Petrochemistry and Mineral Chemistry Studies (Metamorphic Ultramafic Rocks in Yanghou Area, Northern Fujian, China*

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Abstract: Petrochemical studies indicate that the Yanghou metamorphic ultramafic rocks are composed of metamorphosed harzburgite and ultramafic cumulate. Trace element geochemistry and mineral chemistry of the metamorphic harzburgite indicate that they are relicts of depleted mantle. Systematic petrochemical, mineral chemical and geochronological studies led to such a conclusion that the Yanghou metamorphic ultramafic rocks may be the components of Late Sinian-Early Paleozoic ophiolites in South China.

Key words: petrochemistry; mineral chemistry; chronology; metamorphic ultramafic rocks; Yanghou

The Yanghou metamorphic ultramafic rocks are located 100 m west to Yanghou Village, Zhenghe County. Tectonically, they are located in the northern part of the Zhenghe-Dapu fault. The rocks are considered as the intrusions of the Caledonian period (North Fujian Geology Brigade, 1987) and ophiolite components of the Late Proterozoic Qingbaikou period (Nie Ganbo and Wang Yong, 1992; Chen Diyun et al., 1993). Because of their important location, tectonic setting studies of the metamorphic ultramafic rocks are very important for studying tectonic evolution in South China. In order to identify the tectonic settings of the ultramafic rocks, systematic petrochemical and mineral chemical studies are carried out in this paper.

Geology Setting

Field investigations revealed that the Yanghou metamorphic ultramafic rocks are composed of serpentine blocks, measuring from several meters to tens of meters in size. Lensing and schistosity are obviously developed in these serpentine blocks. The smaller the serpentine blocks are, the more developed the lensing and schistosity will be. Some of the blocks are even entirely of schistosity, hence forming schistosity belts. Tectonic analyses indicate that these schistosity belts are actually a series of tectonically shear-sliding planes. In general, from the core to the margin, the serpentine blocks became smaller and smaller in size, the rocks became more fragmented and schistosity or cleavage became more developed (Fig. 1).

The above-described characters of the Yanghou metamorphic ultramafic rockbody imply that it seems to have been tectonically emplaced. During the emplacement process, the rocks experienced a change from a deep plastic environment to a shallow brittle environment, thus leading to schistosity deformation developed in the tenacity-plastic environment and fragmental

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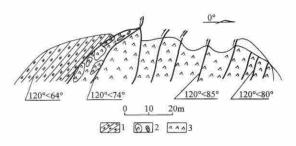


Fig. 1. Cross section of the Yanghou metamorphic ultramafic rockbody. 1. Late Sinian-Early Cambrian epidote-chlorite-albite schist; 2. fault broken zone; 3. metamorphic ultramafic rock.

deformation developed in the brittle environment.

Petrochemistry

The rocks are blackish-green in color, lepidoblastic in texture, massive or schistose in structure. The component minerals are mainly antigorite and chrysotile (>90%). In addition, there are some minor minerals such as calcite and spinellides. The antigorite and chrysotile are for the most part distributed in orientation and show schistosity. Calcite occurred as single crystals or lumpy aggregates (0% – 5%). Spinellide minerals oc-

curred as granulae or pellets (0% - 5%).

The results of chemical analysis (Table 1) indicate that the metamorphic ultramafic rocks studied are greatly variable in chemical composition. According to their chemical compositions, the metamorphic ultramafic rocks can be classified as three types:

Table 1. Major element analyses (%) of Yanghou ultra-mafic rocks and calculated parameters

