade meta-pelites is usually developed with diffusion zoning and biotite does not have uniform compositions[1]. Therefore, it has been disputed to use a garnet-biotite thermometer to get peak temperature. A focus disputation is whether garnet and biotite could preserve their peak compositions or garnet- and biotite-involving thermobarometries could yield peak PT conditions if they are subjected to a cooling event. According to mathematically modelling, Spear et al.[2,3] suggested that the peak compositions of garnet and biotite had been altered violently during the cooling stage and none of them could preserve peak compositions if abundant grain-boundary fluids are present. Detailed studies on microarea compositions of garnet from high-grade metamorphic rocks by Florence and Spear[4] and O'Brien[5] showed that garnet is developed with different diffusion composition profiles when contacting different minerals. This indicates that migration of cations such as Fe and Mg is rather slow among minerals, and that grain-boundary fluids are lacking in rocks or migration distance is rather limited during the cooling stage. Therefore, the garnet and biotite crystals which do not contact each other could preserve peak compositions. On the basis of study on compositional zoning of garnet and biotite from pelitic granulite of Jingshan group in north Jiaodong peninsula, Zhou et al.[1] suggested the Fe-Mg exchange between garnet and biotite or other mafic minerals mainly results from the interface transfer with the grain-boundary fluids playing an assistant role. As a consequence, only some very coarse garnet crystals could preserve peak compositions. Moreover, micro-area compositions of variously sized garnet and biotite crystals neighbored with different minerals were chosen to calculate temperature by a garnet-biotite geothermometer. The calculation results indicated that in biotite-rich rocks with $V_{bi}/V_g > 1$, the cores of matrix biotites which are surrounded by felsic minerals and far away from garnet crystals could preserve peak compositions, and in the biotite-poor rocks with $V_{bi}/V_g < 0.2$, the peak compositions of biotite have been completely changed due to the influence of grain-boundary fluids[6]. All these conclusions were yielded from the traditional petrologic studies, which are

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rather difficult to be proved. With development of the internally consistent thermodynamic data set[7] and the software THERMOCALC, it is possible to forward model an metamorphic evolution of a rock, providing a new method to prove or resolve some petrologic issues[8]. In this paper, we calculate P-T pseudosections with Fe/(Fe + Mg) isopleths of garnet and biotite for two representative pelitic granulite samples from the Jingshan group in the KFMASH system. These pseudosections can show all the probable mineral assemblages and mineral compositions with P-T conditions for specified rocks. Comparing the calculated Fe/(Fe + Mg) values of garnet and biotite in the peak P-T range with the measured Fe/(Fe + Mg) ones, it is concluded that both garnet and biotite could preserve their peak compositions even when they had experienced a cooling event.

1 Geological setting and petrography

The Jingshan group in the Jiaobei terrane lies in the north-central part of the Jiaodong Peninsula, and is an important member of the Jiaoliao Palaeoproterozoic tectonic belt. The Jingshan group is mainly composed of khondalitic sediments including Al-rich schist/gneiss, felsic gneiss and marble intercalated with minor mafic granulites and amphibolites, which are metamorphosed to high amphibolite and granulite facies[9,10]. The Al-rich schist/gneiss occurs as thin layers of dozens of centimeter to meter in the extensive felsic gneisses. It has been dated that the Jingshan group was deposited at about 2.1—2.3 Ga[11] and metamorphoed during 1680—1720 Ma[12]. According to the ratios of garnet and biotite volume contents (V_{bi}/V_g), two representative samples were selected for the study: one is a sillimanite-garnet-cordierite-biotite gneiss with $V_{bi}/V_g > 1$ and the other is a sillimanite-garnet gneiss with $V_{bi}/V_g < 0.2$. The former is mainly composed of garnet (15%), sillimanite (10%), cordierite (15%), biotite (20%), K-feldspar (20%), plagioclase (5%—10%) and quartz (10%). Garnets generally occur as euhedral porphyroclasts of 1—4 mm in size and are often surrounded by biotite, cordierite and K-feldspar. Sillimanite is often prismatic and fibrous. The latter is mainly composed of garnet (30%—35%), sillimanite (15%—20%), K-feldspar (15%—20%), plagioclase (10%), quartz (10%) and biotite (5%). Garnets generally occur as euhedral porphyroclasts of 2—6 mm with a few mineral inclutions. Sillimanites are often prismatic and oriented along the main foliation.

