Determination of Pressure-Temperature Conditions of Retrograde Symplectic Assemblages in Granulites and Amphibolites

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Abstract: Symplectites form during post-orogenic fast uplift processes in orogenic belts, and retrograde Symplectic assemblages mainly consist of plagioclase + quartz \pm orthopyroxene \pm clinopyroxene in mafic granulites or plagioclase + hornblende + quartz ± biotite in amphibolites, usually rimming relict garnet porphyroblasts. Such Symplectic assemblages resulted from retrograde reactions between garnet and other peak-metamorphic minerals by nearly isothermal decompression (ITD), so the Symplectic mineral assemblages could not be at equilibrium with the relict garnet rims and thus the so-called "local equilibrium" between garnet rims and the Symplectic assemblages does not exist. Thus, the *P-T* conditions of the Symplectic assemblages are best determined using only the Symplectic mineral compositions. This is best accomplished using garnet-free thermobarometers, i.e., two-pyroxene or hornblendeplagioclase thermometer in combination with the hornblende-plagioclase-quartz or applying the clinopyroxeneplagioclase-quartz geobarometer to minerals within the symplectites. Taking two mafic granulite samples and two amphibolite samples as examples, reasonable ITD *P-T* paths from the metamorphic peaks to retrogression stages have been derived, but *P-T* paths obtained using the relict garnet rims and the Symplectic minerals gave anomalous results. These examples demonstrate that the *P-T* conditions of the retrograde Symplectic assemblages cannot be estimated using chemical compositions of the decomposed, relict garnet rims in this case.

Keywords: Amphibolite, disequilibrium, geobarometer, geothermometer, granulite.

1. INTRODUCTION

Accurately retrieving metamorphic *P-T* paths is important for understanding the tectonothermal evolution of orogenic belts, since different *P-T* paths can record different tectonic processes. For example, the clockwise, western Alpine type *P-T* paths result from subduction or continental collisional zones [1] and are characterized by prograde and peak metamorphism followed by nearly isothermal decompression (ITD) segments. Such *P-T* paths are related to crustal over thickening followed by erosional exhumation and/or extensional thinning and may be caused by either tectonic unroofing during post-orogenic collapse, such as in extensional terranes, or by very rapid erosion [1- 4]. Examples of these *P-T* paths come from the Tauern Window [5] and the Palaeoproterozoic Trans-North China Orogen [6-9]. The clockwise, Franciscan type *P-T* paths are characterized by retrograde return paths being generally parallel to the prograde *P-T* trajectories [1] and these *P-T* paths are seen in the Franciscan amphibolites [10], the Late Archean basement rocks in the Eastern and Western Blocks of the North China Craton [11,12], Spain [13], and New Zealand [14]. Anticlockwise *P-T* paths, on the contrary, are related to the emplacement of plutons [15,16] or have formed in or beneath areas of voluminous magmatic accretion with or without crustal extension [2].

Metamorphic *P-T* paths are recovered using (1) thermodynamically modeled phase equilibrium relations or (2) by conventional geothermobarometry. Metamorphic *P-T* paths may be reconstructed from Isochemical *P-T* sections (*P-T* pseudosections) using modeling software, such as GIBBS [17,18], THERMOCALC [19], Perple_X [20] or THERIA_G [21]. The *P-T* paths are inferred by comparing the sequential appearance of different mineral assemblages preserved in metamorphic rocks with the calculated assemblages [14, 22-37]. Alternatively, geothermobarometers are applied to mineral assemblages of different metamorphic stages to construct the *P-T* paths [6-8, 9, 13, 38-56]. In any case, metamorphic *P-T* paths are determined on the basis of at least two mineral assemblages formed at different metamorphic stages, or alternatively, from mineral zoning or changing mineral abundance without any change in assemblage.

It should be stated that thermobarometry of highgrade rocks suffers greatly from partial retrograde reequilibration (particularly but not restricted to Fe-Mg exchange) leading to erroneous *P-T* results. Conversely, although pseudosections avoid the problems of retrograde re-equilibration, they have problems associated with changing bulk composition, such as melt loss or gain.