Sample No.	YH21	YH23	YH27	YH36	YH37	GS03	GS04	GS05	YH51	YH52
Rock type			I				П		I	I
SiO ₂	38.35	40.40	39.30	36.43	40.12	43.35	41.71	41.15	35.09	34.71
TiO ₂	0.04	0.03	0.03	0.01	0.01	0.12	0.30	0.23	1.12	1.11
Al_2O_3	1.02	0.95	0.71	0.76	0.81	1.22	3.42	2.06	6.25	6.25
Fe ₂ O ₃	3.31	3.81	1.40	7.31	4.05	4.39	3.76	2.38	7.34	7.95
FeO	2.63	2.93	3.40	2.27	1.59	2.35	4.50	2.95	4.90	4.22
MnO	0.12	0.10	0.11	0.10	0.09	0.11	0.13	0.17	0.21	0.22
MgO	38.12	37.34	38.17	37.19	39.64	31.33	27.10	24.63	33.34	33.72
CaO	1.22	1.22	1.59	0.82	0.54	6.8	17.55	11.46	0.21	0.52
Na ₂ O	0.02	0.10	0.06	0.10	0.07	0.06	0.06	0.06	0.13	0.15
K ₂ O	0.07	0.01	0.01	/	1	0.07	0.06	0.04	0.01	0.03
P ₂ O ₅	0.01	0.01	1	0.02	0.01	0.02	0.09	0.01	0.02	0.02
H ₂ O ⁺	10.43	10.99	11.26	11.65	8.99				11.06	11.16
H_2O^-	0.07	0.04	0.31	0.12	1				0.16	
LOI	4.40	1.72	3.34	3.32	3.59	10.12	11.88	14.89	0.21	0.12
Total	99.71	99.68	99.69	100.10	99.51	100.21	100.56	100.03	100.05	100.18
CIPW stan	dard min	erals								
Ab	0.2	1.0	0.6	1.0	0.7	0.6	0.6	0.6	1.3	1.4
An	3.0	2.4	2.0	1.9	2.2	3.2	10.0	6.2	1.0	2.8
C									6.5	5.8
Di	3.2	3.5	5.8	2.2	0.6	27.2	25.1	47.9		
Hy	21.5	29.5	24.3	14.2	28.4	22.7	20.7	6.1	20.8	15.0
Ol	70.6	62.3	66.5	79.1	67.1	44.6	41.0	37.5	66.0	70.5
Mt	1.0	1.1	0.8	1.5	0.9	1.0	1.3	0.9	1.9	1.9
II	0.1	0.1	0.1	0.1		0.3	0.7	0.5	2.4	2.4
MgO/FeO*	6.8	5.9	8.2	4.2	7.6	5.0	3.4	4.8	2.9	3.0

Results of GS03, GS04 and GS05 are from 1/50000 Regional Geology Survey Reports.

Type I: Poor in $Al_2O_3(0.7\% - 1.0\%)$, $\Sigma FeO(4.7\% - 8.9\%)$ and CaO(0.5% - 1.6%), and rich in MgO(37.2% - 39.6%). These chemical characters are very similar to those of

harzburgite occurring at the bottom of the ophiolite suit in Oman Semail and Cypurus Trodoos (Coleman, 1977). By excluding volatile components and converting FeO to Σ FeO in terms of FeO/Fe₂O₃=9, the calculated CIPW standard minerals are mainly olivine (Ol: 62.3% – 79.1%) and enstenite (Hy: 14.2% – 29.57%).

Type II: Poor in $Al_2O_3(1.2\% - 3.4\%)$, ΣFeO (5.1% - 7.9%) and MgO (24.0% - 31.0%), and rich in CaO (6.8% - 17.6%). These chemical characters are very similar to those of lherzolite. The calculated CIPW standard minerals are mainly clinopyroxene (Di: 25.1% - 47.9%), enstenite (Hy: 6.1% - 22.7%) and olivine (Ol: 37.5% - 44.6%).

Type $\rm III$: Poor in MgO (33.3% - 33.7%) and CaO (0.2-0.5%), and rich in $\rm Al_2O_3$ (6.3% \pm) and $\rm \Sigma FeO$ (11.5% \pm). These compositional characters may indicate that the rocks are dominated by ultramafic cumulates. In this type, CaO may have been leached during serpentization, resulting in disseminated and vein-type carbonation, so anorthite and pyroxene minerals were reduced and abnormal minerals such as corundum occurred in the calculated CIPW standard minerals.

In ACM diagram (Fig. 2), the data points of the type- I rocks fall within the metamorphic peridotite area, whereas those of the type- II and type- III rocks fall within the ultramafic cumulate area. These facts indicate that the type- I rocks may be the relicts of a depleted mantle that has been extracted by MORB, but the type- III and type- III rocks may be segregated from melts which were derived from the depleted mantle. Coexistence of these rocks which are obviously different in origin is also observed in Songshugou, East Qinling (Gao Changlin et al., 1990) and Jormua, New Finland (Liipo, 1995).

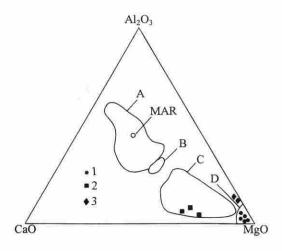


Fig. 2. Al₂O₃-CaO-MgO discrimination diagram of the-mafic-ultramafic rocks (after Coleman, 1977). 1. Type I rocks; 2. type-II rocks; 3. type-III rocks. A. Mafic cumulate; B. komatiite; C. ultramafic cumulate; D. metamorphic olivine; MAR. average composition of mid-ocean basalt.

