Geochemical characteristics of the organic matter in UPPMRs and the implication for fluid–rock exchange due to the retrograde metamorphism in the Dabie–Sulu orogenic belt, North China

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The samples were collected from ultrahigh-pressure para-metamorphic rocks (UPPMRs) around 500–2000 m deep by Chinese Continental Scientific Drilling. The combined method of ultrasonic disintegrator and Soxhlet was strictly conducted to extract the indigenous hydrocarbons from the UPPMRs, to obtain non-contaminated and entire organic matter to reveal the geochemical characteristics and origin of hydrocarbons in the UPPMRs. Through gas chromatography–mass spectrometry analysis, the ratios of Pr/Ph in the soluble hydrocarbon were from 0.04 to 0.87. It was inferred that the precursor of extracts would be deposited in the anoxic setting. Based on the relative content among C₂₇, C₂₈ and C₂₉ steranes, it was found that the main source of organic matter was marine algae. But the isomer ratios of C₃₁ hopane 22S/(22S + 22R) were 0.39–0.69, and the distribution range of C₂₉ sterane 20S/(20S + 20R) was 0.41–0.63, both of which reflected the equivalent maturity of organic matter was no more than 1% (*R*_o%). Therefore, the immature organic matter derived from algae obviously conflicted with its host rock, which experienced ultrahigh-pressure metamorphism. Therefore, this sort of immature organic matter probably is of secondary origin. Furthermore, the chromatography of *n*-alkane almost assumes bimodal distribution, and the data of *T*_{max} ranges from 394 to 565°C, as S₁/total organic carbon (TOC) ratios systematically increase with the corresponding *T*_{max}. Therefore, it could be further proved that the organic matter in the UPPMRs probably is of mixed origin and is mainly derived from immigrant hydrocarbons during the stages of subduction and retrograde metamorphism. The emergence of Zr-in-rutile also indicates that the geological temperature was lower than that during the peak of metamorphism. Therefore, it could be inferred that the kerogen associated with rutile might go through diagenesis regularly at the stage of retrograde metamorphism. It was also shown that the δ¹⁸O value suddenly reduced up to –10‰ corresponding to the highest TOC (1820 µg/g) around the subduction fault. The relationship between the TOC and δ¹⁸O value indicated that the fluid–rock exchange reaction was the main reason for the immature organic matter present in the para-metamorphic rock. The returned subduction and retrograde metamorphism resulted in the activity of the formation fluid, which could prominently impact the geochemical characteristics of the para-metamorphic rock and should also be considered in the geodynamics research of the metamorphic orogenic belt.

Keywords. Ultrahigh-pressure para-metamorphic rock; biomarkers; oxygen isotopes; rutile; retrograde metamorphism; Dabie–Sulu orogenic belt.

1. Introduction

Ultrahigh-pressure metamorphism and continental collision orogenesis was always a research hotspot of geodynamics in the latest decades (Coleman and Wang 1995; Liou *et al.* 2004). New metamorphic mineral assemblage promoted the development of the traditional plate theory. The enormous discovery of coesite and diamond in the metamorphic zones supplied reliable evidence to convince the subduction of crust into mantle (Smith 1984; Chopin 2003). Then the ultrahigh-pressure metamorphism returned and exhumed the shallow crust due to collision orogenesis. Therefore, continental orogenesis usually involved two stages: subduction and exhumation. Numerous research studies have been dedicated to understand the metamorphic mechanism in the process of subduction and exhumation (Hacker and Liou 1998; Carswell and Compagnoni 2003). We could date when the lithosphere started to thicken due to tectonic collision, figure out the formation conditions of metamorphic minerals and reconstruct the thermal history of crustal subduction (Zheng 2008). Fluid activity and material circulation could be other perspectives to explore the geodynamic process.

The main borehole of the Chinese Continental Scientific Drilling (CCSD) is located in the Mesozoic orogeny between the North China and South China plates (figure 1). Previous studies have shown that the peak temperature of metamorphic rocks in the Dabie–Sulu area was up to 850–1000°C, and the pressure was as high as 3.5–6 GPa (Zheng *et al.* 2008). As all these para-metamorphic rocks originated mostly from a sedimentary precursor and suffered high-temperature metamorphism, the traditional view was that most of the organic matters was completely cracked. Such a high temperature and high pressure had exceeded the traditional ‘dead threshold’ of organic matter (Tissot and Welte 1984). Polycondensation and graphitisation occurred in the residual organic matter, resulting in graphite being found in granulite facies rocks. However, according to a number of experiments, high-carbon liquid hydrocarbons still exist at a