2 Micro-compositions of garnet and biotite

Using an electronic probe, the micro-compositions of both garnet and biotite in the two samples were analyzed, which is presented in Table 1. The analyzed garnet is characterized by diffusion zoning

Table 1. Representative micro-compositions of garnets ($d > 1.5$ mm) and biotites from pelitic granulite of the Jingshan group

Sample	Sillimanite-garnet-cordierite-biotite gneiss (Sample N27-1)											Sillimanite-garnet gneiss (Sample P34)					
location	g(r)	g(m)	g(c)	g(m)	g(r)	g(r)	bi(c)	bi(r)	bi(c)	bi(r)	bi(c)	g(c)	g(m)	g(r)	bi(c)	bi(r)	bi(c)
Nearby mineral	bi	bi	bi	kf	kf	cd	g	g	g	g	fel	bi	q	bi	g	g	fel
SiO_2	36.57	38.57	36.51	36.73	36.98	36.44	35.52	36.76	39.05	37.58	35.59	36.44	36.54	38.17	39.36	39.56	39.74
TiO_2	0.16	0.15	0.00	0.05	0.23	0.04	3.38	3.36	3.20	3.53	3.25	0.13	0.11	0.00	4.65	3.74	4.91
Al_2O_3	22.80	21.15	22.94	22.31	22.35	21.26	18.35	17.92	17.70	16.88	19.43	23.27	24.19	22.77	15.95	15.94	14.12
⟨FeO⟩	33.90	32.34	32.31	32.21	32.40	35.05	15.41	15.00	11.69	13.43	16.57	27.00	26.54	27.60	7.56	7.60	8.59
MnO	0.79	1.11	0.69	0.93	0.88	0.78	0.03	0.00	0.00	0.12	0.00	0.49	0.38	0.42	0.00	0.03	0.00
MgO	4.15	4.91	6.25	6.23	5.97	5.00	12.65	12.78	14.07	14.21	11.83	11.51	11.28	10.13	18.45	19.18	16.68
CaO	1.90	1.87	1.51	1.75	1.41	1.74	0.00	0.00	0.00	0.00	0.00	1.14	0.93	1.00	0.00	0.00	0.00
Na_2O	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.12	0.15	0.10	0.02	0.01	0.00	0.11	0.09	0.07
K_2O	0.00	0.00	0.00	0.00	0.04	0.00	9.35	9.11	9.09	9.12	8.05	0.07	0.020	0.02	8.87	8.76	10.90
Total	100.27	100.10	100.21	100.26	100.26	100.31	95.04	95.01	94.92	95.02	94.82	100.07	100.00	100.11	94.95	94.90	95.01
Si	2.907	3.043	2.880	2.901	2.917	2.918	2.670	2.738	2.847	2.778	2.660	2.810	2.807	2.932	2.820	2.833	2.897
Ti	0.010	0.009	0.000	0.003	0.014	0.002	0.191	0.188	0.175	0.196	0.183	0.008	0.000	0.000	0.251	0.201	0.269
Al	2.137	1.967	2.133	2.078	2.079	2.007	1.626	1.574	1.521	1.471	1.712	2.115	2.191	2.062	1.347	1.346	1.213
Fe	2.255	2.135	2.132	2.129	2.138	2.348	0.969	0.935	0.713	0.831	1.036	1.742	1.706	1.773	0.453	0.455	0.524
Mn	0.053	0.074	0.046	0.062	0.059	0.053	0.002	0.000	0.000	0.008	0.000	0.032	0.025	0.027	0.000	0.002	0.000
Mg	0.492	0.578	0.735	0.734	0.702	0.597	1.418	1.419	1.529	1.566	1.318	1.323	1.292	1.160	1.971	2.048	1.813
Ca	0.162	0.158	0.128	0.148	0.119	0.149	0.000	0.000	0.000	0.000	0.000	0.094	0.077	0.082	0.000	0.000	0.000
Na	0.000	0.000	0.000	0.008	0.000	0.000	0.000	0.000	0.017	0.022	0.014	0.003	0.000	0.000	0.015	0.013	0.010
K	0.000	0.000	0.000	0.000	0.004	0.000	0.897	0.866	0.846	0.860	0.768	0.007	0.000	0.002	0.811	0.801	1.014
X	0.821	0.787	0.744	0.744	0.753	0.797	0.406	0.397	0.318	0.347	0.440	0.568	0.569	0.605	0.187	0.182	0.224

