

Sapphirine in the high-grade quartzofeldspathic gneiss of the Larsemann Hills, East Antarctica

Ren Liudong(任留东)¹, Wang Yanbin(王彦斌)¹ and Zhao Yue(赵越)²

¹ Institute of Geology, Chinese Academy of Geological Sciences, Beijing 100037, China

² Institute of Geomechanics, Chinese Academy of Geological Sciences, Beijing 100081, China

Received May 14, 2008

Abstract Study of sapphirine and related mineral association in the high-grade region of the Larsemann Hills, East Antarctica, shows that sapphirine of the area is characterized by its magnesio-, iron- and aluminum-rich, but silica-poor feature, and the obvious intra- and intergrain changes in compositions. The change is mainly manifested as the Tschermark substitution ($\text{Mg, Fe} + \text{Si} = 2\text{Al}$). In the high-grade metamorphism and anatexis process the multistage crystallization of minerals occurred and resulted in the complexity of the mineral association, such as the differentiation of leuco- and melano-components. Among them, the mafic-rich minerals formed earlier, and the differentiation of magnesio- and iron-components is responsible for the earlier presence of iron-rich minerals and later crystallization of magnesio-rich minerals, thus the successive associations of multistage occurred. The rock composition is an important but not critical factor to the occurrence of sapphirine. It is the mobilization of components that accounts for the formation of sapphirine. The multistage evolution of mineral association to some degree reflects the changing composition and opening of the setting. It is therefore deduced that the protolith from which sapphirine is derived is not necessarily magnesio-rich pelite. The heterogeneity of sapphirine composition is resulted from the various media, not the PT changes. Sapphirine formed at 840 ~ 880 °C, not the so-called ultrahigh temperature condition ($> 1000\text{ °C}$). Its formation is related to both the filtration and diffusion processes in high-grade metamorphism and anatexis.

Key words sapphirine, component mobilization, formation condition, Larsemann Hills.

1 Introduction

Sapphirine is a aluminum-rich and silica-deficient mafic mineral. It generally occurs in the granulite-facies rocks, especially in the Precambrian metamorphic rocks^[1]. The mineral can be found both in the low-pressure granulites and some high-pressure rocks, like its occurrence in the metamorphic rocks of the collisional HP/HT orogeny in the Paleozoic, in the magmatic rocks occasionally^[2]. The ultrahigh temperature sapphirine + quartz assemblage was firstly reported in the Napier Complex, East Antarctica^[3]. The association of sapphirine with other minerals usually reflects the special metamorphic setting. To date, the

is simply related with the case.

The sapphirine-bearing metamorphic rock contemporaneously contains sillimanite, hercynite and opaque minerals of Fe-Ti oxides which are usually accompanied by prismatic and cordierite (Fig. 2D). So the general association can include biotite, plagioclase, quartz, corundum, sapphirine, hercynite, tourmaline, prismatic, grandidierite, cordierite, magnetite, ilmenite, hematite and retrograde biotite and chlorite. Among them, the biotite, plagioclase and prismatic are rock-forming minerals, while hercynite and sapphirine are minor or trace in amount. The rock Tong *et al.* [6] reported has sapphirine and orthopyroxene, but borosilicates are absent. Here two samples (samples 126-9 and 20202) with sapphirine are described. The sample 126-9 is biotite plagiogneiss. Besides biotite, plagioclase and quartz, minor prismatic, corundum, hercynite, magnetite, zircon and monazite are present in the sample. While in sample 20202, there are assemblage prismatic, sillimanite, cordierite as the major phases and accessory minerals hercynite, hematite, ilmenite, quartz, zircon and monazite.