temperature of 700°C and a pressure of 3 GPa (Schneider *et al.* 2006). Therefore, it is still confusing whether the hydrocarbons in ultrahigh-pressure para-metamorphic rocks (UPPMRs) could inherit or represent the organic composition of the sedimentary precursor. Current geodynamic research is convinced that the subduction unit represents the oceanic crust precursor, and a ductile shear zone, with a thickness of 150–200 m, has been located (Xu *et al.* 2006). This shear zone supplies a narrow tunnel for the returning and exhumation of the sedimentary precursor and is also associated with complex fluid–rock exchange. But unfortunately, it is unclear as to what sort of fluid activity and organic–inorganic reaction occurred during the subduction and returning process of the para-metamorphic unit.

The stratum of detrital-carbonate experienced an ultrahigh pressure situation with rapid subduction and quick return, and this process only lasted for 10 My (Zhang *et al.* 2008; Cui *et al.* 2009; Zeng *et al.* 2009). The geochemical characteristics of the organic matter in the dynamic metamorphism record the geodynamic process, and this area is the perfectly natural laboratory to observe hydrocarbon behaviour and supply more significant information to explain the geodynamic mechanism of mega orogeny. To reveal the geochemical characteristics of the organic matter in para-metamorphic rocks, 12 samples were collected from the main borehole of CCSD at depths from ca. 500 to ca. 2000 m. The samples involved all varieties of rock types in the entire dynamometamorphic tectonic. The maturity of hydrocarbons in the UPPMRs is discussed using the biomarkers, stable isotopic composition and spectrographic properties of kerogen. The petrography and inclusions of the samples were also used to study the source of hydrocarbons in the para-metamorphic rocks. Based on the research studies on UPPMRs with regard to the geochemical characteristics of organic matter, it would be useful to promote an understanding of the fluid activity during the subduction and returning process of the mega-orogenic tectonic events. This study could possess significant scientific and practical value

Figure 1. The geographic position of CCSD and the distribution of UPPMRs in the Dabie–Sulu area.

for the research of deep dynamic metamorphism of hydrocarbons.

2. Geologic setting

The Dabie–Sulu orogenic belt is one of the most famous ultrahigh-pressure metamorphic zones in the world, due to the collision of the Yangtze and the Sino-Korean craton. The square of this ultrahigh-pressure metamorphic area is $450 \times 75 \text{ km}^2$ and detached into two obvious different parts by the NS-trend Tan-Lu fault (figure 1). The Sulu ultrahigh-pressure metamorphic belt (Sulu UPMB) is located east of the northern sector of the Tan-Lu fault, distributed along the NNE–SSW trending (Liu *et al.* 2009a). The Jiashan–Xiangshui fault is the southern boundary of the Sulu UPMB. The Dabie ultrahigh-pressure metamorphic belt (Dabie UPMB) is situated west of the southern sector of the Tan-Lu fault, coincident with the Qinling mountains (Lou *et al.* 2009). The relative stratum of the Sulu UPMB and the Dabie UPMB was stricken to the NE direction by 500 km by the Tan-Lu strike-slip fault (figure 1).

The main borehole of CCSD was drilled in the area of UPPMR south of Donghai city (figure 1). The main drilling hole of CCSD was the epitome of the Sulu UPMB. The 0–2000 m cores in the CCSD

mainly consisted of orthogneiss and paragneiss, laminated with thin layers of eclogite, retrogressive eclogite and amphibolite. The precursor of this metamorphic rock was the Palaeozoic flysch sediment (Chen *et al.* 2009), which experienced greenschist metamorphism and formed high-pressure para-metamorphic rocks (HPPMR). Based on the analysis of mineral composition, it was found that all the UPPMRs might be derived from the metamorphism of mud rocks and retrogressive metamorphism of amphibolite. Based on the geochronological studies of the Sulu UPMB, the ultrahigh- and high-pressure metamorphic events occurred at $\sim 230 \text{ Ma}$. Meanwhile, the retrograde of hornblende and the overprinting metamorphic of granulite both began at $\sim 210 \text{ Ma}$. On combining the measures of U–Pb dating in the coesite-bearing domains and quartz-bearing rims of the zircons from the paragneiss, it was revealed that the process of ultrahigh-pressure metamorphism and retrograde occurred at about $227 \pm 2 \text{ Ma}$ (Liu *et al.* 2008). Based on a recent study of chronology, it was determined that quick subduction movements had occurred twice in the Sulu UPMB. One occurred at 230–213 Ma and another took place at $\sim 195\text{--}175 \text{ Ma}$ (Liu *et al.* 2009b). The quick exhumations that occurred twice were associated with the processes of temperatures rising and falling twice (Liu *et al.* 2009c), and the stratum

pressure decreasing from 3.5 to 2.8 GPa. Thus, this area is the perfectly natural laboratory to investigate the mechanism of deep geodynamics.

