



ELSEVIER

Contents lists available at ScienceDirect

## Journal of Petroleum Science and Engineering

journal homepage: [www.elsevier.com/locate/petrol](http://www.elsevier.com/locate/petrol)

# Multiple charges to Sinian reservoirs in the middle Sichuan basin, SW China: Insight from the adsorbed/occluded hydrocarbons in solid bitumens

Bin Cheng<sup>a</sup>, Zewen Liao<sup>a,\*</sup>, Tongshan Wang<sup>b</sup>, Hu Liu<sup>a</sup>, Yankuan Tian<sup>a</sup>, Shan Yang<sup>a</sup><sup>a</sup> State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China<sup>b</sup> PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China

## ARTICLE INFO

## Article history:

Received 25 September 2014

Accepted 9 January 2015

Available online 19 January 2015

## Keywords:

Biomarkers

Adsorbed/occluded hydrocarbons

Solid bitumen

Sichuan Basin

SW China

## ABSTRACT

Mild oxidative degradation was used to release the aliphatic hydrocarbons occluded inside the macromolecular structure of solid bitumens collected from Sinian carbonate reservoir, Sichuan basin, SW China. In contrast to the adsorbed aliphatic hydrocarbons extracted from the solid bitumens, the mild oxidative products showed unaltered *n*-alkanes distributions, which had been trapped within the macromolecular structure of the bitumens and protected from biodegradation processes. These observations are quite informative and suggest that at least, two phases of hydrocarbon charging to the Sinian reservoirs might have occurred. The occluded hydrocarbons seem to represent the first phase of hydrocarbon charge while the adsorbed and biodegraded hydrocarbons correspond to the second phase of hydrocarbon charge. However, terpane and sterane distributions in both fractions were preserved and similar, and the carbon isotope analysis results obtained in this work along with the previous geological information, corroborates the idea that Sinian reservoirs hydrocarbons have been sourced from the black shale of Lower Cambrian Qiongzhusi Formation. This study reveals the geochemical significance of adsorbed/occluded aliphatic hydrocarbons in understanding the charging history of oil into reservoirs.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

The Sichuan Basin is one of the prolific hydrocarbon sedimentary basins in the northwestern China (Fig. 1). Studies have revealed that available source rocks in the basin include the mudstones in Sinian strata (Doushantuo Formation) and shales in lower Paleozoic strata (Qiongzhusi and Longmaxi Formations) (Liu et al., 2009). Two phases of hydrocarbon generations from the black shale of Qiongzhusi Formations were presumed to be responsible for multi-stage hydrocarbon-charging to the Sinian reservoirs, based on solid bitumen occurrence and the associated minerals (quartz and calcite) (Huang et al., 2011), as well as the thermal history of Qiongzhusi shale (Yuan et al., 2009). However, it still lacks the straightforward evidence from the point of molecular organic geochemistry.

It has been reported that geological macromolecules such as asphaltene (Liao et al., 2005; 2006a, b, c), solid bitumen (Cheng et al., 2012; Cheng et al., 2014a, 2014b) and kerogen (Cheng et al., 2014b) are able to adsorb and even occlude other small molecules into their macromolecular structures. The occluded hydrocarbons can be well preserved by the macromolecular structures and have been found

useful in the study of organic matter with depleted soluble fractions (Cheng et al., 2012), oil (bitumen)-source correlation (Liao and Geng, 2002; Cheng et al., 2014a) and identification of mixed-source reservoirs (Zhao et al., 2010; Tian et al., 2012a, 2012b).

The solid bitumens, deposited in the Sinian strata and sourced from Lower Cambrian Qiongzhusi Formation in the central Sichuan Basin, SW China, were considered to be generated from thermal cracking of crude oils (Tian et al., 2013). Some researchers have also suggested that the solid bitumens were derived mainly from Sinian–Cambrian ancient oil reservoirs (Xu et al., 2007a, 2007b). In this paper, geochemical results of the mildly oxidative degradation product (occluded fraction) of solid bitumen and conventionally extracted product (adsorbed fraction) are compared in an effort to understand the process of multi-stage oil charging to the bitumen deposited reservoirs.

## 2. Materials and methods

## 2.1. Solid bitumen

Two solid bitumens were collected from the drilling core rocks of wells Gaoshi-1 and Anping-1 (Fig. 1), from the Sinian Dengying Formation of Sichuan Basin, China. The rock samples were ground

\* Corresponding author. Tel.: +86 20 85290190.

E-mail address: [liaoZW@gig.ac.cn](mailto:liaoZW@gig.ac.cn) (Z. Liao).