The data were analyzed by the electron microprobe (EMX-SMT) at Jilin University. Operating conditions were 15 kV and 1×10^{-8} A with a point beam. (c) core, (r) rim, (m) mantle. Mineral symbols: bi, biotite; cd, cordierite; fel, felsic minerals; g, garnet; kf, K-feldspar; q, quartz. $X = Fe/(Fe + Mg)$

with the Mg content higher in the core and decreasing towards to the rim. While the patterns of the garnet zoning are varied, depending on the neighboring minerals. The garnet crystals show well-developed diffusion zoning with the lowest Mg content in the rim when they contact biotites, less-developed diffusion zoning with a moderate Mg content in the rim when contacting cordierite, and almost do not have zoning when contacting felsic minerals. The micro-compositions of biotites are also varied. The biotite crystals neighbored to garnet usually have higher Mg contents than those far away from garnet and are surrounded by felsic minerals. Moreover, the micro-compositions of biotite vary even in a single crystal, occasionally, with a slight compositional zoning. The Mg content in the rim is always somewhat higher than that in the core. These variations of garnet and biotite micro-compositions indicate that the Fe-Mg exchange between garnet and biotite or other mafic minerals mainly results from the interface transfer with the grain-boundary fluids playing a less important role. However, Fe and Mg could also be transferred through grain-boundary fluids because the weak diffusion zonings are found in the rims of some garnet crystals even when they contact felsic minerals. How the peak compositions of garnet and biotite are changed through the contact interface and the grain-boundary fluids during cooling stage needs to be quantitatively calculated with the pseudosection approach.

3 *P-T* projection in the KFMASH system

P-T projections are the familiar petrogenetic grids in the literature, showing the invariant and univariant equilibria in a PT space for all the bulk compositions in a model system. *P-T* projections are the bases for the other phase diagram calculations. On a consideration that the discussed pelitic granulites are poor in Mn and contain some CaO which is mainly distributed between garnet and plagioclase and affects a little the equilibria of the other minerals, we, the same as that in most literatures, choose the classic KFMASH (K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O) system to discuss the phase relations of the pelitic granulites. The PT range is selected as 650—950 ℃ and 4—14 kbar. For the subsolidus conditions, quartz and H_2O are assumed to be in excess, and for the suprasolidus conditions, only quartz is assumed to be in excess. The calculated *P-T* projection using THERMOCALC 3.1 is shown in Fig. 1, which consists of 5 invariant points and 34 univariant lines in the PT range of interest.

4 *P-T* pseudosections

Since *P-T* projections show all the phase equilibria in a PTX space for all the bulk compositions, it is impossible to see the phase relations for a specified rock in the *P-T* projections. So it is necessary to calculate pseudosections based on their specific bulk compositions. For example, *P-T* pseudosections can show all the probable mineral assemblages and mineral compositions in the P-T space for the discussed rocks.