3. Samples

Twelve samples of UPPMRs from 700 to 2000 m from the main borehole of the CCSO project were distributed in the lithologic units. At the top was the epidote biotite amphibolite plagioclase gneiss (eclogite gneiss) from 583 to 1130 m (see sample No. 1–5 in table 1 and figure 2), including multiple layers of kyanite eclogite and amphibolite. The middle unit was the amphibolite biotite plagioclase gneiss and biotite alkali feldspar gneiss from a depth of 1130–1596 m (see sample No. 6–8 in table 1 and figure 2). The third unit was the phengite eclogite, degeneration rutile eclogite including the amphibolite and biotite alkali feldspar gneiss (see sample No. 9–12 in table 1 and figure 2). The lithological type of each sample is exactly presented in table 1.

In addition, a strong seismic reflector existed at a depth of 1600 m, which was the boundary between the overlying granitic gneiss and the underlying phengite, eclogite and gneiss (see the shear boundary in figure 2). The main trend of the upper strata was ESE (100°E), the inclination ranged from 30° to 40°; but in the lower strata, the main trend was SSE (160°E) and the inclination exceeded 50°. At 1600 m upward, the breccia zone was developed, in which the phenomenon of rounding existed (figure 2), according to which it was presumed that there was a tectonic surface of extension shear between the two strata, which was

developed in the late extension stage of the exhumation structure.

4. Methods

The powdered sample (ca. 50) was Soxhlet extracted with methanol (MeOH)/dichloromethane (DCM) (1/9; v/v) for 72 h. The resulting extracts were separated into fractions using a column (30 × 0.8 cm, column volume (V_0) = 7 ml) packed with silica gel (activated at 120°C for 16 h) by elution with hexane (8 ml) for the saturated fraction and DCM/hexane (1:2, v/v; 10 ml) for the aromatic fraction. But, it had not been clear whether this traditional method was suitable to reveal the entire hydrocarbons in the metamorphic rocks. So, the ultrasonic disintegrator was used to extract the hydrocarbons included in the UPPMR. The whole extraction experiment was conducted strictly, including washing the surface of the cores with H₂O₂ and cutting the exterior to clean samples. During the procedure of extraction, all of the solvents had been 20 times concentrated to guarantee a blank during extraction.

The difficulty of investigating the organic characteristics of UPPMR was the separation of kerogen from fluoride (Durand 1980; Zhu 1981). Different from the kerogen from sedimentary rocks, the insoluble organic matter of UPPMR contained fluoride, which could not be isolated completely by conventional flotation. Therefore, special flotation fluid (ZnCl–KI in acetic acid, 2.06 g/cm³) was used to isolate kerogen. After flotation, the samples were centrifuged for 20 min at 600 rpm.

Table 1. The samples information of Chinese Continent Science Drilling 700–2000 m (Donghai).

	No. of samples	Depth (m)	Main lithology
1	B387R304P1a	735–742	Calcite biotite hornblende plagioclase gneiss
2	B425R329P7u	798–800	Pyrite limestone adamellite gneiss
3	B426R329P7z	801–802	Epidotic hornblende schist
4	B442R342P1c	820.91–832.70	Epidotic hornblende biotite plagioclase gneiss
5	B623R439P6a	1121–1129	Epidotic hornblende gneiss
6	B644R458P2c	1263–1273	Epidotic hornblende plagioclase gneiss
7	B819R556P4b	1564–1571	Magnetite felsic gneiss
8	B820R558P2	1571–1579	Chlorite biotite hornblende schist
9	B952R626P5a	1828–1837	Phengite eclogite
10	B956R627P4a	1838–1840	Hornblende plagioclase gneiss
11	B957R627P4t	1841.13–1844	Epidotic biotite hornblende schist
12	B966R629P3t	1850–1857	Phengite eclogite

Figure 2. The profile of crustal fold, thrusting structure and ductile shear zone with the lithological composition of UPPMRs cross the CCSD main borehole (after Zheng 2008).