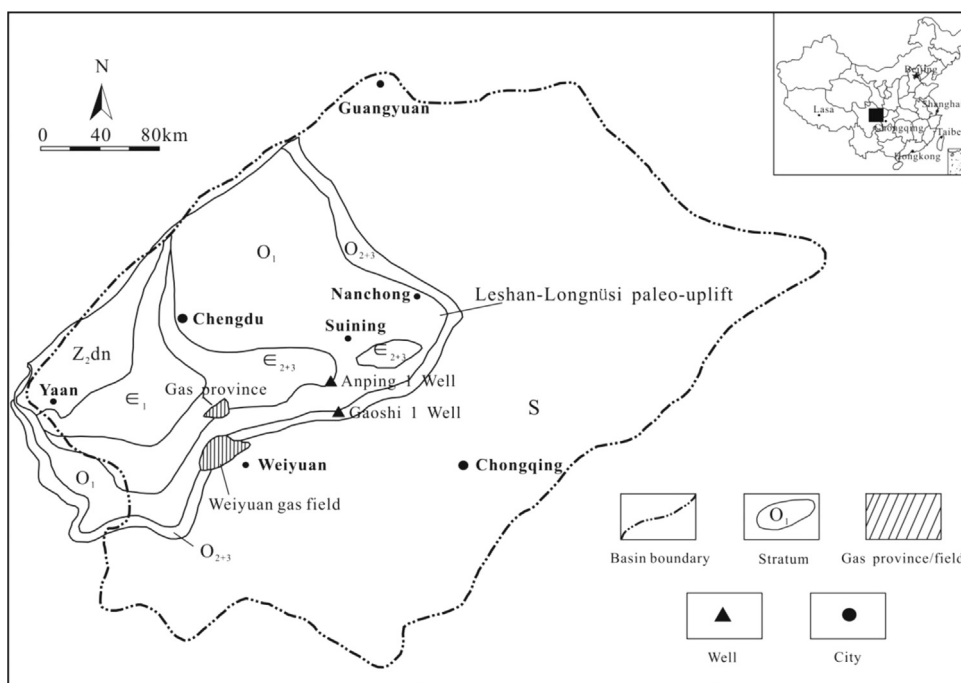


Fig. 1. Diagram showing the paleo-geology and the distribution of main structures of Sinian Dengying Formation in Sichuan Basin before Permian (From Liu et al., 2012, with minor modification).

to 80 mesh, and then put into 500 ml centrifuge bottles (PTFE). HCl and HF solutions were used to treat the rocks repeatedly to remove the carbonate and silicate minerals, like the kerogen preparation with the details of the procedure from Fu and Qin (1995), and the solid bitumens were collected after centrifugation.

### 2.2. Acquisition of the adsorbed/occluded compounds from solid bitumens

Solid bitumen samples were grouped into two portions. A portion was extracted for 120 h with chloroform to obtain the soluble chloroform bitumen "A" as the adsorbed fraction in solid bitumens. The other portion was successively extracted for 120 h with *n*-hexane, acetone and dichloromethane, in order to exclude interference from adsorbed components, and was subsequently subjected to oxidation process. All solvents used were of analytical grade and redistilled prior to use.

Benzene (~28 ml) was used as solvent (dispersant) for oxidative degradation treatment while H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>COOH (about 12 ml/12 ml) was served as the oxidation system for the extracted solid bitumens. Samples were allowed to react for 48 h under magnetic stirring at room temperature, and product was filtered through a Büchner funnel by adding dichloromethane. The obtained liquid phase was then transferred to a 250 ml separating funnel (made of PTFE), followed by the addition of ultrapure water to separate the organic and inorganic phases. The organic phase was collected as occluded hydrocarbons in the solid bitumens. Detailed procedures have been reported by Liao et al. (2006a, 2006b, 2006c).

The solvent soluble organic product (adsorbed fraction) and the oxidative degradation product (occluded fraction) were further fractionated by column chromatography on silica/alumina (2:1, *v/v*) and eluted using *n*-hexane and toluene to obtain the saturated and aromatic hydrocarbon fractions, respectively.

### 2.3. Instrumental analysis

Analyses performed on the solid bitumen included rock pyrolysis utilizing a Rock-Eval 6.0 Standard Pyrolysis Analyzer, elemental

analysis using a Vario EL III Element Analyzer, stable carbon isotope analysis on a Thermo Finnigan Delta XL stable isotope ratio mass spectrometer.

The saturated hydrocarbons were analyzed by gas chromatography–mass spectrometry (GC–MS), using a Thermo Scientific Trace GC Ultra-DSQ II MS analyzer equipped with the column of HP-1MS (60 m × 0.32 mm × 0.25 μm). The GC oven was held isothermally at 80 °C for 4 min, ramped to 295 °C at 4 °C/min, then holding for 20 min. The ion-source temperature was 260 °C, and the temperature of injector was 290 °C. Helium was used as the carrier gas with a constant flow rate of 1.2 ml/min. The ion-source was operated in the electron impact (EI) mode with electron energy of 70 eV.