Mineral Chemistry

Spinellide

Spinellide minerals [spinel-chrome-magnetite (Mg, Fe2+)(Cr, Al, Fe3+)2O4] are ubiquitous accessory minerals in the ultramafic rocks. They show significant differences in chemistry during fractional crystallization or partial melting, with Cr and Mg being strongly partitioned into the solid, and Al into the melt. In addition, the partitioning of Mg and Fe2+ between spinel minerals and silicate melts is strongly temperature-dependent and the ratio of Fe2+ to Fe3+ is sensitive to variations in f_{O_2} . Thus the composition of spinellide minerals is extremely sensitive to host rock petrogenesis and is called the "petrologic litmus paper". Due to these characteristics and as its signature value Cr#

(100Cr/(Cr+Al)) is stable during later metamorphism, spinellide minerals are widely used in original environment discrimination for ultramafic rocks (Dick and Bullen, 1984; Bonatti and Michael, 1989; Arai, 1994).

Detailed slice observation for type- I metamorphic ultramafic rocks (sample YH27) indicates that spinellide minerals in the Yanghou metamorphic ultramafic rocks exhibit cataclastic texture and zonal structure. The minerals were scattered as irregular blocks. The core parts of the blocks are brown and the marginal parts are opaque black in mono-polarized light. The mineral grains show three zones in the back scattered electron image. The core parts are dark gray, the marginal parts are light gray, and the transitional parts are grayish-white. These indicate that the average atomic numbers tend to increase gradually from the central to the marginal parts.

Electron probe analyses of the different zones (Table 2) indicate that there are significant differences in chemical composition between the core and marginal parts. In the core, transitional and marginal parts, the constituent minerals are mainly magnesian alumochromite, ferruginous chrome-magnetite and magnetite, respectively. From the core to the marginal parts, the contents of Al_2O_3 , Cr_2O_3 and MgO are gradually reduced, and those of FeO and Fe_2O_3 are gradually increased (Fig. 3). The signature index Cr^{\sharp} for the core parts is within the range of 0.56-0.59, very similar to that of type-III spinel proposed by Dick (1984) and this type of spinel may be the product of a highly depleted relic mantle. The signature index Cr^{\sharp} for the transitional parts is very high (0.56-0.59), showing a transitional trend toward magnetite. Studies have indicated that the spinel zones with these characters were formed from spinel alteration during serpentinization and metamorphism of the metamorphic ultramafic rocks.

Table 2. Electron microprobe analyses and calculated parameters for spinel minerals

Zone			Core pa	art (%)	(Transi	tional pa	rt (%)	17	M	larginal	part (9	6)
TiO ₂	0.11	0.04	0.07	0.08	0.06	0.25	0.21	0.12	0.21	0.11	0.21		0.01	0.06	
Al_2O_3	22.11	21.73	21.99	21.19	23.12	23.78	1.10	0.65	1.22	1.33	0.41	0.10			0.12
Cr_2O_3	47.48	46.89	46.64	45.98	45.41	45.21	39.34	38.99	38.88	38.25	37.10	15.29	9.54	9.06	2.44
$\mathrm{Fe_2O_3}$	0.79		0.07	0.52			28.44	32.24	29.26	32.41	30.69	51.95	60.61	60.74	66.26
MgO	11.94	7.97	8.05	8.16	9.02	7.74	1.59	1.58	1.47	3.39	1.34	0.96	0.34	0.46	0.50
CaO	0.04	0.05	0.00		0.13	0.04				0.18		0.11	0.04	0.01	0.15
MnO	0.79	1.22	1.29	1.52	0.90	1.35	2.96	3.42	2.98	3.26	2.89	1.44	0.80	0.41	0.09
FeO	16.19	21.45	21.67	21.77	20.19	20.96	26.11	22.77	26.68	20.69	26.05	29.40	29.84	29.33	28.77
NiO	0.09	0.08			0.11	0.03	0.24	0.22	0.18		0.32	0.57	0.54	0.51	0.70
Tot	99.54	99.43	99.78	99.22	98.94	99.36	99.99	99.99	100.88	99.65	99.01	99.82	101.72		99.03
Mg#	0.55	0.39	0.38	0.38	0.43	0.38	0.06	0.05	0.05	0.07	0.05	0.02	0.02	0.02	0.02
Cr#	0.59	0.59	0.59	0.59	0.57	0.57	0.96	0.98	0.96	0.95	0.98	0.99	1.00	1.00	0.94
Mineral		Magn	esian al	umochr	omite		Fer	ruginou	s chrom	e-magn	etite		Mag	netite	