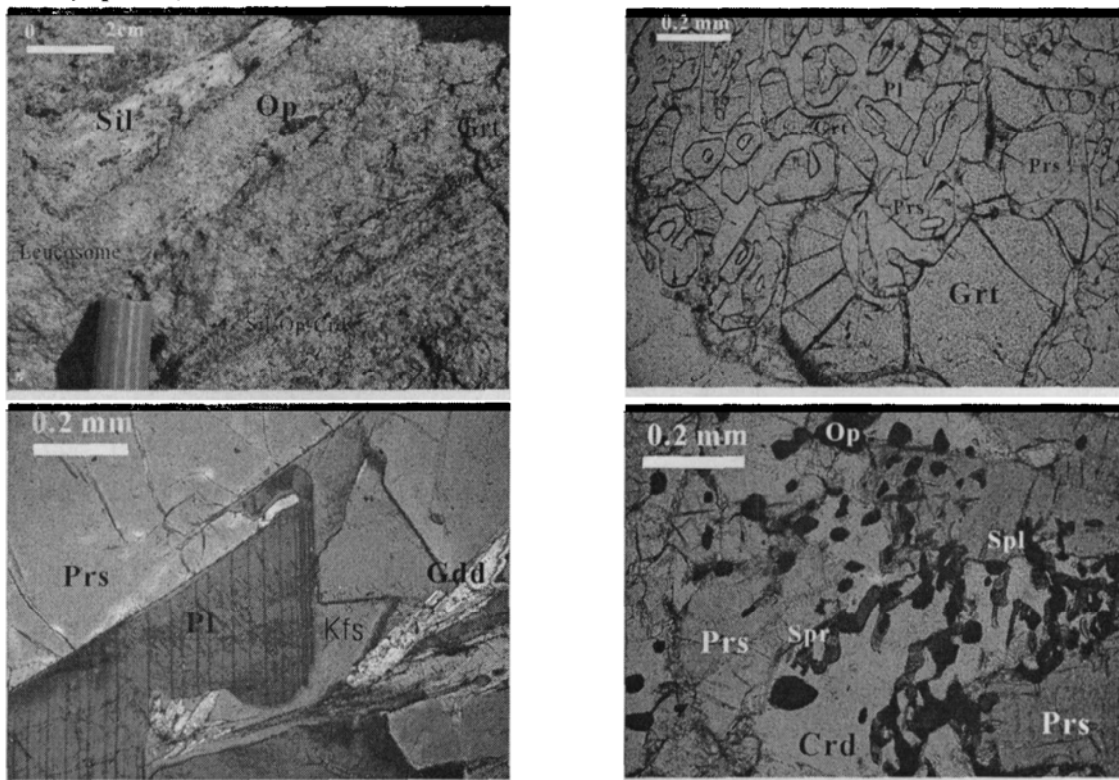


Fig. 2 Some mineral textures in the Larsemann Hills. A-outcrop scale texture between Sil, Grt, Op and Crd; B-garnet is substituted by Prs-Pl, plane polarized; C-the association of Prs-Pl and Gdd-Kfs, cross polarized; D- Spr-Prs-Crd-Spl-HIM-Pl assemblage in sample 20202, plane polarized.

Due to the progressive metamorphism, structure effect and local changes in compositions of rock and/or volatiles, the mineral crystallization sequence became rather complicated, such as accompanying sillimanite (fibrolite and subsequent prismatic sillimanite) in the biotite plagioclase, some oxides (magnetite, ilmenite, hematite or abbreviated as HIM and corundum) may form. After that, thin lensoid hercynite or sapphirine crystallized along the margin or fractures of magnetite (Fig. 3). In texture relationships, sapphirine and hercynite are intimately related to each other, so the two may form at nearly the same stage.

Tong *et al.* [6] noticed that sometimes hercynite is present as inclusion in sapphirine, but no reaction relations were observed between them. So hercynite and sapphirine may coexist and the former began to crystallize earlier, but the latter's crystallization ended late. The ilmenite exsolution in hematite is also shown as long lenses in shape, so the formation of both the Hcy and Spr are possibly postdated the crystallization of the oxides. In addition, Hcy-Spr are noticed to be included in prismatine (Fig. 2D), Hcy-Spr and Prs are overgrown the HIM assemblage, so Hcy, Spr and Prs may be derived from the Fe-Ti oxides. Grandierite and cordierite can be observed along the margin or cleavages of prismatine [13]. Finally, occurred small amount of sillimanite, tourmaline, biotite and chlorite, therefore there may be the following crystallization sequence. The minerals abbreviations are mainly after that of Kretz [14]:

Bt1 + Pl + Qtz ± Trn ± Ap → Fib → Sil-HIM ± Crn → Grt-Pl-Kfs → Spl-Spr ± Crn → Bt2 → Prs-Pl ± Qtz ± Mna ± Xnt, Gdd-Kfs ± Qtz → Crd → Trn-Bt-Sil → Phl-Chl

At each stage of the sequence the minerals crystallized nearly contemporaneously.

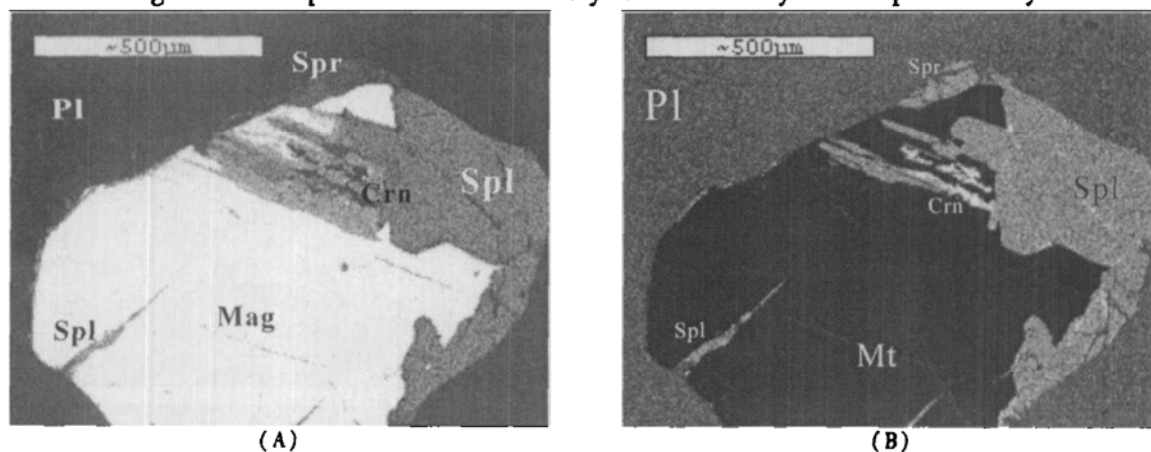


Fig. 3 BSE images of the assemblage Spr-Spl-Crn-Bt along the margin of magnetite in sample 126-9. A- Fe image; B-Al image. The sapphirine outline at the top corner of magnetite in Al-image(B) is obvious and blurred in Fe-image(A). The background is plagioclase(An9.5).