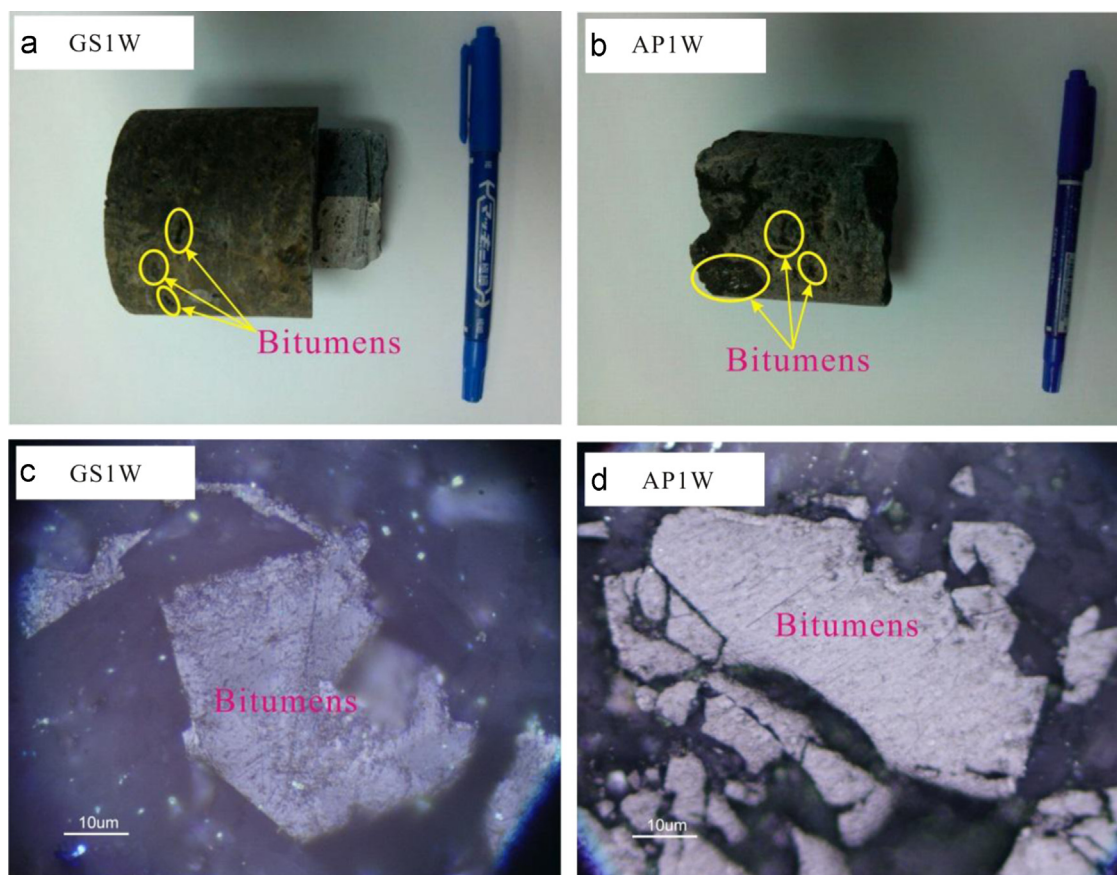
## 3. Results and discussion

In this work solvent extracts of solid bitumens were defined as the adsorbed component. Saturated hydrocarbons released from oxidative degradation treatment of extracted solid bitumens were defined as the occluded fraction. More details can be referred from some previous reports (Liao et al., 2005, 2006c).

### 3.1. Basic geochemical data for the solid bitumens

The bitumens were scatteredly deposited in the rock pores of the samples Gaoshi-1 and Anping-1 (Fig. 2). Solid bitumens prepared from core samples have an H/C atomic ratio of 0.37–0.39 and O/C atomic ratio of 0.04,  $T_{max} \sim 607$  °C and PI > 0.1 (Table 1), indicating high maturity of the samples.

The sulfur content of the solid bitumen was relatively high at 5.2 wt% and 5.7 wt%. The bulk stable carbon isotope compositions for the two solid bitumens were –35.2‰ and –35.7‰ (VPDB), and –30.5‰ for the chloroform extracts (Table 1). The stable carbon isotopes of both chloroform extracts are heavier than solid bitumens by around 5‰, indicating an exceptional geochemical process of solid bitumen generation.



**Fig. 2.** Drilling core samples and microscopic photos of solid bitumens. (a) Drilling core sample from Gaoshi 1; (b) drilling core sample from Anping 1; (c) microscopic photo of solid bitumen from Gaoshi 1; (d) microscopic photo of solid bitumen from Anping 1.

**Table 1**  
Basic geochemical data of the solid bitumens.

Sample	H/C	O/C	S/C	PI	$T_{\max}$ (°C)	$R_b$ (%)	TOC (wt%)	$\delta^{13}C_B$ (‰)	$\delta^{13}C_{-A}$ (‰)	"A" (mg/g)
GS1W	0.37	0.04	0.03	0.18	607	3.1	0.45	-35.2	-30.5	293
AP1W	0.39	0.04	0.03	0.16	608	3.2	0.6	-35.7	-30.5	283

"A" represented the chloroform extracts of solid bitumens, and B represented the bulk solid bitumen.

### 3.2. Distribution of alkanes from adsorbed/occluded fractions

The *n*-hexane extracts (adsorbed) of both solid bitumens displayed similar *n*-alkane distributions (Fig. 3) by normal alkanes ranging from  $C_{15}$  to  $C_{27}$  and maximizing at  $C_{18}$ . In addition, the chromatograms of adsorbed fraction exhibited certain "unresolved complex mixture" (UCM) peaks (Fig. 3a and c), indicating that these samples had generally suffered from biodegradation while the relative abundance of *n*-alkanes suggests hydrocarbon input from later charging.

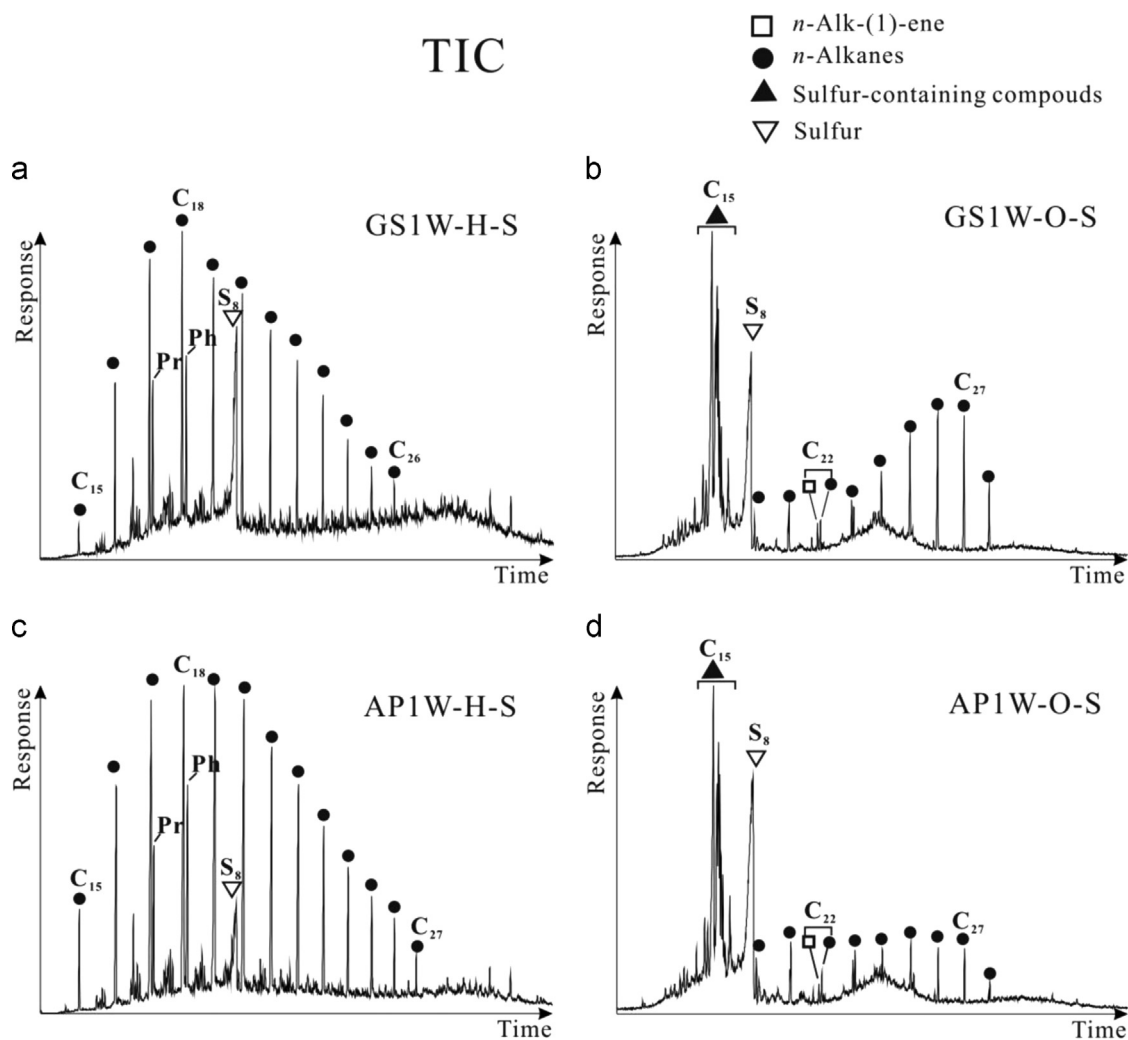
In the occluded fractions, the detected compounds included  $C_{15}$  bicyclic sulfides, elemental sulfur ( $S_8$ ), series of normal alkanes and  $C_{22}$  *n*-alk-1-ene, with sulfides as the main peaks (Fig. 3b and d). Bicyclic terpenoid sulfide is presumably derived from thermal maturation reaction of carotenoids (Mathis and Schenck, 1982). *n*-alk-1-ene is generally believed to be unstable under geological conditions and is considered to originate from the concerted reaction of linear alkyl esters under low thermodynamic impact (Alexander et al., 1992, 1997; Cheng et al., 2014a). The detection of bicyclic terpenoid sulfides and *n*-alk-1-ene from the occluded fraction showed that the hydrocarbons within the structure were