Rocks that have undergone post-collisional, fast uplift may produce and preserve retrograde textures including symplectites or coronas. In garnet-bearing

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mafic granulites or amphibolites, such processes usually produce the so-called "white-eye socket" Symplectic assemblages [57, 58] consisting of plagioclase + quartz ± orthopyroxene ± clinopyroxene (in mafic granulites) or plagioclase + hornblende + quartz ± biotite (in amphibolites) rimming relict garnet porphyroblasts. Such Symplectic assemblages are common in mafic granulites and commonly indicate isothermal decompression into the orthopyroxenebearing, medium-*P* granulite facies [2, 59]. Decompression is suggested by the increase in Ca content in the newly-formed Symplectic plagioclase combined with the decrease in Ca in adjacent garnet rims [60]. It is quite necessary to estimate accurately *P-T* conditions of such retrograde Symplectic assemblages in order to understand accurately orogenic processes. In theory, *P-T* conditions of such assemblages should be determined using the chemical compositions of the Symplectic assemblages. Unfortunately, there is a wrong but ubiquitous routine work in determining the *P-T* conditions of the retrograde assemblages: almost all over the world, workers suppose that there exist the socalled "local equilibrium" between the older generation minerals (*e.g.*, garnet) and the younger mineral assemblages (*e.g.*, the retrograde minerals in corona or symplectite), thus estimate the retrograde *P-T* conditions by applying thermobarometry using the mineral compositions of both the garnet rim and minerals in the corona or symplectite, as done in the literature elsewhere for mafic granulites [39,41,48,60- 85]. Not surprisingly, one always obtains incorrect retrograde *P-T* conditions and accordingly, derived bias conclusions concerning tectono-metamorphic processes. Correctly computing *P-T* conditions of retrograde assemblages is quite scarce hitherto, to our knowledge.

Such retrograde "white-eye socket" Symplectic assemblages have been found to be present both in the mafic granulite enclaves in TTG gneisses [6- 9,47,58] elsewhere in the Trans-North China Orogen (TNCO) [86, 87], as well as mafic granulites in Antarctica [28]. In this paper, we have determined the *P–T* conditions of such retrograde Symplectic assemblages using the chemical compositions of the minerals in the symplectite assemblages themselves and the results show that erroneous *P–T* conditions have been obtained where using garnet rims in thermobarometric computation.

In this work, symbols of minerals are adopted from the scheme of Whitney and Evans [88]. Abbreviations of geothermobarometers used hereafter are as follows:

CPQ= the clinopyroxene – plagioclase – quartz geobarometer [89].

COPQ= the two – pyroxene geothermometer [90] paired with the clinopyroxene – plagioclase – quartz geobarometer [89].

GCPQ= the garnet – clinopyroxene geothermometer [91] combined with the garnet – clinopyroxene – plagioclase – quartz geobarometer [92].

GHPQ= the plagioclase – hornblende thermometer [93] coupled with the garnet – hornblende – plagioclase – quartz geobarometer [94].

GOPQ= the garnet – orthopyroxene geothermometer adjoined the garnet – orthopyroxene – plagioclase – quartz geobarometer [95].

HPQ= plagioclase – hornblende geothermometer [93] fixed with the hornblende $-$ plagioclase $-$ quartz geobarometer [96].

Chemical compositions of the minerals were determined using a wavelength dispersive electron microprobe Cameca SX51 equipped at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China. The analytical conditions were 15 kV accelerating voltage, 20 nA beam current, 5 µm electron beam diameter and 20 seconds of counting time. The program PAP was used for matrix corrections. Reported mineral compositions are averaged values of up to twenty spot analyses for every component. Ferric contents of garnet, orthopyroxene and clinopyroxene were determined according to the method of Droop [97]. For amphibole, ferric iron contents were determined according to the method of Holland and Blundy [93]. Chemical compositions of the minerals used for the *P-T* determinations are listed in Tables **1-4**.