4.1 Soluble organic matter detected by gas chromatography-mass spectrometry (GC-MS)

GC-8060/MD-800 equipment was used for GC-MS testing from Finnigan Corporation, USA. The capillary column was ZB-5 (J&W Co., USA), which was suitable for detection by mass spectrometry. To test all the organic compounds, the scan range of MS was 35.00–550.00 amu. Helium was the carrier gas, with a constant current of 1 cm³/min. The temperature programme is as follows: a constant temperature of 50°C for 5 min; 50–220°C with a rate of 4°C/min; 220–320°C with a rate of 2.0°C/min; a constant temperature of 320°C for 25 min and the gasification chamber temperature was 300°C. An HP-5 capillary column was adopted in the GC with a length of 30 m, a diameter of 0.25 mm and a film thickness of 0.25 μm.

4.2 Detection by Rock-Eval

The hydrocarbon potential of UPPMR was evaluated using Rock-Eval 2plus (France) at the assessment station of petroleum (RIPED, China). The conditions of instruction are as follows: adsorbed organic matter (S₁) was tested by heating 3 min at 300°C and bounded organic matter (S₂) was detected with the temperature rising from 300°C to 600°C at a heating rate of 50°C/min. Then the S₁ and S₂ were burnt to CO₂, which was quantified at 390°C in a trap well.

4.3 Fourier transform infrared (FTIR) spectrum of kerogen

The mixture of 0.68 mg kerogen and 150 mg KBr was smashed for 10 min, and then the powered sample was squashed into a round sheet under 10 Mpa. FTIR spectroscopy was performed using TFS-113V (Bruker Co., Germany). The analysis conditions of the FTIR spectrum were luminous flux = 15,000, XSP = 4000 cm⁻¹, XEP = 400 cm⁻¹, NSS = 16 and VEL = 16.

4.4 Analysis of the carbon and oxygen isotopes

The carbon isotope of the prepared pure kerogen was analysed using Thermo Delta V Advantage, an ion source vacuum of 8.6–8.9 × 10⁻⁷ mbar and an ion source voltage of 3.07 kV. In the temperature programme, the temperature rose from 33°C at a rate of 8°C/m to 80°C and then rose up to 250°C at a rate of 5°C/m for 20 min of constant temperature.

An aliquot of UPPMR samples (ca. 10 g) reacted with 100% phosphoric acid under vacuum at 50.0 ± 0.1°C for 36 h. The collection of the resulting CO₂ was analysed for oxygen isotope using a Delta-XP mass spectrometer of continuous flow (Finnigan Co., USA).

5. Results and discussion

Based on the Rock-Eval data, the $T_{\max}$ of average UPPMR samples is above 450°C (except sample No. 11) (figure 3), which is the commonly equated

Figure 3. The comparison of maturity, potential content and biomarker characteristics of hydrocarbons in the UPPMR samples detected by Rock-Eval and GC-MS.

high maturity of sedimentary rocks ($> \sim 1.2\%$ R_o) consisting of UPPMRs. Meanwhile, the total organic carbon (TOC) in most of the UPPMR samples is quite lower than that of typical TOC in sedimentary rocks, as the majority ranges from 111 to 516 $\mu\text{g/g}$ (except sample No. 11). The production index is 0.13–0.22 (figure 3), which also indicates high maturity. The S_1 of almost all samples is 0.01 mg/g, and S_2 is abnormally low, ranging from 0.04 to 0.07 mg/g (figure 3), which was initially found to be the residual hydrocarbons in the UPPMRs. However, the T_{max} of all samples widely spans from 394°C to 565°C. The T_{max} of the special No. 11 sample was just 394°C and quite below the oil-window of sedimentary rocks ($T_{\text{max}} = 435^\circ\text{C}$) (Tissot and Welte 1984) rather than of high maturity. The percentage of pyrolysis hydrocarbons in TOC was from 13.83% to 60.87%, which implicates that both the thermal evolution of all UPPMR and the maturity of pyrolysis hydrocarbons varied and are not consistent. Especially, the

highest TOC appeared in the paragneiss and plagio-hornblende schist (sample No. 11), which was 1820 $\mu\text{g/g}$ at a depth of 1842 m near the boundary of the shear zone. So, further investigation of the biomarkers in soluble hydrocarbons is needed to figure out whether the organic matter is residual in average UPPMRs.