fairly well protected from the impact of the later geochemical depositional processes.

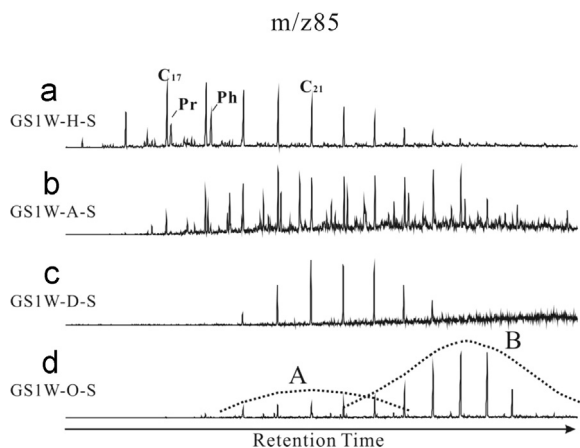
Some contrasted differences in the *n*-alkane distributions between the adsorbed and occluded fractions are observed and summarized as follows:

- (1) For Gaoshi 1 solid bitumen, the *n*-hexane, acetone and dichloromethane extracts display a narrow *n*-alkanes distribution ranging from  $C_{15}$ – $C_{27}$  to  $C_{19}$ – $C_{25}$  (Fig. 4a–c), while the occluded components generally have *n*-alkane distributions ranging from *n*- $C_{16}$  to *n*- $C_{28}$  and maximizing at *n*- $C_{27}$  (Fig. 4d). The *n*-alkane distribution of the occluded fraction was very asymmetric showing two superimposed unimodal *n*-alkane distributions. Based on this observation, *n*-alkanes could be classified into groups A and B (Fig. 4d). The *n*-alkane distribution in group A ranges from *n*- $C_{18}$  to *n*- $C_{24}$ , similar to that of the dichloromethane extract (Fig. 4c). Group B displays totally different *n*-alkane distribution in comparison to any solvent extract of solid bitumen, ranging from *n*- $C_{23}$  to *n*- $C_{29}$ .
- (2) For Anping 1 solid bitumen, the *n*-hexane, acetone and dichloromethane extracts display similar distributions ranging from  $C_{15}$ – $C_{27}$  to  $C_{18}$ – $C_{25}$  (Fig. 5a–c). On the other hand, for the occluded components the *n*-alkane distribution had a scope of  $C_{17}$ – $C_{28}$  with  $C_{27}$  as the main peak, which can be separated into two peak groups, A and B, the same as for Gaoshi 1 occluded fraction (Fig. 5d).

From the extracts of Sinian solid bitumens of middle Sichuan basin, Xu et al. (2007a, 2007b) discovered unimodal distribution of *n*-alkanes for most samples and bimodal distribution for a few samples. The authors supposed that the bimodal

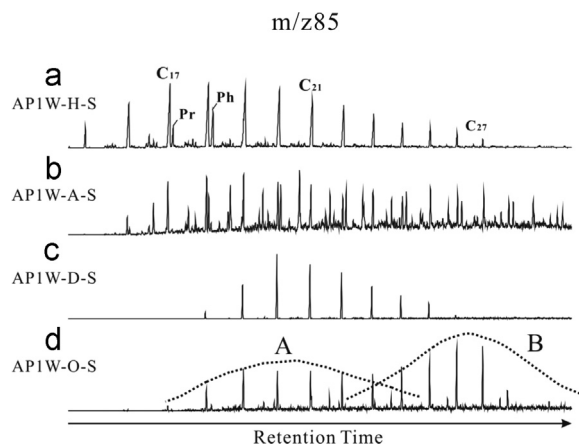


**Fig. 3.** TIC chromatograms of *n*-hexane eluates from the adsorbed/occluded fractions of solid bitumens. (a) Adsorbed fraction of solid bitumen from Gaoshi 1; (b) occluded fraction of solid bitumen from Gaoshi 1; (c) adsorbed fraction of solid bitumen from Anping 1; (d) occluded fraction of solid bitumen from Anping 1.