3 Composition feature

The compositions of sapphirine and related minerals are shown in table 1. The analysis is measured in the Electronic Microprobe Analysis Laboratory of the Institute of Mineral and Resources, CAGS, by the JEOL JXA8800 microprobe, with the electronic beam accelerating voltage 20KeV, and the current 2×10^{-8} A.

Compared with other localities in the world, like that from the Napier complex($X_{Mg} = 0.746$) [15], 2000, Eastern Ghats, India($X_{Mg} = 0.757 \sim 0.62$), and Greenland($X_{Mg} = 0.82 \sim 0.95$) [16], the sapphirine($X_{Mg} = 0.702 \sim 0.716$) in the study region has relatively high contents of Fe, Al and low Si, Mg (Table 1). Take the first spot as an example, the formula of sapphirine can be expressed as:

$(Mg_{2.575}Fe_{1.029}Al_{0.478}Ti_{0.003}Cr_{0.010}Mn_{0.001}Zn_{0.002})_{4.108}Al_{8.000}(Si_{1.309}Al_{0.691})_{2.000}O_{20}$ or $(Mg_{2.575}Fe_{0.706}^{2+}Fe_{0.215}^{3+}Al_{0.478}Ti_{0.003}Cr_{0.010}Mn_{0.001}Zn_{0.002})_{4.000}Al_{8.000}(Si_{1.309}Al_{0.691})_{2.000}O_{20}$ or simplified as: $(Mg, Fe, Al)_4Al_8(Si, Al)O_{20}$.

3.1 Composition correlation in sapphirine

One of the most prominent feature of sapphirine composition in the samples is that the major elements of the formula can vary a lot from one grain to another. Tong *et al.* [6] also noticed the phenomenon. This can be described by the correlation among different oxide compositions.

According to the correlation analysis of the oxide composition in sapphirine (Table 1), it is known that either the components of Al_2O_3 , MgO , FeO , or the correlation between SiO_2 and MgO , are positively correlated, but negative correlation between Al_2O_3 and SiO_2 , implying that these components are the major factors in the composition changes of the mineral.

In the sapphirine formula, the correlation between Mg-Fe is basically positive, occasionally negative or positive between Si and Fe, $\text{Mg} + \text{Fe}$, and the latter two show negative correlation with Al, suggesting the predominant Tschermak substitution $(\text{Mg}, \text{Fe}) + \text{Si} = 2\text{Al}$ in sapphirine. If Fe is subdivided into Fe^{2+} and Fe^{3+} , there may be positive correlation between Si, Mg and Fe^{2+} , negative correlation between Si and Fe^{3+} , Al and Fe^{2+} , Fe^{2+} and Fe^{3+} , that is,

$$(\text{Mg}, \text{Fe}^{2+}) + \text{Si} = 2(\text{Al}, \text{Fe}^{3+})$$

Considering the co-existence of Al^{IV} and Al^{VI} in sapphirine, we know that positive correlation between Fe^{3+} and Al^{VI} , and negative correlation between $\text{Fe}^{2+} - \text{Al}^{\text{VI}}$ and Al^{IV} , Mg and Al^{VI} , demonstrating the substitution of $(\text{Mg}, \text{Fe}^{2+})$ by Al^{VI} :

$$(\text{Mg}, \text{Fe}^{2+}) + \text{Si} = (\text{Al}^{\text{VI}}, \text{Fe}^{3+}) + \text{Al}^{\text{IV}}$$

which is identical with the substitution put forward by Higgins *et al.* [17].

Comparing the X_{Mg} of the mafic minerals in the two samples (Table 1), it can be seen that the X_{Mg} of the rock-forming minerals Prs and early Bt_1 in 20202 is relatively large, but X_{Mg} of the minerals in 126-9 is small. The contrary situation for the trace amount of Hcy-Spr-Bt₂ (late biotite): the X_{Mg} is larger in 126-9. Compared with the early Bt_1 , the late biotite (Bt_2) is rich in Mg, Al, Si and Zn, but poor in Na and Fe (Table 1), which is consistent with the crystallization sequence or the evolving direction of decreasing amount of $(\text{MgO} + \text{FeO})$ and X_{Fe} . If the Prs composition is controlled by the bulk chemistry, then the composition of Spr may be constrained by quite different factors. Of course the co-existing assemblage Hcy-Spr-Bt₂ formed in the same stage, and their formation might be related to the mobility of components (like the involvement of foreign components). That is the bulk chemistry has not the lasting effect on the minerals. It is generally considered that the protolith of the Spr-bearing rock is the magnesio-rich pelite, but the rock hosting Spr in the region is quite possible to be derived from the biotite plagioclase, in other words, the protolith composition feature can not be deduced by analyzing the composition of the sapphirine. $X_{\text{Mg}}^* = \text{Mg} / (\text{Mg} + \text{Fe}^{2+})$, the $\text{Fe}^{2+} - \text{Fe}^{3+}$ contents are calculated after Droop [18] (1987); $X_{\text{Mg}} = \text{Mg} / (\text{Mg} + \text{Fe})$, the Fe refers to the total $\langle \text{Fe} \rangle$; n. d. -not determined.