Serpentine

The behavior of major elements during serpentinization has been well documented. Generally, serpentinization is an isochemical process (Coleman, 1977). Since the 1980s, more and more evidence has indicated that during serpentinization, only Al₂O₃ is relatively stable, and other elements such as Ca, Mg, Fe and Na are all active to some extent (Bonatti and Michael, 1989; Lippard and Shelton, 1986). Because of strong serpentinization of the Yanghou metamorphic ultramafic rocks, the primary dark minerals are seldom observed and their original chemical compositions are difficult to analyze.

In order to discuss the basic mineral compositions of the metamorphic ultramafic rocks, we analyzed metamorphosed harzburgite (serpentine) with the electron probe (Table 3). The analytical results indicate that the serpentine is relatively stable in chemical composition and is

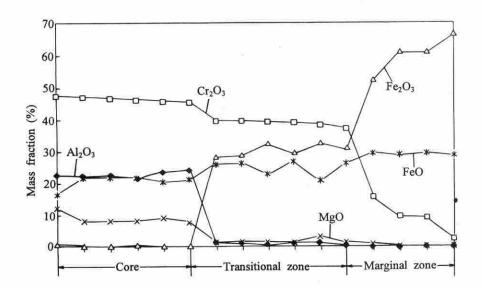


Fig. 3. Major composition variations of spinels in the different zones. characterized by high MgO and low FeO, indicating they are the products of a depleted relic mantle. This conclusion is coincident with spinellide mineral compositions.

Table 3. Electron microprobe analyses (%) of serpentine in the Yanghou area (sample YH27)

Sequence No.	SiO ₂	TiO ₂	Al_2O_3	Cr ₂ O ₃	FeO	MgO	MnO	NiO	Na ₂ O	K ₂ O	H_2O	Total
1	43.13	0.03	0.56	0.17	2.91	39.87	0.03	0.04	0.02	0.02	12.80	99.59
2	43.8	0.02	0.40		2.82	40.29	0.1	0.11		0.03	12.93	100.50
3	43.29		0.67	0.20	3.25	40.81	0.04	0.14			13.00	101.40
. 4	44.50	0.03	0.80	0.25	3.28	39.92	0.03	0.15			12.12	101.08

Trace Element Geochemistry

Rare-earth elements (REE)

The REE contents and chondrite-normalized distribution patterns of the type-I and type-II rocks (Table 4 and Fig. 4) are obviously different. Their characters are described as follows.

The REE contents of the type- I metamorphic ultramafic rocks are relatively low [Σ REE = $(0.91-1.63) \times 10^{-6}$] and the chondrite-normalized REE patterns are "U"-shaped [(La/Sm)_N=2.42-4.01; (Gd/Yb)_N=0.69-0.95; (La/Yb)_N=2.36-3.64)]. These are very similar to the REE characters of the relic mantle (Frey, 1984). Compared to the REE contents of harzburgite in a typical ophiolite suit, the total LREE contents of this type of rocks are relatively high (Fig. 4). Considering the widespread serpentinization of the samples, it could be deduced that the high LREE contents may be the result of alteration developed after diagenesis (Gillis et al., 1992; Michard, 1989).

The REE contents of type- \blacksquare metamorphic ultramafic rocks are much higher [Σ REE = $(5.96-6.08)\times10^{-6}$], and the chondrite-normalized REE patterns are right declined in the LREE part and flat in the HREE part [$(La/Sm)_N = 1.28-1.38$; $(La/Yb)_N = 1.43-1.58$; $(Gd/Yb)_N = 0.91-0.94$] (Fig. 4). These are the REE characters of pyroxene and olivine (Frey, 1984; Michard, 1989). In conjunction of the fact that this type of rocks is rich in

Al₂O₃, TiO₂ and poor in MgO, it could be interpreted that the rocks are cumulate rocks composed mainly of pyroxene and olivine.