**Fig. 4.**  $m/z$  85 mass chromatograms of the adsorbed/occluded fractions from Gaoshi 1 solid bitumen. (a) *n*-hexane extract of solid bitumen; (b) acetone extract of solid bitumen; (c) dichloromethane extract of solid bitumen; (d) the oxidative degradation treatment of solid bitumen (occluded fraction).

distribution was related to high thermal maturity. However, Yuan et al. (2009) suggested that this bimodal distribution pattern may be a result of more than one charging such that the early charging contributed to the higher carbon number *n*-alkanes (such as group B in Figs. 4 and 5), whereas the later



**Fig. 5.**  $m/z$  85 mass chromatograms of the adsorbed/occluded fractions from Anping 1 solid bitumen. (a) *n*-Hexane extract of solid bitumen; (b) acetone extract of solid bitumen; (c) dichloromethane extract of solid bitumen; (d) the oxidative degradation treatment of solid bitumen (occluded fraction).

charging contributed to the lower carbon number *n*-alkanes (as group A in Figs. 4 and 5).

The high thermal index of bitumen reflectance (equivalent  $R_b$  of 3.1% and 3.2%) indicated that the solid bitumens have undergone distinctly thermal evolution after its formation. The thermal

alteration is expected to have equal influence on both fractions (adsorbed and occluded) of the solid bitumens. Therefore, thermal alteration could not be responsible for their hydrocarbon distribution difference.

The adsorbed components were obviously depleted in high carbon number *n*-alkanes (group B in Figs. 4 and 5), which suggest a possible biodegradation of the first charging along the uplifted crust and might have also received hydrocarbon input from the later charging. The occluded fraction of the solid bitumen is capable of providing useful information on the history of the hydrocarbon charging into the reservoir. The unimodal distributions of *n*-alkanes from the adsorbed fractions observed in this work are consistent with the general findings of Xu et al. (2007a, 2007b). The bimodal distributions from the occluded fractions of solid bitumens are also comparable to previous results (Xu et al., 2007a, 2007b). These two kinds of distributions associated with the adsorbed/occluded compounds are depicted in Fig. 6.

### 3.3. Terpane and sterane compounds from adsorbed/occluded fractions

Terpane biomarkers in the *n*-hexane extracts of the two bitumen samples display similar distributions (Fig. 7), and are represented by C<sub>20</sub>–C<sub>29</sub> tricyclic terpanes and C<sub>29</sub>–C<sub>35</sub> hopanes. The relative abundance of homohopane series decreased with increasing carbon number (Fig. 8). The tricyclic terpanes in the occluded fractions of the two solid bitumens were wrapped into the “unresolved complex mixture” (UCM) which may be introduced by the oxidative degradation treatment (Fig. 7b and d).

For each solid bitumen, the terpane compounds showed similar distribution features between the adsorbed and occluded fractions as follows:

- (1) In Gaoshi 1 solid bitumen, the adsorbed and occluded fractions have the C<sub>29</sub>-norhopane/C<sub>30</sub>-hopane ratios 0.50 and 0.51, respectively (Table 2). The relative abundance of C<sub>31</sub>–C<sub>35</sub> homohopanes and values of hopane parameters ( $T_s/T_m$  and  $C_{31}22S/(22S+22R)$ ) for two fractions were similar (Fig. 8, Table 2). Similar values of hopane thermal maturity parameters (Table 2) indicated that these two fractions of solid bitumen have undergone almost equal thermal evolution after its formation.

- (2) In Anping 1 solid bitumen, the adsorbed and occluded fractions have the C<sub>29</sub>-norhopane/C<sub>30</sub>-hopane ratios 0.41 and 0.46, respectively (Table 2). Like in Gaoshi 1 bitumen, the relative abundance of C<sub>31</sub>–C<sub>35</sub> homohopanes for two fractions of Anping 1 bitumen was also similar (Fig. 8). The same observation is related to  $T_s/T_m$  and  $C_{31}22S/(22S+22R)$  ratios (Table 2).

For each solid bitumen, between the adsorbed and occluded fractions the regular sterane compounds showed similar distribution features (characterized by a V-type distribution) and have similar biomarker parameter ratios as shown in Table 2. Thermal maturity parameters calculated from sterane distributions in the solid bitumens for both adsorbed and occluded fractions are comparable (Table 2). This result shows that the two fractions have been exposed to the equal thermal stress.

### 3.4. Geochemical development of solid bitumens

From the adsorbed fractions of solid bitumens, the *n*-alkane distributions showed distinct “UCM” peaks (Fig. 3) and obvious difference from the occluded ones. This indicated that the adsorbed fraction was possibly from the later oil charging. The *n*-alkane distributions in the occluded fractions are classified into two groups A and B (Figs. 4 and 5), indicating that the fractions contain hydrocarbon input of more than a single charge. So it seems that the Sinian reservoirs of central Sichuan basin had experienced at least two times of hydrocarbons charging maybe from the same set of source rocks at different thermal evolution stages. This point can be strengthened by their similar distributions of terpane and sterane compounds from both the adsorbed and occluded fractions (Figs. 7 and 9; Table 2). The group B peaks in Figs. 4 and 5 represent the earlier charge, while the group A peaks signify hydrocarbons from the later charge.

Thermal simulation experiments of kerogens showed that *n*-alkanes generated from the later stage of higher maturation level would be more enriched in <sup>13</sup>C compared to those generated at an earlier stage by up to 4‰ (Jia et al., 2011; Tang et al., 2005). The stable carbon isotopes of the chloroform extracts of the bitumens were reasonable that the isotope ratio of the extracts was heavier than the bulk bitumens by around 5‰ as listed in Table 1. This suggests that the chloroform fraction contains hydrocarbons from the later charge.