3.2 The mafic compositions in minerals and their changes

The mafic minerals are noticed to have the decreasing $(\text{MgO} + \text{FeO})$ contents:
 $\text{Spl}(37.78 - 40.16) > \text{Bt}(26.76 - 27.94) \geq \text{Spr}(24.49 - 26.75) \geq \text{Prs}(23.58 - 24.61)$

Table 1. Electron microprobe analyses of sapphirine and related minerals in the quartzofeldspathic gneisses from the Larsemann Hills, East Antarctica
20202

Samples	120-5										20202									
	Spr	Spr	Spl	Bt2	Bt1	Tm	Km	Pl	Spr	Spr	Crđ	Spl	Pl	Prs	Cdd	Bt1	B2			
SiO ₂	10.84	10.89	0.03	38.24	37.91	35.55	29.93	62.87	15.45	13.05	50.82	0.05	61.83	29.79	21.23	36.62	38.5			
TiO ₂	0.03	0.03	0.01	4.09	4.36	1.19	0.12	0.01	0.077	0.059	0.013	0.01	0.02	0.19	0.012	3.435	4.688			
Al ₂ O ₃	64.41	65.07	62.61	14.93	14.75	30.73	39.75	23.2	57.06	59.53	34.11	58.35	23.85	42.01	51.05	15.44	14.3			
Cr ₂ O ₃	0.11	0.11	0.31	0.03	0.05	0.09	0	0.01	0.09	0.04	0.02	0.44	0	0.02	0.002	0.04	0.04			
MgO	14.3	14.34	12.07	17.7	17.57	8.14	14.68	0	14.57	14.81	11.51	9.14	0	14.58	11.53	18.7	16.82			
CaO	0	0	0	0.02	0	1.23	0.02	3.96	0.008	0.003	0.004	0	5.64	0.014	0.01	0	0			
MnO	0.01	0.02	0	0	0.01	0	0	0	0.001	0.028	0	0.026	0.006	0.027	0	0.01	0			
FeOt	10.19	10.83	25.71	9.8	10.37	5.73	9.93	0.01	12.18	11.68	3.59	31.02	0.049	9	4.59	8.6	9.94			
FeO	7.436	7.681	24.76						12.18	8.910	3.59	29.04								
Fe ₂ O ₃	3.060	3.500	1.06						0	3.079	0	2.20								
ZnO	0.027	0.007	0.068	0.008	0	0.016	0.027	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			
Na ₂ O	0	0.01	0.01	0.1	0.12	1.83	0.07	8.59	0.004	0	0	0.001	7.97	0.044	0	0.13	0.07			
K ₂ O	0	0	0	10.68	10.57	0.08	0	0.69	0.001	0.001	0.02	0.001	0.53	0.004	0.001	10.05	10.87			
P ₂ O ₅	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.009	0	0	0.002	0.091	0.022	0.087	0.011	0.014			
F	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.007	0.006	0	0	0.006	0	0	0.015	0.025			
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.005	0	0.009	0	0.001	0.009	0.002	0.328	0.332			
Total	100.23	101.64	100.94	95.6	95.7	84.58	94.53	99.34	99.45	99.52	100.09	99.24	99.99	95.71	88.51	93.31	95.51			
O	20	20	4	11	11	20	21.5	8	20	20	18	4	8	21.5	107	11	11			
Si	1.300	1.290	0.001	2.793	2.775	4.823	4.006	2.797	1.884	1.587	5.022	0.001	2.745	3.916	2.069	2.733	2.827			
Ti	0.003	0.003	0.000	0.225	0.24	0.122	0.012	0	0.008	0.006	0.001	0	0.001	0.018	0.001	0.193	0.259			
Al	9.105	9.088	1.949	1.286	1.273	4.914	6.272	1.219	8.204	8.529	3.973	1.897	1.248	6.509	5.862	1.358	1.238			
Cr	0.010	0.010	0.006	0.002	0.003	0.01	0	0	0.008	0.004	0.001	0.010	0	0.002	0	0.002	0.002			
Fe ³⁺	0.276	0.312	0.021						0	0.282		0.046								
Fe ²⁺	0.746	0.761	0.547	0.599	0.635	0.651	1.112	0	1.242	0.906	0.296	0.670	0.002	0.99	0.374	0.537	0.611			
Mg	2.557	2.533	0.475	1.928	1.918	1.649	2.93	0	2.65	2.685	1.695	0.376	0	2.857	1.675	2.08	1.841			
Ca	0.000	0.000	0	0.002		0.179	0.003	0.189	0.002	0.000	0	0	0.268	0.002	0.001	0	0			
Mn	0.001	0.002	0	0	0	0	0	0	0	0.002	0	0.001	0	0.003	0	0.001	0			
Zn	0.002	0.001	0.001	0	0	0.002	0.002	0	0	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			