Fig. 2 is the *P-T* pseudosection in the KFMASH system calculated for the sillimanite-garnet-cordierite-biotite gneiss (Sample N27-1) from the Jingshan group. The diagram is dominated by divariant, trivariant and quadrivariant fields with 5 univariant reactions. The dashed lines in the diagram are $X_{(g)}(=Fe/(Fe+Mg))$ isopleths of garnet and the dotted lines are $X_{(bi)}(=Fe/(Fe+Mg))$ isopleths of biotite. Fig. 2 shows that the $X_{(g)}$ and $X_{(bi)}$ values tend to decrease with increasing temperature in general. This conforms that garnet and biotite from high-grade metamorphic rocks always have a higher Mg content. The slopes of $X_{(g)}$ and $X_{(bi)}$ isopleths vary clearly with mineral assemblages. For instance, the slopes of both $X_{(g)}$ and $X_{(bi)}$ isopleths are rather steep in the divariant fields g-ms-bi-kf-liq, g-bi-kf-sill-liq and g-bi-cd-kf-liq, where the variations of $X_{(g)}$ and $X_{(bi)}$ values are mainly controlled by temperature. However, the slopes of the isopleths are flat in divariant fields g-ms-bi-ky, g-cd-kf-sill-liq and g-cd-kf-opx-liq where the variations of $X_{(g)}$ and $X_{(bi)}$ values are mainly controlled by pressure. This indicates that the contents of Mg and Fe in garnet and biotite are dependent on both PT conditions and mineral assemblages. When temperature is above ~850 ℃ and pressure is over ~8 kbar, biotite and cordierite disappear and the $X_{(g)}$ values tend to be invariant, being 0.536—0.539 and 0.532—0.536 in trivariant field g-kf-sill-liq and quadrivariant field g-sill-liq, respectively. The observed assemblage g-bi-cd-kf-sill-liq in the sillimanite-garnet-cordierite-biotite gneiss is univariant in the KFMASH, separating the two divariant fields g-bi-kf-sill-liq and g-bi-cd-kf-liq. The mole proportions of minerals yield a peak PT condition of 780—810 ℃ and 6—7 kbar (Fig. 2).