2. MAFIC GRANULITES

2.1. Mafic Granulite Sample Lu02

In eastern Shandong Province, mafic granulites, amphibolites and metamorphic ultramafic rocks are exposed as discontinuous boudins or lenses within the late Archean TTG gneisses [55], basement of the North China Craton [86]. Sample Lu02 is a high-pressure mafic granulite enclave in TTG gneiss and was collected from the Jiaobei terrane and in this sample three generations of metamorphic assemblages are recognized (Figure **1a**). Weak chemical zoning of the

Table 1: Representative EMPA Data for Minerals in Mafic Granulite Sample LU02 Shown in Figure 1a

Table 2: Representative EMPA Data for Minerals in Mafic Granulite Sample EP1-12 Shown in Figure 1c

		Symplectite Assemblage (M3)						
	Grt ₂	PI ₂	Hbl ₂	Cpx ₂	PI ₃	Hbl ₃	Cpx ₃	Opx ₃
MgO	6.13	0.00	11.90	11.65	0.01	12.32	13.43	19.96
CaO	7.36	11.86	11.95	21.73	18.74	12.07	23.29	0.40
Na ₂ O	0.00	5.73	1.57	0.58	1.25	1.38	0.37	0.00
K_2O	0.00	0.07	0.39	0.01	0.00	0.22	0.00	0.00
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr ₂ O ₃	0.13	0.00	0.08	0.02	0.00	0.09	0.07	0.03
NiO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.92	99.90	97.01	99.13	99.25	96.89	100.65	99.88
				Cations Per Formular Unit				
Si	2.980	2.428	6.572	1.837	2.105	6.713	1.917	1.943
Ti	0.000	0.001	0.141	0.016	0.000	0.100	0.006	0.000
AI	1.940	1.535	1.911	0.252	1.857	1.775	0.101	0.078
$Fe2+$	1.606	0.006	1.529	0.234	0.009	1.481	0.202	0.796
$Fe3+$	0.085	0.000	0.251	0.084	0.000	0.257	0.077	0.034
Mn	0.055	0.000	0.009	0.003	0.000	0.002	0.004	0.005
Mg	0.711	0.000	2.623	0.654	0.001	2.705	0.741	1.126
Ca	0.614	0.578	1.894	0.877	0.936	1.905	0.923	0.016
Na	0.000	0.505	0.450	0.042	0.113	0.394	0.027	0.000
Κ	0.000	0.000	0.074	0.000	0.000	0.041	0.000	0.000
Zn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$\rm Cr$	0.008	0.000	0.009	0.001	0.000	0.010	0.002	0.001
Ni	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
X(alm)	0.538							
X(pyr)	0.238							
X(gros)	0.206							
X(sps)	0.018							
X(An)		0.53			0.89			

⁽Table 2). Continued

Table 3: Representative EMPA Data for Minerals in Amphibolite Sample HB32D Shown in Figure 2a

Table 4: Representative EMPA Data for Minerals in Amphibolite Sample HN424 Shown in Figure 2c

		Matrix Assemblage (M2)		Symplectite Assemblage (M3)								
	Grt ₂	PI ₂	Hbl ₂	Cpx ₃	PI ₃	Hbl ₃						
ZnO	0.00	0.00	0.00	0.00	0.00	0.00						
Cr ₂ O ₃	0.02	0.00	0.02	0.07	0.01	0.02						
NiO	0.03	0.03	0.03	0.00	0.00	0.00						
Total	99.8	100.5	98.4	100.6	100.3	98.7						
Cations Per Formular Unit												
Si	2.80	2.61	6.33	1.95	2.64	6.40						
Ti	0.00	0.00	0.24	0.00	0.00	0.23						
$\mathsf{Al}\xspace$	2.00	1.39	2.08	0.07	1.35	1.97						
$Fe2+$	1.58	0.00	1.00	0.36	0.00	1.04						
$Fe3+$	0.39	0.00	1.55	0.06	0.00	1.45						
Mn	0.16	0.00	0.03	0.01	0.00	0.03						
Mg	0.43	0.00	1.83	0.65	0.00	1.93						
Ca	0.65	0.37	1.82	0.88	0.35	1.84						
Na	0.01	0.62	0.55	0.03	0.64	0.51						
Κ	0.00	0.01	0.21	0.00	0.01	0.21						
Zn	0.00	0.00	0.00	0.00	0.00	0.00						
Cr	0.00	0.00	0.00	0.00	0.00	0.00						
Ni	0.00	0.00	0.00	0.00	0.00	0.00						
$X(\text{alm})$	0.56											
X(pyr)	0.15											
X(gros)	0.23											
X(sps)	0.06											
X(An)		0.37			0.35							