From the GC-MS analysis, the maturity parameters of isomer biomarkers released that the revolution of soluble organic matter in the UPPMR had not achieved the thermodynamics equilibrium under geological conditions (figure 3) such as the ratios of C_{32} hopane $22S/(22S + 22R)$ were 0.53–0.61, the ratio of $T_s/(T_s + T_m)$ was from 0.40 to 0.66 and the ratio of C_{29} sterane $20S/(20S + 20R)$ was 0.41–0.63, all of which indicate that the thermal maturity of soluble hydrocarbons was in the oil-window stage (see discussion in section 5.1). The exact reflectivity of analogous vitrinite was only $\sim 0.3\%$, and the analogous vitrinite reflectivity in the strata below the shear zone was

only 0.1% (figure 3). Thus, a few parts of organic matter in UPPMR should be secondary rather than residual hydrocarbons. In accordance with the previous thermal simulation, the stability of long-chain alkanes was proved under the conditions of high pressure and increased activation energy of the reaction (Price and Wenger 1992), because the ultrahigh-pressure conditions inhibited the reaction of demethylation, aromatisation and dehydrogenation in the maturation process of the organic matter. This might provide some enlightenment for the revolution of the organic matter under the conditions of ultrahigh pressure and temperature. Therefore, the analysis data of samples would be discussed around whether the organic matter in the samples had experienced metamorphism together with UPPMR. The revolutionary mechanism of the organic matter in the UPPMR also needs to be elucidated.

5.1 Characteristics of the soluble organic matter in the UPPMR

Regarding the integrity of the soluble organic matter in the UPPMR, the powered sample was extracted using a combination of Soxhlet first and ultrasonic extraction in sequence next. The organic matter in mineral inclusions could be recovered by ultrasonic shattering. As shown, the main peak n -C₂₀ in the chromatography of Soxhlet extraction and the main peak n -C₃₀ in the chromatography of bitumen resulted from the ultrasonic extraction (figure 4). Therefore, the two parts of the soluble organic matter were merged as the entire soluble organic matter.

With the GC-MS analysis, the main peak of n -alkane ranged from C₂₀ to C₃₁ in the soluble organic matter of 12 samples, and was bimodal (figure 5). From the traditional view of the bimodal pattern, the origin of light n -alkanes is from microorganisms, and the heavy n -alkanes are from terrigenous plants. But based on the Pr/Ph ratio from 0.04 to 0.87, it was indicated that the organic matter might develop in the anoxic environment. Especially, the concentration of heavy n -alkanes is quite lower than that of light n -alkanes in most of the samples. Therefore, the contribution of plants is limited. In a previous research, it was revealed that the chromatography of n -alkanes derived from subsea *Spirulina* possessing the bimodal property. When the maturity elevated at 200°C during the simulation experiment, the high carbon number disappeared. But at 250°C, the bimodal property reappeared (Li 2002). Therefore, based on the chromatography of n -alkanes in sample No. 4 (B442R342P1c), it was concluded that the origin of the organic matter in UPPMR was possible from marine algae. So, further discussion would be necessary to clarify the evolution stage of the organic matter in the UPPMR samples.

With regard to organic maturity, the ratio of C₃₂ hopane 22S/(22S + 22R) was 0.53–0.61, which indicated that the thermal revolution of the organic matter was in the oil-window stage. The range of the $T_s/(T_s + T_m)$ ratios was from 0.40 to 0.66 (figure 6); all the maturity parameters had not reached equilibrium, which also revealed that the thermal revolution of the organic matter had not reached the stage post maturity. During the thermal maturity process of the organic matter, the biological configuration of biomarkers would transform

Figure 4. Comparison of gas chromatography disposed by Soxhlet and ultrasonic extraction from sample No. 6 (B644R458P2c). (a) Soxhlet extraction and (b) ultrasonic extraction.

Figure 5. The TIC chart of the saturated hydrocarbon in sample No. 4 (B442R342P1c).

Figure 6. The m/z 191 mass chromatogram of sample No. 11 (B957R627P4t). Notes: 1. C_{20} Tricyclic Terpene (TT); 2. C_{21} TT; 3. C_{23} TT; 4. C_{24} TT; 5. C_{25} TT; 7. C_{26} Tetracyclic Terpene; 8. C_{28} TT; 9. C_{29} TT; 10. $18\alpha(H)$ -22,29,30-trisnorhopane (Ts); 11. $17\alpha(H)$ -22,29,30-trisnorhopane; (Tm); 12. C_{29} TT; 13. C_{30} TT; 14. $17\alpha(H)$, $21\beta(H)$ -30-norhopane; 15. $18\alpha(H)$ -30-norhopane (C_{29} Ts); 16. $17\alpha(H)$, $21\alpha(H)$ -30-norhopane; 17. $17\alpha(H)$, $21\beta(H)$ -hopane; 18. $17\beta(H)$, $21\alpha(H)$ -hopane; 19. $17\alpha(H)$, $21\beta(H)$ -29-homohopane 22S; 20. $17\alpha(H)$, $21\beta(H)$ -29-homohopane 22R; 21. Gammacerane; 22. $17\alpha(H)$, $21\beta(H)$ -29-bishomohopane 22S; 23. $17\alpha(H)$, $21\beta(H)$ -29-trishomohopane 22S.

into the geological configuration, and the relative concentration of isomers corresponds to a certain maturity point of the organic matter (Zhang and Huang 2005). So, based on the four maturity parameters, it could be concluded that the thermal revolution of the organic matter in the UPPMR was equivalent to the $VR_o^E = 0.5$ – 0.9% . It might also be indicated that the organic matter of UPPMR had not experienced ultra-pressure metamorphism.