Samples	126-9								20202								
	Spr	Spr	Spl	Bt2	Bt1	Trn	Krn	Pl	Spr	Spr	Crd	Spl	Pl	Prs	Gdd	Bt1	Bt2
Na	0	0	0.001	0.014	0.017	0.481	0.018	0.741	0.002	0	0	0	0.686	0.011	0	0.019	0.009
K	0	0	0	0.994	0.986	0.014		0.039	0	0	0.003	0	0.03	0.001	0	0.957	1.018
P	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.001	0	0	0.0001	0.0034	0.002	0.007	0.0007	0.0009
F	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.003	0.002	0	0	0.0008	0	0	0.0035	0.0058
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.001	0	0.0015	0	0.0002	0.002	0.0003	0.0415	0.0413
Xmg*	0.774	0.769	0.465						0.681	0.748	0.851	0.359					
Xmg				0.763	0.751	0.717	0.725							0.742	0.818	0.795	0.751
An								0.195					0.281				
Fe ³⁺ %	0.270	0.291	0.037						0	0.237		0.064					

$> \text{Gdd}(16.12) \geq \text{Crd}(15.10) \geq \text{Trn}(13.87)$, that is:

$$\text{Spl} > \text{Spr} \geq \text{Prs} > \text{Gdd} \geq \text{Crd}$$

The sequence is consistent with the formation order in the metamorphic evolution of the region, suggesting the mafic-rich minerals form relative early in metamorphism.

In addition, the X_{mg} of the mafic minerals has the similar tendency:

$\text{Spl}(0.344 - 0.456) < \text{Spr}(0.681 - 0.715) \leq \text{Trn}(0.717) < \text{Prs}(0.725 - 0.742) < \text{Bt}(0.717 - 0.795) < \text{Gdd}(0.818) < \text{Crd}(0.851)$. As the $\text{Fe}^{2+}/\text{Fe}^{3+}$ of Trn, Prs, Gdd can not be estimated easily, the Fe^{2+} is calculated with the TFe contents.

If the opaque Fe-Ti oxide minerals are included, and biotite and tourmaline (representing the initial prograde or late retrograde association) are excluded, it can be seen that the increasing sequence of the mafic minerals is identical with that of the formation sequence; the value of X_{mg} of them as:

$$\text{Op} < \text{Spl} < \text{Spr} < \text{Prs} < \text{Gdd} < \text{Crd}$$

So in the progressive formation of sapphirine and related minerals, the mafic minerals in early stage are relatively rich in Fe components, while that in late stage rich in Mg compositions.

3.3 Other components

Sapphirine is thought to have certain contents of boron. When co-existing with Prs the B_2O_3 contents of Spr may exceed 0.3wt%^[19]. The volatile component B_2O_3 may also have influence on other major components in contents and mobility, such as in the co-existence of Fe^{3+} and Mg^{2+} , the $(\text{BO}_3)^{3-}$ preferentially combines with Fe^{3+} . Only in the situation when without or deficient in Fe^{3+} (forming HIM, for example), does $(\text{BO}_3)^{3-}$ combine with Mg^{2+} .

4 Pressure and temperature estimate

As no garnet or orthopyroxene present in the samples, most of the geothermobarometers can not be used for estimates of the pressure and temperature conditions of metamorphism. Here only the sapphirine-spinel geothermometer is adopted^[20]: $T = 800 + 228 \ln K_d - 273$, where $K_d = (\text{Fe}/\text{Mg})_{\text{Spl}}/(\text{Fe}/\text{Mg})_{\text{Spr}}$. The mean temperature for two samples is 837 °C (sample 126-9) and 884 °C (sample 20202), respectively, and the total average 872 °C. With the substitution $\text{Mg} + \text{Si} = \text{Al} + \text{Al}$, the Al-rich Spr tends to be formed in LP/HT condition^[17], which is consistent with the temperature estimate (Tables 1, 2)

Table 2. Temperature estimates from the sapphirine-spinel pair (°C)

126-9			20202						
Spot1	Spot2	average	Spot1	Spot2	Spot3	Spot4	Spot5	Spot6	average
840	833	837	831	897	904	871	897	906	884

According to the composition of the Mg-cordierite inclusion in hyperthene in the Bt-Prs-Hy-Crd gneiss interlayered with the Spr-bearing rock, Tong *et al.*^[6] obtained the condition as of 0.75Gpa and 850°C, on which the possible pressure obtained with the GASP

barometer^[21] is less than 9.0 kbar^[9]. The All theses estimates are lower than the ultra-high temperature(> 1000 °C), and are consistent with the relative Fe-rich Spr variety of the area, because only the Mg-rich Spr can be formed in relative high temperature and pressure^[22]. In spite of the possible component exchange in the retrograde process, the Spr in the region is included in the Mg-richer minerals like Prs and Crd(sample 20202, Figure 2D) or contacts Prs and Crd(sample 126-9, Figure 3) directly, and the overall lower X_{Mg} value than that of the high temperature types, implying the retrograde effect is not substantial even it does occur. Furthermore, both the non-co-existence of Spr and Qtz and the absence of mesoperthite exclude the possibility of ultrahigh temperature in the study area.

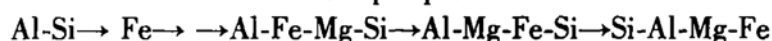
5 Origin analysis

In the closed system, sapphirine may includes spinel, and Dasgupta and Sengupta^[16] put forward the reaction $\text{Spl} + \text{Qtz} + \text{Sil} = \text{Spr}$. The Spr enclosing Spl or Crn forms the reaction texture or corona, which was taken as the symbols of disequilibrium^[17]. The Spr at Eastern Ghats, India, demonstrates the similar reaction: spinel is enveloped by Spr or Crd^[23].