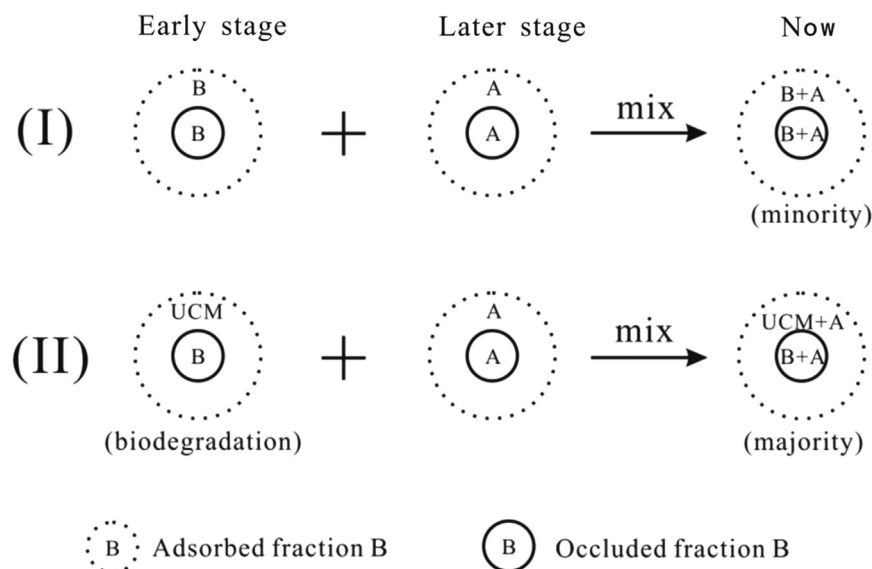
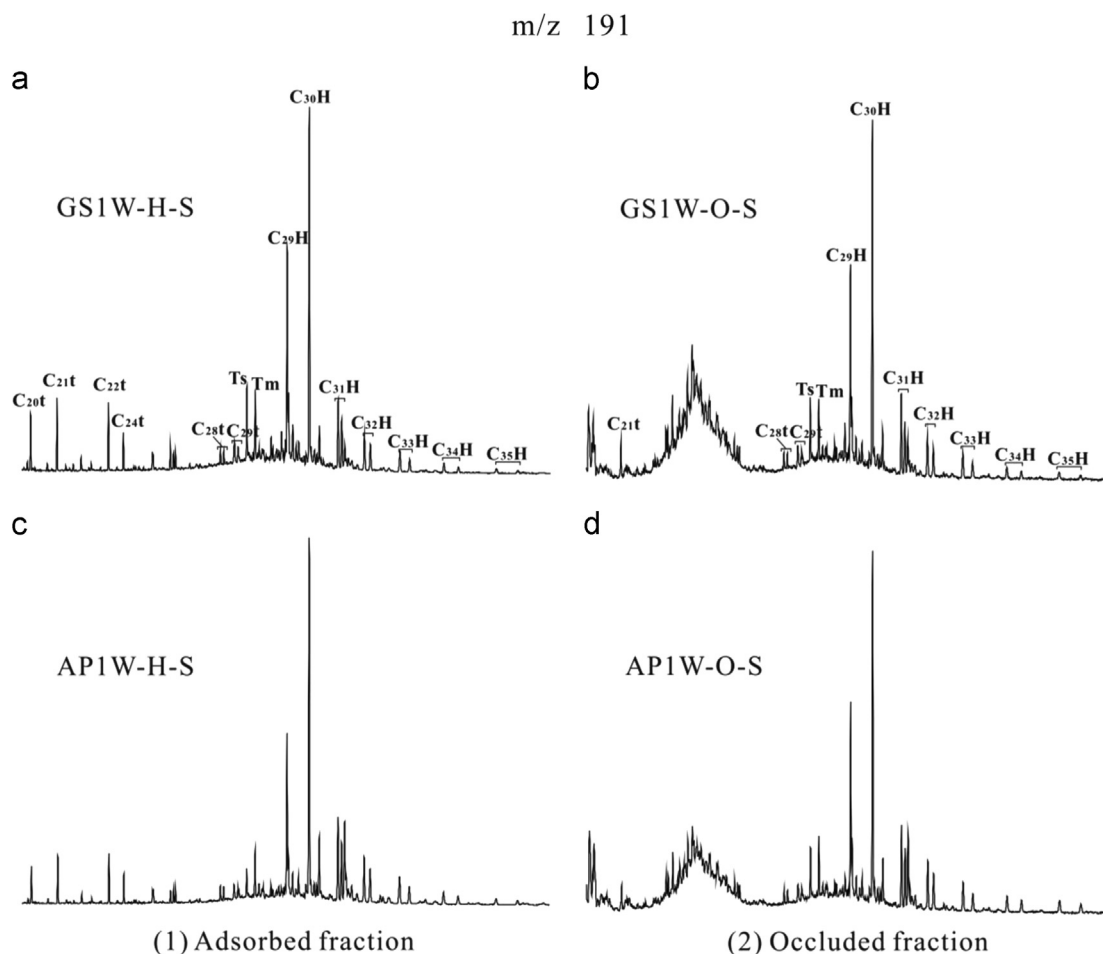
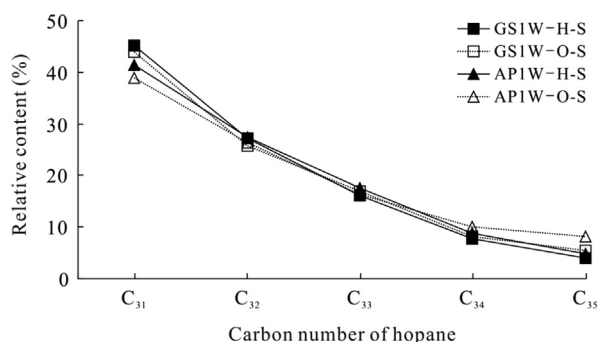


Fig. 6. The evolution patterns of adsorbed/occluded fractions in solid bitumens by more than one charging. (I) Two charging without biodegradation (II) two charging with the first one suffered from biodegradation.