(Table 4). Continued

garnet was detected. The inclusion assemblage (M1) within garnet porphyroblast is mainly consisted of clinopyroxene + hornblende + plagioclase \pm quartz, the metamorphic peak assemblage (M2) is mainly composed of garnet and matrix minerals (clinopyroxene + hornblende + plagioclase + quartz ± magnetite) and the retrograde Symplectic assemblage (M3) is generally constituted by clinopyroxene + orthopyroxene + hornblende + plagioclase + quartz \pm ilmenite. The *P-T* conditions of the metamorphic peak (M2) were estimated to be of 11.5kbar/885°C and 12.3kbar/810°C through applying the GCPQ and GHPQ thermobarometers, respectively. The *P-T* conditions of the retrograde Symplectic assemblages (M3) were estimated to be of 9.0kbar/802°C and 1.8kbar/802°C, respectively, using the garnet-free hornblende-plagioclase thermometer combined with the HPQ and CPQ barometers and thus ITD *P-T* paths were obtained for the retrograde metamorphic process

(Figure **1b**) which is the case. Alternatively, when using the garnet rim compositions combined with the Symplectic assemblages (M3), erroneous results of 13.0kbar/770°C (GCPQ) and 11.9kbar/780°C (GHPQ) were yielded, respectively, and thus bias *P-T* paths were obtained (Figure **1b**).

2.2. Mafic Granulite Sample EP1-12

Sample EP1-12 is a garnet-bearing mafic granulite metamorphosed in the Late Neoproterozoic-Cambrian, collected from the Grove Mountains, East Antarctica [28]. The prograde assemblages (M1) are inclusion assemblages (plagioclase + hornblende + rutile) preserved in the garnet cores, and garnets and the matrix assemblages (clinopyroxene + plagioclase + hornblende + quartz) constitute the metamorphic peak assemblages (M2), and the retrograde Symplectic assemblages (M3) are fine-grained vermicular

Figure 1: Photomicropetrographs and metamorphic *P-T* paths of the mafic granulites. (**a**) Sample Lu02 and its metamorphic *P-T* paths (**b**). (**c**) Sample Ep1-12 and its metamorphic *P-T* paths (**d**). Mineral abbreviations: Grt, garnet; Cpx, clinopyroxene; Opx, orthopyroxene; Pl, plagioclase. Thermobarometer symbols: GCPQ, the garnet – clinopyroxene geothermometer [91] combined with the garnet – clinopyroxene – plagioclase – quartz geobarometer [92]; GHPQ, the plagioclase – hornblende thermometer [93] coupled with the garnet – hornblende – plagioclase – quartz geobarometer [94]; HPQ, plagioclase – hornblende geothermometer [93] fixed with the hornblende – plagioclase – quartz geobarometer [96]; HP-CPQ, the plagioclase – hornblende thermometer [93] coupled with the clinopyroxene – plagioclase – quartz geobarometer [89] GOPQ, the garnet – orthopyroxene geothermometer adjoined the garnet – orthopyroxene – plagioclase – quartz geobarometer [95]; COPQ = the two – pyroxene geothermometer [90] paired with the clinopyroxene – plagioclase – quartz geobarometer [89].