In the situation of Laesemann Hills, there is the same relation between Spr and Spl. Though quartz is present^[6], but no association relation of Spr and Qtz can be observed, neither the direct contact of Spr with Sil can be seen. Texturally, Spr-Spl is derived from magnetite(Fig. 3). Of course, in the formation of Spr other components like Mg, Al and Si may be involved.

5.1 Component activation

For the complicated changes of the sapphirine composition and mineral associations, some considered that the changes result from the spatial zonations of minerals by the way of diffusion^[24]. It is essential in composition exchanges between two or more rocks for this kind of zoning. But in the Laesemann Hills, the complex associations generally occur in the same rock, even of the same thin section scale. So the mineral changes must reflect the evolving metamorphic stages: the early HIM show the mobility and precipitation of the Fe^{3+} (Fe^{2+}) and Ti elements. In the beginning period of Mg(Fe^{2+}) and Al activation formed the Spl-Spr, which may be described in this way: the gradual transition from the Fe-Ti oxides to other minerals under Mg, Al-rich setting, as the following(the bold means the major components) :



The above evolution manifests the differential mobility of components: the iron oxides are immobile, and the activation of Mg, Al is emerging compositions. The sequence is as the following: opaque minerals \rightarrow deep dark-colored minerals \rightarrow dark-colored minerals \rightarrow light-colored minerals. The differentiation occurs between the dark and light-colored minerals. If the system is closed, both the dark and light-colored associations will be present together^[25].

On the basis of the background assemblage of Bt-Pl-Qtz in the biotite plagiogneiss, the separation and combination of components intrigued by differential strain finally resulted in the quite different mineral associations from that of the original gneiss. As the migrating degree and metamorphic stages vary, the following progressive metamorphic assemblages can be found:

Assemblage 1 (Hem, Mt) \rightarrow Assemblage 2 (Spl-Spr \pm Opx) \rightarrow Assemblage 3 (Prs-Gdd \rightarrow Crd-Gdd)

The progression reflects the changing compositions in crystallization, and the system is open at least for the reaction space of sapphirine. Besides, the composition in a single sapphirine grain is heterogeneous. It is well known that at the scale of the thin section or smaller grain, the pressure and temperature condition cannot change essentially, that is, the heterogeneity can not be caused by the spatial change in PT value. The more probable reason is that the media was changing in composition, or some local equilibrium domains may form.

If enough boron components are involved, there may be the borosilicates Prs and Gdd, which are the result of the mutual effect of both the mafic and boron components, and finally cordierite crystallizes. The activation of boron component began early and ended late in the system. When sapphirine-spinel crystallize the SiO₂ component is unsaturated, the local setting is basic or silica-deficient. The quartz may be present as relics and the co-existence of Spr-Qtz is not found. The later occurrence of Prs-Gdd suggests the abundance of B-SiO₂ components.

5.2 Possible effect of anatexis

As to the relationship with anatexis, Riesco *et al.* [26] mentioned two-stage partial melting mechanism for metapelites, the quartz-rich veins formed in early anatexis migrated away with the residues deficient in quartz. Further peritectic melting was responsible for the trace amount of melts that were difficult to escape and some silica-unsaturated minerals, like corundum and spinel. The melting and crystallization of the anatexis melts are two irreversible processes, which result in the difference between the compositions of minerals and melt, and substantial differentiation among the chemical compositions. More specifically, the composition coalescence and separating occur:

1) the separation of melanocratic and leucocratic components: SiO₂, Al₂O₃, CaO, Na₂O, K₂O = Sil \pm Pl || FeO, TiO₂, MgO = Mt, Hem, Ilm

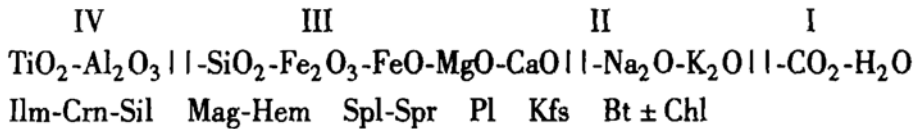
2) the separation of mafic components: FeO = Hem, Mt || MgO \rightarrow Spl-Spr \rightarrow Prs-Gdd \rightarrow Crd

3) the coalescence of components: Bt, Fl, Qtz

In this sense, the so-called protoliths from which the Spr- or borosilicates were derived are not necessarily the magnesio-rich pelite^[15]. The formation of the minerals of interest may involve the migration of components at rather degree, or the open system. This may correspond to the late stage melting as reported by Riesco *et al.* [26]. While the general anatexis association (Grt-Opx-Pl-Kfs-Qtz) occur at the early stage melting.

5.3 Sapphirine formation mechanism

As regarding the sapphirine formation mechanism, the mineral sequence is consistent with the predicted one by the metasomatism theory^[27], suggesting the mobility of components is related to both the diffusion and infiltration processes^[28], at the beginning the mobile components dominate, and decrease in late stage. For the occurrence of sapphirine, the role of the MgO component is crucial.