**Fig. 7.**  $m/z$  191 mass chromatograms of the adsorbed/occluded fractions from Gaoshi 1 and Anping 1 solid bitumens. (a)  $n$ -Hexane extract of solid bitumen from Gaoshi 1 Well; (b) the oxidative degradation treatment of solid bitumen from Gaoshi 1 Well; (c)  $n$ -hexane extract of solid bitumen from Anping 1 Well; (d) the oxidative degradation treatment of solid bitumen from Anping 1 Well.



**Fig. 8.** Relative abundance of homohopanes from the adsorbed (solid legend) and occluded fractions of solid bitumens Gaoshi 1 and Anping 1.

Thermal history and hydrocarbon generation simulation results (Fig. 10) showed that the Qiongzhusi Formation source rocks had undergone two phases of hydrocarbon generation, including the first one during the period of Late Ordovician to the end of Silurian and the second one during the period of Middle-Late Permian (Zhang et al., 2007; Yuan et al., 2009). The Sinian reservoirs had received input of hydrocarbons from both periods of hydrocarbon generation. This observation is supported based on the relationship between asphalt and mineral deposition, in that their filling sequence appeared as dolomite  $\rightarrow$  bitumen  $\rightarrow$  dolomite  $\rightarrow$  bitumen  $\rightarrow$  quartz (Huang et al., 2011). The adsorbed/occluded fractions of solid bitumens had recorded the two charging history of petroleum fluids as

the early oil charging  $\rightarrow$  biodegradation  $\rightarrow$  later oil charging. This sequence is in accordance with the tectonic movement and the thermal evolution of source rocks in this area as showed in Fig. 10.

#### 4. Conclusions

The Sinian solid bitumens from middle Sichuan basin, SW China, were developed from oil cracking. They have an H/C atomic ratio of 0.37–0.39, O/C ratio of 0.04, Rock-Eval parameter  $T_{max} \sim 607$  °C, and the bitumen reflectance  $R_b$  of 3.1–3.2%, indicating high maturity level. The stable carbon isotope composition of chloroform extracts of solid bitumens is around  $-30.5\text{‰}$ , which is 5‰ heavier than that of the bulk solid bitumens.

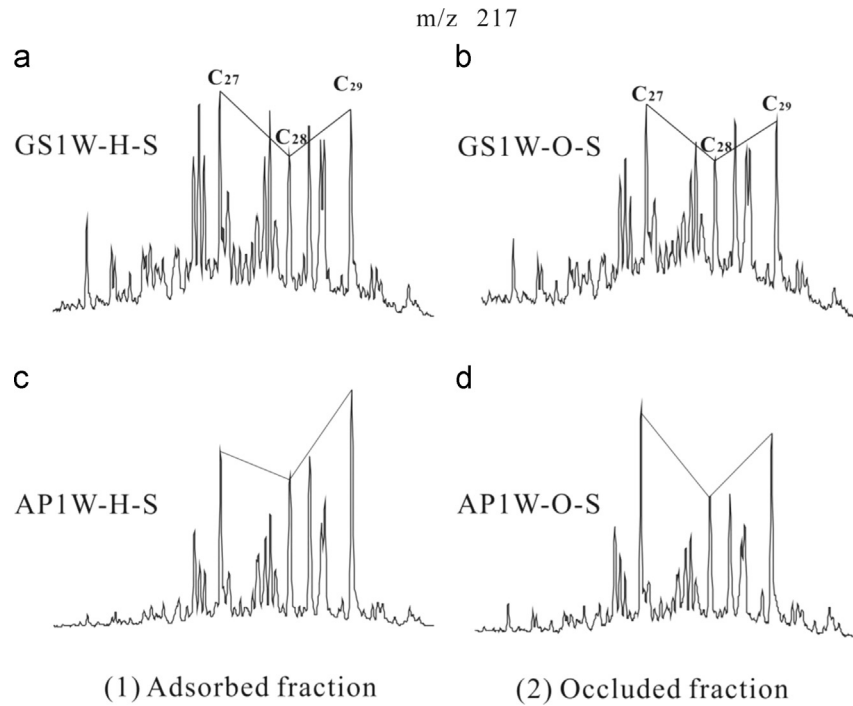
The adsorbed fraction of the solid bitumens displays a unimodal  $n$ -alkane distribution with predominance of  $n$ -C<sub>18</sub> while occluded fraction exhibited a bimodal  $n$ -alkane distribution with a predominance of  $n$ -C<sub>27</sub>. The  $n$ -alkane unimodal distributions of adsorbed fractions are similar to the group A peaks of occluded fractions. The terpane and sterane distributions in both fractions of the bitumens are similar and suggesting equal thermal experience, which strengthened the point that these hydrocarbons have been sourced from the same set of source rocks, the black shale of Lower Cambrian Qiongzhusi Formation.

The Sinian reservoirs of middle Sichuan basin had experienced at least two hydrocarbons charging from the Cambrian black shale. The alkanes in the adsorbed fraction of solid bitumens are believed to represent the later charged hydrocarbons and the occluded

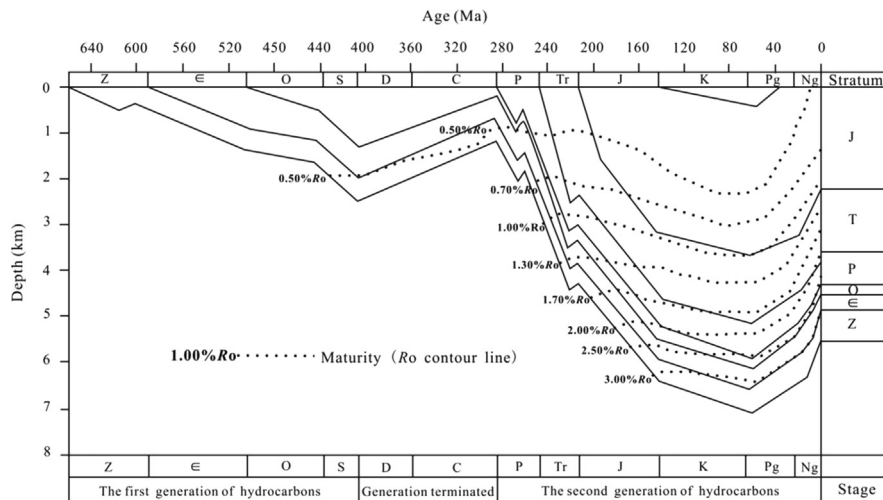
**Table 2**  
Terpane/sterane parameters from the adsorbed/occluded fractions of two solid bitumens.