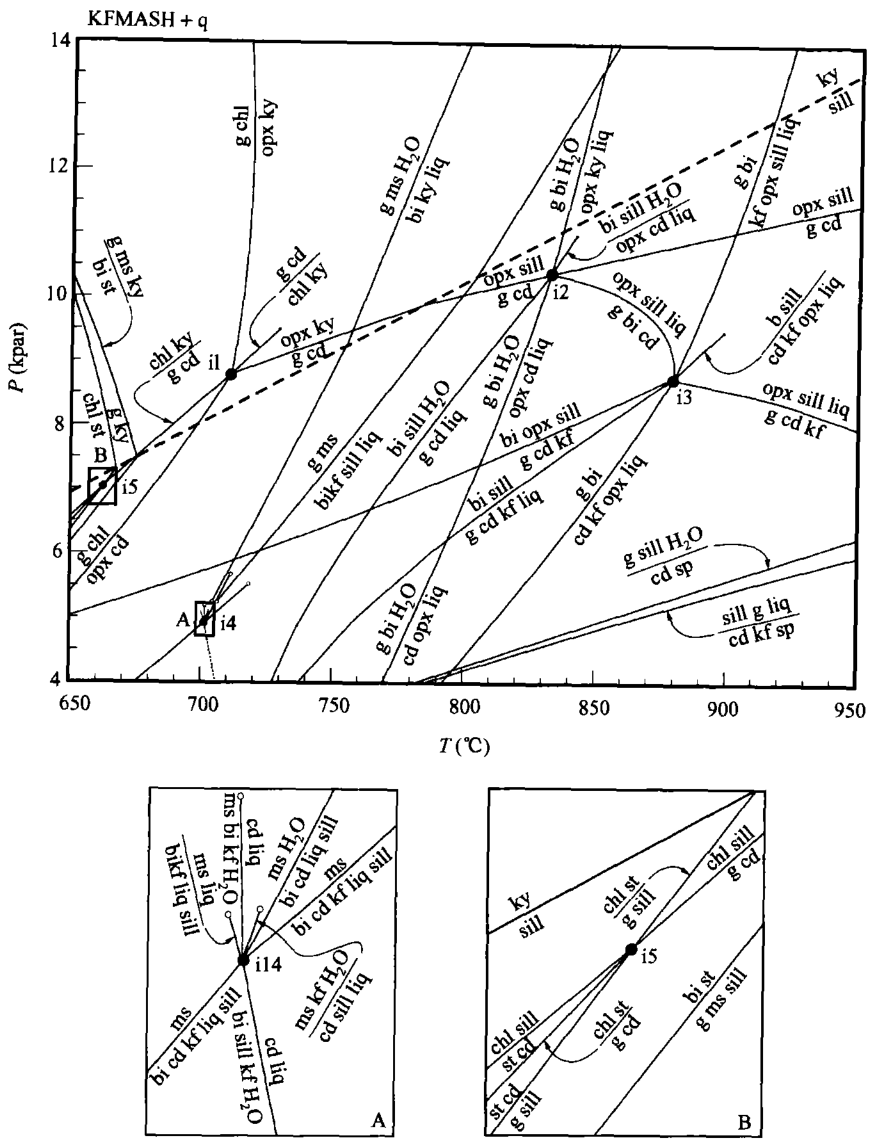

Fig. 1. *P-T* projection in the KFMASH system. For the subsolidus conditions, quartz and H_2O are assumed to be in excess, and for the suprasolidus conditions, only quartz is assumed to be in excess. i1-i5 are invariant points. Mineral symbols: bi, biotite; cd, cordierite; chl, chlorite; ct, chloritoid; g, garnet; H_2O, water; kf, K-felspar; ky, kyanite; liq, melt; ms, muscovite; opx, orthopyroxene; sill, sillimanite; sp, spinel; st, staurolite.

Fig. 3 is a *P-T* pseudosection calculated for the sillimanite-garnet gneiss (Sample P34) from the Jingshan group, which contains 6 univariant lines and is a little different from Fig. 2 especially in the lower temperature region. In the two figures, even the same mineral assemblages have different PT ranges. The observed mineral assemblage g-bi-kf-sill-liq in the sillimanite-garnet gneiss is divariant in the KFMASH. On the basis of the rather low content of biotite in the rock, it is concluded that the PT condition of the peak assemblage maybe lies in the higher temperature part of the divariant field g-bi-kf-sill-liq, adjacent to the biotite-out trivariant field g-kf-sill-liq. The peak PT condition is 830—850 ℃ and 8—9 kbar (see pane in Fig. 3) from the mole proportions of minerals.

5 Discussion and conclusion

Garnet and biotite are two of the most important minerals in metamorphic rocks. Whether they could preserve metamorphic peak compositions or not is the key point for getting reliable peak PT conditions by garnet- and biotite-involving thermo-barometries. As mentioned above, the detailed studies on micro-compositions of garnet and biotite indicate that the $X_{(g)}$ of 0.744 at the core of the analyzed coarse garnet crystal