In comparing the mineral assemblages in the spr-bearing rock and the general quartzofeldspathic gneiss, it is noticed that they have both similar and different aspects:

Sil ~ ~ ~ ~ ~ Op → Bt-Pl → ~ ~ ~ ~ ~ Grt-Opx-Kfs → ~ ~ ~ ~ ~ Spl-Crd → ~ ~ ~ ~ ~ Bt ± Sil
 Structural first hydration dehydration (peak) second hydration (retrograde)

Differentiation:

Sil ~ ~ Crn ≥ Op → Bt-Pl → ~ ~ ~ ~ ~ Pl-Kfs → ~ ~ ~ ~ ~ Spr, Spl, Crn → Prs-Gdd → Crd → ~ ~ ~ ~ ~ Fl-Bt-Qtz,
 Early Al ± Fe enriching process late Mg-Al-Fe enriching process

Here the "dehydration(peak)" refers to the peak dehydration assemblage in metamorphism, "first hydration" means the biotitization after the sillimanite, and the "second hydration" is the retrograde biotite in late metamorphism. The formation of Sil is actually the Al ± Fe enriching process (Sil ± Op). Quartz is present and the Hem-Ilm ± Mt synneusis texture usually occurs. This is also the segregation process of the Al-Si ± Fe rich components from others (Mg ± Fe-Ca-K-Na). In the late Mg-Al-Fe enriching process (Spl ± Spr-Crd), the system is often deficient in silica and quartz is generally absent, while the assemblage Spl ± Spr forms.

It can be seen that metasomatism is obvious in the formation of sapphirine and the Spr-bearing rocks show more stages of mineral evolution than that of the general fluid-absent melting gneisses, suggesting that the fluid or volatile is another factor in constraining the metamorphic evolution of minerals.

In summary, the formation of sapphirine and related minerals can be controlled the united actions of component diffusion and infiltration in high-grade metamorphism and anatexis. The system is open in feature. Sapphirine formed in solid state reactions may need the high or ultrahigh temperature condition. The closed system khondalite with Spr^[29] may be a different process from the region.

6 Conclusions

The rare sapphirine in the Larsemann Hills is stable with the association of hercynite and is characterized by the magesio-, iron- and aluminum-rich, but silica-poor feature, the obvious intra- and intergrain changes in compositions are controlled by the Tschermark substitution (Mg, Fe) + Si = 2Al.

The multistage crystallization of minerals and differentiation of leuco- and melano-components resulted in the complexity of the mineral association. The mafic-rich minerals

formed earlier, and the differentiation of magnesio- and iron-components is responsible for the earlier presence of iron-rich minerals and later magnesio-rich minerals crystallization, thus the successive multistage associations occurred. The multistage evolution of mineral associations to some degree reflects the changing composition and open system.

The rock composition is an important but not critical factor for the occurrence of sapphirine. The protolith from which sapphirine is derived is not necessarily magnesio-rich pelite.

Sapphirine formed at 840 ~ 880 °C, not the so-called ultrahigh temperature condition (>1000 °C). It is deduced that the heterogeneity of sapphirine composition is related to the changing media, not to the PT conditions. The occurrence of sapphirine is caused by both the filtration and diffusion processes in high-grade metamorphism and anatexis.

Acknowledgements The project is supported by the National Natural Science Foundation of China (No. 40572041), the Chinese Geological Survey (Grant No. 1212010711509) and Programme of Excellent Young Scientists of the Ministry of Land and Resources (MLR) and Basic outlay of the Ministry (J0704). The logistic was supported by the Chinese Arctic and Antarctic Administration. The anonymous reviewers are thanked for their valuable comments of the early version of the paper.

References

- [1] Baba S (1999): Sapphirine-bearing orthopyroxene-kyanite/sillimanite granulites from South Harris, NW Scotland: evidence for Proterozoic UHT metamorphism in the Lewisian. *Contribution to Mineralogy and Petrology*, 136: 33–37.
- [2] Sarkar S *et al.* (2003): Petrological evolution of a suite of spinel granulites from Vizianagram, Eastern Ghats Belt, India, and genesis of sapphirine-bearing assemblages. *Journal of Metamorphic Geology*, 21: 899–913.
- [3] Dallwitz WB (1968): Co-existing sapphirine and quartz in granulite from Enderby Land. *Antarctica. Nature*, 219: 476–477.
- [4] Liu XS, Jin W, Li SX (1992): Low-pressure granulite facies metamorphism of the Paleoproterozoic orogenic event in central Inner Mongolia. *Acta Geologica Sinica*, 66: 244–255.
- [5] Zhang JX, Meng FC (2005): Geological implication of the sapphirine-bearing high-pressure basic granulite in the southern Altyn Mountains. *Chinese Science Bulletin*, 50: 167–171 (in Chinese).
- [6] Tong LX, Liu XH, Xu P *et al.* (1996): Occurrence of sapphirine-bearing hyperthine-quartzite in the Larsemann Hills, east Antarctica and its geological implication. *Chinese Science Bulletin*, 41: 1205–1208 (in Chinese).
- [7] Tong LX, Liu XH, Zhang LS *et al.* (1997): Assemblage and metamorphic feature of the earlier residue minerals in the granulite facies rocks of the Larsemann Hills, east Antarctica. *Acta Petrologica Sinica*, 13: 127–138.
- [8] Zhao Y, Song B, Wang YB *et al.* (1992): Geochronology of the late granite in the Larsemann Hills, East Antarctica. In: Y. Yoshida, K. Kaninuma and K. Shiraishi (eds.), *Recent Progress in Antarctic Earth Science*; Terra Scientific Publishing Company, Tokyo, 153–169.
- [9] Ren L, Zhao Y, Liu XH *et al.* (1992): Re-examination of the metamorphic evolution of the Larsemann Hills, East Antarctica. In: Yoshida Y, Kaminuma K, Shiraishi K (eds.), *Recent Progress in Antarctic Earth Science*; Terrapub, Tokyo, 145–153.
- [10] Carson CJ, Dirks PHGM, Hand M *et al.* (1995): Compressional and extensional tectonics in low-medium pressure granulites from the Larsemann Hills, East Antarctica. *Geological Magazine*, 132: 151–

170.