Table 4. REE analyses (× 10 -9) for the Yanghou metamorphic ultramafic rocks

		12 W / 1			10000	-					
Sequence No.	YH21	YH23	YH27	YH36	YH37	YH50	YH51	л т	Aver. III	Semail	Troodos
Element			I			Ι	II	Aver. 1	Aver. III	Seman	1 roodos
La	309	270	175	177	223	701	752	231	727	26	68
Ce	534	510	295	344	401	1707	1777	417	1742	55	72
Pr	68	60	45	64	40	265	55	261	_	6	90
Nd	297	220	127	140	181	1185	1217	193	1201	26	26
Sm	59	45	33	46	35	345	342	44	344	5	8
Eu	20	14	12	14	12	109	110	14	110	1	4
Gd	62	50	48	47	51	384	367	52	376	7	13
Tb	9	8	8	9	8	69	65	8	67	_	1
Dy	91	68	54	60	47	403	394	64	399	16	18
Ho	17	10	9	10	12	95	89	12	92	==	3
Er	74	42	40	25	30	273	273	42	273	19	22
Tm	9	5	7	5	4	44	45	6	45	160	1
Yb	72	50	50	40	54	33	326	53	328	31	16
Lu	11	11	10	13	9	57	55	11	56	-	4
TOT	1632	1363	913	994	1107	5958	6078	1202	6018	192	346
δEu	1.01	0.90	0.92	0.92	0.87	0.92	0.95	0.93	0.93	0.57	1.31
$(La/Sm)_N$	3.29	3.77	3.34	2.42	4.01	1.28	1.38	3.33	1.33	3.21	5.35
(Gd/Yb) _N	0.69	0.81	0.77	0.95	0.76	0.94	0.91	0.78	0.92	0.18	0.63
(La/Yb) _N	2.89	3.64	2.36	2.98	2.78	1.43	1.56	2.92	1.49	0.57	1.31

Analyzed by ICP - MS at the Institute of Geology, Chinese Academy of Sciences.

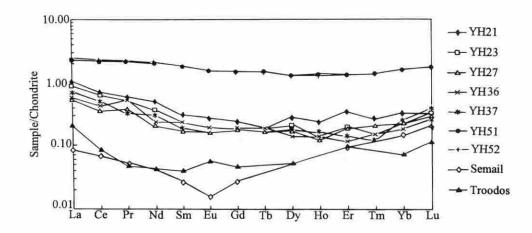


Fig. 4. Chondrite-normalized REE patterns in the Yanghou metamorphic ultramafic rocks. Semail represents the metamorphosed harzburgite REE patterns of Semail ophiolite, Oman (Lippard and Shelton, 1986); Troodos represents the metamorphosed harzburgite REE patterns of Troodos ophiolite, Cypurus (Lippo et al., 1995).

Large ion lithophile elements (LILE) and high field strength elements

Trace element analyses are listed in Table 5. Rb and Ba of all the samples analyzed are obviously higher than those of the primary mantle, which may be the alteration result of serpen-

tinization. The contents of high field strength elements (Nb, Ta, Zr, Hf) in the type-I rocks are 4 – 20 times lower than those of the primary mantle; but those of the type-II rocks are much higher (Nb and Ta are 4 – 6 times higher than those of the primary mantle). This reflects that the two types of rocks are obviously different in origin. From the data on trace element contents, it could be deduced that the type-II rocks represent a relic mantle which had experienced strong partial melting, and the type-III rocks may be the segregation products of basaltic melts derived from high partial melting of a mantle.

First transitional group elements (FTGE)

In the FTGEs, the distribution coefficients (Kd) of Sc, Cr, Co and Ni are high (Kd>1) and these elements are classified as the compatible elements; the distribution coefficients of Fe and Mn are about 1, and these elements could be classified as the moderately compatible elements; the distribution coefficients of Ti, V, and Cu are relatively low (Kd<0.2) and these elements could be classified as the moderately incompatible elements. In addition, Cr and Ni tend to remain in mantle mineral phases (olivine and pyroxene), so the magma derived from the mantle is generally depleted in Cr and Ni relative to chondrites, but pyrolites and relict mantle have no such characters. Because of these characters, the FTGEs are of importance for revealing magma source region and diagenesis process.

The two types of rocks show obvious differences in FTGE contents (Table 5). As compared to the primary mantle, the type-I rocks are highly enriched in Cr, Co and Ni, and this is a character of the highly depleted relic mantle; as to the type-II rocks, the contents of Cr, Co and Ni are much lower than those of the primary mantle. In the chondrite-normalized FTGE distribution patterns (Fig. 5), the type-I rocks display the patterns characterized by depletion in incompatible elements (Ti, V) and enrichment in compatible elements (Cr, Ni); but the type-II rocks show a mantle-source rock pattern characterized by enrichment in incompatible elements (Ti, V) and depletion in compatible elements (Cr, Ni). Such complementary variations indicate that the two types of rocks are closely related with each other with respect to their origin. FTGE characters also indicate that the type-I rocks are characteristic of a relic mantle, but the type-II rocks may be derived from the mantle (segregation cumulating origin). These are coincident with the results from the major elements, rare-earth elements and incompatible elements.