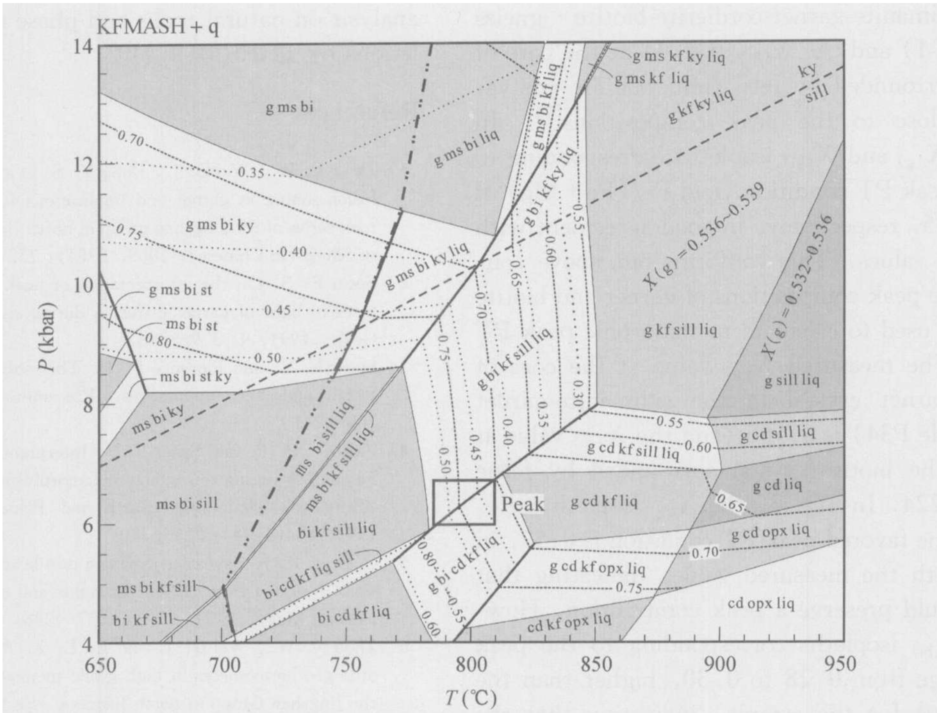

Fig. 2. *P-T* pseudosection for the sillimanite-garnet-cordierite-biotite gneiss (Sample N27-1) from the Jingshan group in the KFMASH system. For the subsolidus conditions, quartz and H_2O are assumed to be in excess, with the bulk composition of Al_2O_3:MgO:FeO:K_2O = 41.44:20.81:24.29:13.46 on a mole basis, and for the suprasolidus conditions, only quartz is assumed to be in excess, with the bulk composition of H_2O:Al_2O_3:MgO:FeO:K_2O = 21.22:32.64:16.40:19.14:10.60. The pseudosection shows divariant fields (unshaded), trivariant fields (lighter-shaded), quadrivariant fields (darker shaded). The dashed lines are $X_{(g)}$ (= Fe/(Fe + Mg)) isopleths of garnet and the dotted lines are $X_{(b)}$ (= Fe/(Fe + Mg)) isopleths of biotite. The thick lines are univariant lines. The thick double dotted dashed line is water-saturated solidus. The pane in the diagram is the peak PT range yielded from mineral assemblage. Mineral symbols refer to Fig. 1.