- [11] Stüwe K, Braun HM, Peer HM (1989): Geology and Structure of the Larsemann Hills area, Prydz Bay, East Antarctica. *Australian Journal of Earth Sciences*, 36: 219 – 241.
- [12] Ren LD, Zhao Y (2004): Occurrence of prismatine at the Zhongshan Station area, East Antarctica, and the changes of its definition. *Acta Petrologica Sinica*, 20: 759 – 763.
- [13] Ren LD, Wang YB, Chen TY *et al.* (2001): A possible mechanism of cordierite formation in the quartzofeldspathic gneisses—A case study on the high-grade region of the Larsemann Hills, East Antarctica. *Acta Petrologica et Mineralogica*, 20(1): 29 – 35.
- [14] Kretz R (1983): Symbols for rock-forming minerals. *American Mineralogist*, 68: 277 – 279.
- [15] Grew ES, Yates MG, Barbier J *et al.* (2000): Granulite-facies beryllium pegmatites in the Napier Complex in Khmara and Amundsen Bays, western Enderby Land, East Antarctica. *Polar Geoscience*, 13: 1 – 40.
- [16] Dasgupta S, Sengupta P (1995): Ultrametamorphism in Precambrian granulite terranes: evidence from Mg-Al granulites and calc-silicate granulites of the Eastern Ghats, India. *Geological Journal*, 30: 307 – 318.
- [17] Higgins JB, Ribbe PH, Herd RK (1979): Sapphirine, I: Crystal chemical contributions. *Contribution to mineralogy and Petrology*, 68: 349 – 356.
- [18] Droop GTR (1987): A general equation for estimating Fe^{3+} concentrations in ferromagnesian silicates and oxides from microprobe analysis using stoichiometric criteria. *Mineralogical Magazine*, 51: 431 – 436.
- [19] Grew ES, Chernosky JV, Werding G *et al.* (1990): Chemistry of kornorupine and associated minerals, a wet chemical, ion microprobe, and X-ray study emphasizing Li, Be, B and F contents. *Journal of Petrology*, 31: 1025 – 1070.
- [20] Owen VJ, Greenough JD (1991): An empirical sapphirine-spinel Mg-Fe exchange thermometer and its application to high-grade xenoliths in the Popes Harbour dykes, Nova Scotia, Canada. *Lithos*, 26: 317 – 332.
- [21] Essene EJ (1989): The current status of thermobarometry in metapelitic rocks. In *Evolution of Metamorphic Belts*. ed. JS Daly, RA Cliff and BWD Yardley, Geological Special Publication, 43: 1 – 44.
- [22] Kelsey DE, White RW, Holland TJB *et al.* (2004): Calculated phase equilibria in $\text{K}_2\text{O}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ for sapphirine-quartz-bearing mineral assemblages. *Journal of Metamorphic Geology*, 22: 559 – 578.
- [23] Rao AT (1999): Sapphirine granulites from Marturu near Anakapalle in the Eastern Ghats Granulite Belt, India. In A. T. Rao, V. Divakara Rao, and M. Yoshida (eds.) *Gondwana Research Group Memoir, No. 5, Eastern Ghats Granulites*. 139 – 144. Visakhapatnam, India.
- [24] Dunkley DJ, Clarke GL (1999): Diffusion metasomatism in silica-undersaturated sapphirine-bearing granulite from Rumdoodle Peak, Framnes Mountains, east Antarctica. *Contribution to Mineralogy and Petrology*, 134: 264 – 276.
- [25] Zhang CG, Wei CJ (2004): Phase equilibria for metapelites in the system $\text{K}_2\text{O}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ (KFMASH). *Acta Petrologica Sinica*, 20: 725 – 736.
- [26] Riesco M, Stüwe K, Reche J *et al.* (2004): Silica depleted melting of pelites. Petrogenetic grid and application to the Susqueda Aureole, Spain. *Journal of Metamorphic Geology*, 22: 475 – 494.
- [27] Korzhinskii DS (1970): *Theory of metasomatic zoning*. Oxford: Clarendon Press, 111 – 146.
- [28] He TX, Lu LZ, Li SX *et al.* (1980): *Metamorphic Petrology*. Beijing: Geological Publishing House (in Chinese).
- [29] Santosha M, Tsunogae T, Li JH *et al.* (2007): Discovery of sapphirine-bearing Mg – Al granulites in the North China Craton; Implications for Paleoproterozoic ultrahigh temperature metamorphism. *Gondwana Research*, 11: 263 – 285.