	Table 5.	Trace	element	analyses of	of the n	netamorphic	ultramafic	rocks ($(\times 10^{-9})$)
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Sample No.	Rb	Ba	Nb	Zr	Hf	Ta	Se	Cr	Ni	Co	V
YH21	2.7	72	0.19	0.47	0.02	0.01	8	2064	2719	109	30
YH23	1	50	/	1	/	1	7	2144	2741	113	27
YH27	0.3	49	0.19	0.57	0.02	0.01	8	1350	2280	117	37
YH51	1.3	16	2.58	7.20	0.24	0.26	35	86	1188	66	199
PM	0.6	7	0.71	11.20	0.31	0.04	17	1020	2400	105	59

Note: FTGEs are analyzed by the XRF method at the Institute of Geology, Chinese Academy of Sciences; the other elements by the ICP-MS method at the Institute of Geology, Chinese Academy of Sciences. PM—primary mantle composition (Rollinson, 1993).

Discussions on Rock-Forming Age

Because of their special composition, it is very difficult to determine the petrogenic age of the ultramafic rocks. In this paper, we think that the rock-forming time of the Xiongshan basic

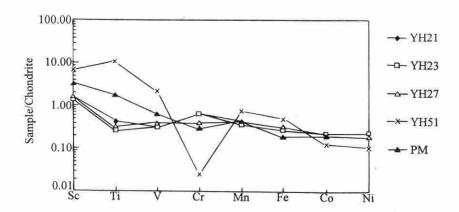


Fig. 5. Chondrite-normalized FTGE patterns in the metamorphic ultramafic rocks.

dike swarm complex and the Daoxiang Group metasedimentary rocks can represent that of the ultramafic rocks because they are closely associated in the same area.

The Sm/Nd isochron age of the Xiongshan basic dike swarm complex is 585.7 ± 30 Ma and the calculated $\varepsilon_{Nd}(T)$ is up to +6.9 (Ren Shengli et al., 1996). It is indicated that the dike swarm complex may be originated from a depleted mantle source region left behind MORB extraction, and the complex and harzburgite in the ultramafic rocks may have parent-daughter relations in origin.

In the Daoxiang Group metasedimentary tuff (epidote-chlorite-albite schist), there have been found micro paleo-fossils (Trematosphaeridium heltedahlii Tim, Trematosphaeridium sp., Protosphaeridium Timofeev, Laminavites antiguissimus Eichw, etc.), which belong to Upper Sinian to Lower Ordovician (Xu Yiwei and Lin Yuping, 1990). The Pb/Pb isochron age of the marble from the "Daoxiang Group" is about 460 Ma (Ren Shengli et al., 1996). Marble from the same layer was found fossilized with Turuchanica temete sp. and Chitinozoa, which belong to Upper Sinian to Lower Cambrian (Xu Yiwei and Lin Yuping, 1990). Previous studies showed that the Pb/Pb isochron ages of marbles could reflect their metamorphic recrystallization age (Jahn and Cuveller, 1994), so it could be inferred that the "Daoxiang Group" was formed in the Late Sinian-Early Cambrian, and metamorphosed at 460 Ma.

In a 1/50,000 regional survey, the North Fujian Brigade determined a K/Ar isotopic age of 424 ± 10 Ma for amphibolite (may be the product of metamorphism) in the metamorphic ultramafic rocks.

From the above-mentioned facts, it could be deduced that the Yanghou metamorphic ultramafic rocks were formed at about 585 Ma ago and may be metamorphosed in the time period of 424 – 460 Ma.

Conclusions

From petrogeochemistry and mineral chemistry studies, it could be concluded that the Yanghou metamorphic ultramafic rocks are derived from the relic mantle extracted by melts and ultramafic cumulate. Geological occurrence and geochronological studies indicate that the ultramafic rocks may be formed in Late Sinian-Early Paleozoic, and alteration, metamorphism and tectonic emplacement were developed after the rocks were formed. From the petrochemistry,

mineral chemistry and geochronology data, it is concluded that the Yanghou metamorphic ultramafic rocks are the components of the ophiolite suite in South China.

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