The distribution range of the C_{29} sterane 20S/(20S + 20R) ratio was from 0.41 to 0.63 and the C_{29} sterane $\beta\beta/(\alpha\alpha + \beta\beta)$ ratio was 0.31–0.44. Both of the maturity parameters of steranes were close to the equilibrium of mature evolution, because the epimerisation equilibrium of S/(S + R) and $\beta\beta/(\alpha\alpha + \beta\beta)$ was 0.55 and 0.7, respectively, (Moldowan *et al.* 1986). The ratio of

S/(S + R) in some samples was beyond 0.55 which might have been disturbed by the biodegradation of bacteria (Clegg *et al.* 1998). Therefore, it can be explained that the organic matter in the UPPMR has secondary origin. As is well known, if the hydrocarbons experienced the metamorphism of ultrahigh pressure and temperature (Wang *et al.* 2008; Richard *et al.* 2008), the steranes could not be detected or the abundance would be an order of magnitude less than that in normal sedimentary rocks (figure 7). Therefore, the maturity parameters of steranes also reflected the same level of maturity as the parameters of hopanes ($R_o = 0.6$ – 0.9%).

Referring to the triangular chart of the relative content of C_{27} , C_{28} and C_{29} sterane (figure 8), the source of the organic matter was confirmed as mainly algae (Peters *et al.* 1994). This conclusion

Figure 7. The m/z 217 mass chromatogram of sample No. 11 (B957R627P4t). Notes: 8. $13\alpha,17\beta$ - C_{28} diasterane 20R(24S+24R); 9. $5\alpha,14\alpha,17\alpha$ - C_{27} sterane 20R; 10. $5\alpha,14\beta,17\beta$ - C_{27} sterane 20S; 11. $5\alpha,14\beta,17\beta$ - C_{27} sterane 20S; 12. $5\alpha,14\alpha,17\alpha$ - C_{27} sterane 20R; 13. $13\alpha,17\beta$ - C_{29} diasterane 20R; 14. $13\alpha,17\beta$ - C_{29} diasterane 20S; 15. $5\alpha,14\alpha,17\alpha$ - C_{28} sterane 20S; 16. $5\alpha,14\beta,17\beta$ - C_{28} sterane 20R; 17. $5\alpha,14\beta,17\beta$ - C_{28} sterane 20S; 18. $5\alpha,14\alpha,17\alpha$ - C_{28} sterane 20R; 19. $5\alpha,14\alpha,17\alpha$ - C_{29} sterane 20S; 20. $5\alpha,14\beta,17\beta$ - C_{29} sterane 20R; 21. $5\alpha,14\beta,17\beta$ - C_{29} sterane 20S; 22. $5\alpha,14\alpha,17\alpha$ - C_{29} sterane 20R.

Figure 8. Relative contents of the C_{27} , C_{28} and C_{29} sterane in the samples of UPPMRs and the origin of organic matter.

was also uniform with the result shown by the characteristics of n -alkanes in samples. According to the regional dynamic metamorphism research, it was indicated that the UPPMR was derived from the metamorphism of marine strata from neoproterozoic to palaeozoic in the Yangtze craton. So, there might be a chance that the organic matter was generated from the syndeposition of algae in the neoproterozoic to palaeozoic strata via the

metamorphism at high temperature and pressure. But the parameters of sterane isomers indicated median maturity, which conflicted with the theory of metamorphism. So, the only reliable explanation was that the organic matter did not experience the ultra-high temperature and pressure of metamorphism. If that actually happened, it is consistent with the evidence of organic maturity indicated by kerogen and bitumen.

5.2 Characteristics of kerogen from No. 11 sample

The only kerogen was extracted from the No. 11 sample using a centrifuge at a low-rotational speed. Based on comparing the FTIR spectrum of kerogen from the No. 11 sample (figure 9), the major functional groups involved are CH_3CH_2 and C–H. The absorption intensity of CH_3CH_2 and C–H is 0.1163 and 0.1116, respectively, which is higher than that of the aromatic-CH bond (see $I_{870\text{ cm}^{-1}}$ and $I_{750\text{ cm}^{-1}}$ in figure 9). It was indicated that the type of kerogen is prone to type II or II₁, although a little bit of the absorption peak of the oxygen bond appeared at $I_{1720\text{ cm}^{-1}}$. The origin of incorporated oxygen will be discussed in the paragraph on oxygen isotopes.