symplectites consisted of clinopyroxene + orthopyroxene + hornblende + plagioclase rimming embayed, relict garnet porphyroblasts (Figure **1c**). No chemical zoning of the garnet was detected. Thermodynamic *P-T* pseudosection calculation suggests that such mafic granulite has recorded a clockwise *P-T* path passing from 830°C/9.2kbar (M1) through 840°C/11.8kbar (M2) to 840°C/8.2kbar (M3), demonstrating the retrograde segment (M2→M3) being an ITD–type path [28]. The *P-T* conditions of the metamorphic peak (M2) were estimated using geothermobarometers to be of 11.8kbar/744°C (GCPQ) and 9.3kbar/745°C (GHPQ), respectively, and the *P-T* conditions of the retrograde Symplectic assemblages (M3) were estimated to be of 1kbar/708°C using the garnet-free COPQ thermobarometers. Thus the retrograde process was determined to be an ITD *P-T* path from the M2 to M3 stages. However, when using garnet-bearing thermobarometers, erroneous *P-T* conditions of either 8.7kbar/- 828°C (GHPQ) or 4.4kbar/537°C (GCPQ) or 7.4kbar/- 774°C (GOPQ) for the M3 assemblages have been yielded, leading to clearly bias *P-T* paths (Figure **1d**). This again demonstrates that the porphyroblastic garnet rims should not be included in the *P-T* estimations of symplectites.

3. AMPHIBOLITES

3.1. Amphibolite Sample HB32D

Garnet-bearing amphibolites and garnet- and kyanite-bearing metapelitic gneisses are intercalated elsewhere in the late Palaeoproterozoic Zanhuang

metamorphic complex, Trans-North China Orogen and this terrane had experienced upper amphibolite to granulite facies metamorphism characteristic of clockwise *P-T* paths including retrograde ITD segments [9] in the Palaeoproterozoic [98]. Sample HB32D was collected from the Zanhuang terrane and three generations of mineral assemblages are preserved in this sample (Figure **2a**). The prograde assemblage (M1) is mainly consisted of quartz + plagioclase + hornblende ± biotite included within garnet porphyroblasts. The metamorphic peak assemblage (M2) is dominantly composed of garnet porphyroblasts and the matrix minerals (plagioclase + hornblende + quartz ± clinopyroxene ± biotite). The retrograde coronitic symplectites (M3) are consisted mainly of plagioclase + hornblende + quartz ± magnetite ± pyrite intergrowths rimming embayed, relic garnet porphyroblasts. No chemical zonation of garnet was found. The *P-T* conditions of the metamorphic peak (M2) were determined to be 10.5kbar/688°C by the GHPQ and 12.8kbar/668°C by the GCPQ thermobarometers, respectively. The HPQ thermo-barometer

yielded *P-T* conditions of the Symplectic assemblage (M3) to be of 5.7kbar/696°C. Thus the ITD *P-T* path was obtained (Figure **2b**) which is the case. However, when applying the GHPQ thermobarometer using chemical compositions of the garnet rim and minerals in the symplectite, the *P-T* conditions of the symplectite assemblages (M3) were estimated to be of 10.6kbar/710°C, thus an erroneous, prograde *P-T* path of the retrograde process was retrieved (Figure **2b**).

3.2. Amphibolite Sample HN424

Sample HN424 was collected from a metamorphosed gabbroic dyke within TTG gneiss in the Lushan Terrane, southern terminal of the Palaeoproterozoic Trans-North China Orogen. Three episodes of metamorphic mineral assemblages were found in this rock (Figure **2c**). The first generation assemblages (M1) are inclusion minerals (quartz + ilmenite) preserved in the garnet porphyroblasts although the *P-T* conditions cannot be determined due to lack of suitable geothermometers and geobaro-

Figure 2: Photomicropetrograph and metamorphic *P-T* paths of the amphibolites. (**a**) Sample HB32D and its *P-T* paths (**b**). (**c**) Sample HN424 and its *P-T* paths (**d**). Mineral abbreviations and thermobarometer symbols are the same as in Figure **1**.