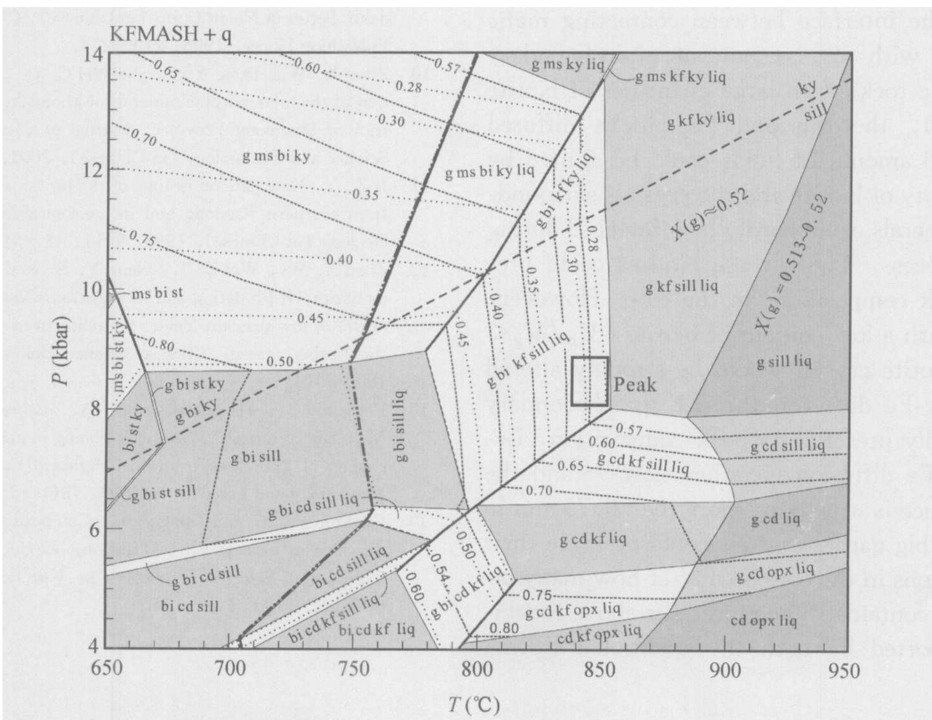

Fig. 3. *P-T* pseudosection for the sillimanite-garnet gneiss (Sample P34) from the Jingshan group in the KFMASH system. For the subsolidus conditions, quartz and H_2O are assumed to be in excess, with the bulk composition of Al_2O_3:MgO:FeO:K_2O = 42.92:23.04:25.08:8.95 on a mole basis, and for the suprasolidus conditions, only quartz is assumed to be in excess, with the bulk composition of H_2O:Al_2O_3:MgO:FeO:K_2O = 16.39:35.88:19.27:20.97:7.49. The others refer to Fig. 2.

in the sillimanite-garnet-cordierite-biotite gneiss (Sample N27-1) and the $X_{(bi)}$ of 0.44 at the core of the biotite surrounded by felsic minerals are equivalent to or close to the peak compositions[7]. In Fig. 2, the $X_{(g)}$ and $X_{(bi)}$ isopleths corresponding to the favored peak PT condition yield Fe/(Fe+Mg) of 0.75 and 0.45, respectively, in good agreement with the measured values. This conforms our above conclusion for the peak compositions of garnet and biotite which can be used to calculate metamorphic peak PT conditions. The measured $X_{(g)}$ value at the core of the coarse garnet crystal in the sillimanite-garnet gneiss (Sample P34) is 0.568, and the $X_{(bi)}$ value at the core of the biotite crystal surrounded by felsic mineral is 0.224. In Fig. 3, the $X_{(g)}$ isopleth corresponding to the favored peak PT condition is 0.57, in agreement with the measured value, indicating that the garnet could preserve a peak composition. However, the $X_{(bi)}$ isopleths corresponding to the peak condition range from 0.28 to 0.30, higher than the measured value for the sample, indicating that the compositions of the biotite have been altered and could not represent the peak, even the biotite crystal is far away from garnet and surrounded by felsic minerals. This probably results from the too low content of biotite in the sillimanite-garnet gneiss. The garnet diffusion zonings are mainly developed by the Fe-Mg exchange on the interface between contacting mafic minerals[4,5,13] with an assistant of grain-boundary fluids[1]. In the rocks with large quantities of biotite ($V_{bi}/V_g > 1$), the Mg and Fe cations diffused through a small amount of fluids could be diluted by the large quantity of biotite and the crystals surrounded by felsic minerals could hardly be influenced during the cooling process. Thus, these biotites could preserve their peak compositions in the core. However, in the rocks with a low content of biotite ($V_{bi}/V_g < 0.2$), each biotite crystal would be strongly altered by the the Mg-Fe diffusion through grain-boundary fluids and hardly preserve its peak composition. Because the Mg-Fe diffusion is rather slow[14] and the diffusion distance is usually no more than 0.75 mm in garnet[1], the big garnet crystals could preserve their peak compositions in the core no matter how many biotites the rock contains. Therefore, the above conclusions are supported by both the traditional EPMA analysis on natural rocks and phase equilibrium calculations by THERMOCALC.

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