Especially, an absorption peak of rutile appeared in the kerogen concentrate. Based on previous research studies (Xu *et al.* 2004), the rutile was the common accessory minerals in the process of metamorphism, whose origin can be divided into two types. One type of rutile was of regular nanometre-size deformed twins, associated with garnet and omphacite, with a modulated texture. It indicated a strong strain effect on rutile crystals, and might be tightly related to the subduction, return and subsequent continental collision. Another type of rutile was included in the garnets or omphacites. The crystal of the latter type was well preserved in the host minerals, and had not undergone crystal distortion during exhumation and subduction. By means of the new Zr-in-rutile geothermometer reported by Zack *et al.* (2004), the formation temperature of rutile in the epidotic schist of CCSD at a depth of 1841 m was estimated

to be from 690°C to 787°C (Chen *et al.* 2005). This was slightly lower than the conclusion from continental dynamics studies. It was very likely that the rutile in the No. 11 sample formed in the inclusions of garnet or omphacite. At the stage of tectonic return, the eclogite suffered from amphibolite-facies retrograde metamorphism, so that formation fluid was quite active. Then the diffusion exchange of ion in the rutile resulted in the formation temperature of the Zr-in-rutile geothermometer being lower than that of the metamorphism peak. So, this evidence indicated that the kerogen associated with the rutile might mature regularly at the stage of retrograde metamorphism.

The $\delta^{18}\text{O}$ value of rocks in the main hole of CCSD from the ground surface to 1700 m depth was slightly increasing. From the near surface to 1000 m depth, the $\delta^{18}\text{O}$ value of UPPMR was well below zero. This indicated the shallow rocks had experienced the fluid–rock exchange with atmospheric precipitation. Accompanied by an increase in the depth from 1000 to 1700 m, the $\delta^{18}\text{O}$ value of rocks raised more than zero and increased up to $\delta^{18}\text{O} = 2.4\text{‰}$ at a depth of 1660 m. However, it is worth noting that the $\delta^{18}\text{O}$ value of the No. 11 sample at 1842.6 m suddenly changed to -10‰ . The TOC of the No. 11 sample was 1820 $\mu\text{g/g}$ for most of the samples. The variation trend of the oxygen isotope was coupled with TOC, which mutually explains both the oxygen isotope and the organic content (figure 10). The relationship between the TOC and $\delta^{18}\text{O}$ value indicated that the fluid–rock exchange reaction was the main reason for the relative abundant TOC and low-maturity organic matter detected in the No. 11 samples.

Figure 9. The FTIR spectrum of the kerogen from sample No. 11 (epidote biotite amphibolite).

Figure 10. The relationship between TOC and the oxygen isotope of the para-metamorphic rock samples.

The carbon isotope of kerogen separated from the epidote biotite amphibolite was detected at $\delta^{13}\text{C} = -31.4\text{‰}$. In a previous research, the inclusions of $\text{N}_2\text{-CH}_4$ in the eclogite were first discovered by Fan *et al.* (2005). Based on the petrography study of $\text{N}_2\text{-CH}_4$ inclusions, these pure gaseous inclusions were mostly primary and mainly exhibited as isolated and little groups in banded quartz veins in the eclogite, associated with the salt-water inclusions of high-medium salinity. It was implied that the $\text{N}_2\text{-CH}_4$ inclusions were probably captured in HP-UHP metamorphism. The $\delta^{13}\text{C}$ value of CO_2 in the salt-water inclusions was from -32‰ to -28‰ , close to the $\delta^{13}\text{C}$ of the organic matter deposited in marine sediments (Mook 2001). Therefore, the origin of carbon from the inclusions captured in the HP-UHP metamorphism might be the organic origin, and not disturbed by the effect of the mantle fluid. It could also be implied that the protogenetic organic matter was probably cracked into CH_4 and CO_2 at ultrahigh pressure and temperature, with the rapid subduction in <10 My. But no fluidic hydrocarbon inclusions had been discovered so far. Therefore, the primary record of hydrocarbons is unfortunately deficient.