meters. The chemical compositions of the garnet grains are nearly homogeneous. The metamorphic peak assemblages (M2) are represented by garnet porphyroblasts and matrix minerals (plagioclase + hornblende + quartz ± biotite) and the *P-T* conditions were estimated to be of 8.1kbar at 763°C by applying the GHPQ thermobarometer. The retrograde Symplectic assemblages (M3) are consisted of hornblende + plagioclase + quartz ± clinopyroxene rimming embayed, relic garnet porphyroblasts and the *P-T* conditions of 4.3kbar at 747°C were determined by HPQ thermobarometry. Thus, an ITD *P-T* path was retrieved (Figure **2d**). But, when applying the GCPQ thermobarometers using both the garnet rims and the Symplectic assemblages the *P-T* conditions were estimated to be 9.1kbar at 618°C and thus a fake cooling and pressure-increasing *P-T* path was rebuilt (Figure **2d**).

4. DISCUSSION

Although the absolute and random errors of the geothermobarometers used here are not discussed, these thermometers and barometers are the most reliable ones among the different versions. However, the trends of the derived *P-T* paths are not distorted by the inherited errors of these thermobarometers, because the errors are well below the *P-T* differences between the different generations of mineral assemblages formed at different metamorphic stages.

In nature, it is commonly seen that supercooled water (such as of -15° C) freezes directly at temperatures far below 0°C at 1 bar in the winter, deviating greatly below from the equilibrium state of ice and water in the *P-T* space, thus one cannot take it for granted that water consolidates to ice at 0°C/1bar exactly. Quite similar phenomena exist on the formation of retrograde symplectites or coronas in granulites or amphibolites. In mafic granulites, symplectites or coronas were generated by the decomposition reactions between garnet rims and adjacent matrix minerals (*e.g.*, clinopyroxene ± orthopyroxene \pm hornblende \pm plagioclase \pm biotite), and in many amphibolites the retrograde assemblages were also formed by the decomposition reactions between garnet rims and adjacent matrix minerals (*e.g.*, hornblende ± plagioclase ± biotite ± clinopyroxene). Suppose that an equilibrium decomposition reaction occurs at 8 kbar and 750°C in a mafic granulite, then, in nature, when pressure decreases to well below 8 kbar (rather than at 8 kbar exactly) at the temperature of \sim 750 $^{\circ}$ C, the reaction may be much more easily to occur. It is thus anticipated that most decompression, decomposition reactions deviate significantly from the equilibrium reaction conditions. If one believes that the garnet rims were at thermodynamic equilibrium with the newly formed, adjacent Symplectic or coronitic minerals when a decomposition reaction occurs, then the probability may be comparable to that of a passing-by meteoroid hitting an astronomer! This is the most important reason why we cannot estimate the *P-T* conditions of the Symplectic assemblages using chemical compositions of both the Symplectic minerals and the garnet rims.

But we do not imply that one particular Symplectic or coronitic assemblage itself is necessarily at equilibrium, either. In fact, if there is chemical heterogeneity among different grains of the same mineral or even if there is chemical heterogeneity in one grain in the symplectite, then disequilibrium does exist in such a Symplectic assemblage. In such case *P-T* conditions of the symplectites or coronas cannot be determined by thermobarometers any longer.

CONCLUSION

(a) The garnet rims were hardly at, but usually deviate significantly from, thermodynamic equilibrium with the newly formed, adjacent minerals within the symplectite or corona, when the decomposition reaction occurred;

(b) The *P-T* conditions of the retrograde symplectites or coronas can only be determined by minerals formed within the symplectites or coronas themselves, and it is strongly suggested that garnet rims should be excluded from the computation. In granulites or amphibolites, *P-T* conditions of the symplectites or coronas can be determined by applying the two–pyroxene or hornblende–plagioclase thermometers simultaneously combined with the clinopyroxene–plagioclase–quartz or hornblende– plagioclase–quartz barometers.

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