5.3 Maceral characteristics of UPPMRs

The maceral observation in the oil-immersed reflection was the direct evidence for the origin of the organic matter in the UPPMR. The main maceral in samples was the mineral-bituminous matrix, as shown in figure 11. This kind of maceral was formed by the condensation of organic matter associated with minerals (Carr 1999). Based on the

Figure 11. The detected reflectivity of organic matter and mineral in the samples of UPPMRs with oil-immersed reflection. (a) Bitumen in sample No. 1 (B387R304P1a), $\times 240$ and (b) bitumen and unidentified mineral in No. 5 (B623R439P6a), $\times 240$.

morphology of maceral, the origin of the mineral-bituminous matrix might be a degraded or algae amorphous mass (Huang *et al.* 2003; Rao *et al.* 2006a, b; Wang *et al.* 2006). The reflectivity of the organic matter was 0.1–0.4%, implying that the organic matter was at the immature stage. Meanwhile, the reflectivity of the mineral was 0.4–2.6%, which was much lower than that of normal minerals. The reflectivity of the calcite in sample No. 11 (B957R627P4t) was 2.6%, which indicated that the calcite did not experience

the metamorphism of ultrahigh pressure and temperature. So, in other words, this mineral-bituminous groundmass was of secondary origin. It is inferred that the mineral-bituminous matrix might be carried in stratum by the activity of the formation fluid during the return of subduction accompanied by retrograded metamorphic minerals. Moreover, the results of Rock-Eval also revealed that the organic matter in the UPPMR was mainly trapped at the stage of subduction return, because the S_1/TOC of most samples was $>50\%$. It was illustrated that the majority of the organic matter in the UPPMR was absorbed on the surface of the minerals.

6. Conclusions

- (a) With the GC-MS analysis of the soluble organic matter from 12 samples, the marine origin of the organic matter and the anoxic sedimentary setting were observed. Referring to the bimodal chromatography of *n*-alkanes and the triangular chart of C_{27} , C_{28} and C_{29} sterane, the source of the organic matter was confirmed as mainly algae, likely marine plankton. With regard to maturity, the steranes could be detected in most of the samples, and the distribution range of C_{29} sterane $20S/(20S + 20R)$ was from 0.41 to 0.63 and the value of C_{29} sterane $\beta\beta/(\alpha\alpha + \beta\beta)$ was 0.31–0.44. Both of the maturity parameters reflected the same level of maturity as the parameters of hopanes ($R_o = 0.6$ – 0.9%) which conflicted with the theory of metamorphism. So, the only reliable explanation was that the organic matter was from the active formation fluid during the process of subduction return and retrograde metamorphism.
- (b) In addition, the absorption peak of rutile appeared in the kerogen of sample No. 11 (B957R627P4t). Since the retrograde metamorphism of amphibolite-facies, the diffusion exchange of the ion in the rutile resulted in the metamorphism temperature of the Zr-in-rutile geothermometer being lower than that of the metamorphism peak. It was also indicated that the $\delta^{18}O$ value of the No. 11 sample at 1842.6 m suddenly reduced up to -10% . The corresponding TOC of the No. 11 sample was $1820 \mu\text{g/g}$, which is the highest of all samples. The relationship between the TOC and $\delta^{18}O$ value indicated that the fluid-rock exchange reaction was the main

reason why the relative abundant TOC and low-maturity organic matter had been detected in the No. 11 sample. This sample (No. 11) is located near the shear zone, which was activated during the process of subduction return. The rock type of sample No. 11 is epidote amphibolite facies, which is a product of low-grade metamorphism. Thus, it could be inferred that the retrograde metamorphism resulted in the fluid-rock exchange at the returning stage of metamorphism.

- (c) The main maceral in the samples was the mineral-bituminous matrix, which was the source of the origin of the degraded or algae amorphous mass. The reflectivity of the organic matter and the mineral in the samples of UPPMR were much lower than the maturity of the organic matter and normal minerals, respectively. So, it was indicated that the calcite associated with mineral-bituminous groundmass did not experience the metamorphism of ultrahigh pressure and temperature. Moreover, the results of Rock-Eval also revealed that the organic matter in the UPPMR was mainly trapped at the stage of subduction return, because the S_1/TOC of most samples was $>50\%$. It was illustrated that the majority of organic matter in the UPPMR was absorbed on the surface of the minerals. The $\delta^{13}C$ of CO_2 in the salt-water inclusions was from -28% to -32% , close to the $\delta^{13}C$ of the organic matter deposited in marine sediments. It was implied that the protogenetic organic matter was probably cracked into CH_4 and CO_2 at ultrahigh pressure and temperature, with the rapid subduction in <10 My. Then, the subduction return and retrograde metamorphism resulted in the dramatic activity of the formation fluid.

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