Sample	$T_s/T_m$	$C_{29}H/C_{30}H$	$C_{31}\text{-}S/(S+R)$	$C_{29}\text{-}S/(S+R)$	$C_{27}/\text{total}$	$C_{28}/\text{total}$	$C_{29}/\text{total}$	$\alpha\alpha\alpha C_{27}/\text{total}$	$\alpha\alpha\alpha C_{28}/\text{total}$	$\alpha\alpha\alpha C_{29}/\text{total}$
GS1W-H-S	0.97	0.51	0.59	0.50	0.30	0.29	0.41	0.30	0.31	0.39
GS1W-O-S	0.95	0.50	0.61	0.51	0.28	0.27	0.45	0.28	0.33	0.40
AP1W-H-S	0.46	0.41	0.60	0.41	0.22	0.30	0.48	0.24	0.30	0.46
AP1W-O-S	0.79	0.46	0.59	0.40	0.29	0.29	0.42	0.33	0.29	0.38

$C_{29}H/C_{30}H$ :  $17\alpha\text{-}21\beta(H)\text{-}30\text{-nor-hopane}/17\alpha\text{-}21\beta(H)\text{-hopane}$ ;  $C_{31}\text{-}S/(S+R)$ :  $C_{31}\text{-hopane-}22S/(22S+22R)$ ;  $C_{29}\text{-}S/(S+R)$ :  $\alpha\alpha\alpha C_{29}$  regular sterane- $20S/(20S+20R)$ ;  $C_{27}/\text{total}$ :  $(C_{27}$  regular steranes)/ $(C_{27-29}$  regular steranes);  $C_{28}/\text{total}$ :  $(C_{28}$  regular steranes)/ $(C_{27-29}$  regular steranes);  $C_{29}/\text{total}$ :  $(C_{29}$  regular steranes)/ $(C_{27-29}$  regular steranes);  $\alpha\alpha\alpha C_{27}/\text{total}$ :  $\alpha\alpha\alpha C_{27}/(C_{27-29}$  regular steranes);  $\alpha\alpha\alpha C_{28}/\text{total}$ :  $\alpha\alpha\alpha C_{28}/(C_{27-29}$  regular steranes);  $\alpha\alpha\alpha C_{29}/\text{total}$ :  $\alpha\alpha\alpha C_{29}/(C_{27-29}$  regular steranes).



**Fig. 9.**  $m/z$  217 mass chromatograms of the adsorbed/occluded fractions from Gaoshi 1 and Anping 1 solid bitumens. (a)  $n$ -Hexane extract of solid bitumen from Gaoshi 1 Well; (b) the oxidative degradation treatment of solid bitumen from Gaoshi 1 Well; (c)  $n$ -hexane extract of solid bitumen from Anping 1 Well; (d) the oxidative degradation treatment of solid bitumen from Anping 1 Well.



**Fig. 10.** The history of hydrocarbon-generation in Cambrian source rocks in the Anping-Gaoshiti structural belt in the middle Sichuan Basin, China (modified from Yuan et al., 2009).

fraction corresponds to both the earlier and the later charged hydrocarbons owing to their effective protection from biodegradation by the macromolecular structure of the solid bitumen.

## Acknowledgments

This work has been financially supported by the National Key Science Projects Program of China (Grant 2011ZX05008-002) and the State Key Laboratory of Organic Geochemistry (Grant No. sklog2012A02). We thank Dr. Lekan Faboya for improving the English writing of the original manuscript. We are very grateful to Prof. Ksenija Stojanović for the careful review to our manuscript, which helps much to improve the paper.

## References

- Alexander, R., Kralert, P.G., Kagi, R.I., 1992. Kinetics and mechanism of the thermal decomposition of esters in sediments. *Org. Geochem.* 19 (1-3), 133–140.
- Alexander, R., Kralert, P.G., Sosrowidjojo, I.B., Kagi, R.I., 1997. Kinetics and mechanism of the thermal elimination of alkanes from secondary stanyl and triterpenyl esters: implications for sedimentary processes. *Org. Geochem.* 26 (5/6), 391–398.
- Cheng, B., Liao, Z.W., Tian, Y.K., Zhao, J., 2012. Release of the hydrocarbons occluded inside solid bitumen in Jurassic Shaximiao Formation of northwestern Sichuan Basin and its geochemical significance. *Geochimica* 41, 425–432 (in Chinese with English abstract).
- Cheng, B., Hu, S.Z., Shen, C.B., Liao, Z.W., Liu, H., Du, J.Y., Tian, Y.K., 2014a. The geochemical characterization of adsorbed/occluded hydrocarbons inside solid bitumen in the Kuangshanliang area of northwestern Sichuan Basin and its significance. *Pet. Sci. Technol.* 32 (18), 2203–2211.
- Cheng, B., Yang, C.P., Du, J.Y., Zhao, J., Liao, Z.W., 2014b. Determination of the series of even carbon numbered *n*-alk-(1)-enes trapped inside geomacromolecules. *Mar. Pet. Geol.* 51, 49–51.
- Fu, J.M., Qin, K.Z., 1995. *Kerogen Geochemistry*. Guangdong Scientific Publication Press, Guangzhou, pp. 1–292 (in Chinese).
- Huang, W.M., Liu, S.G., Xu, G.S., Wang, G.Z., Mang, W.X., Zhang, C.J., Song, G.Y., 2011. Characteristics of Paleo oil pools from Sinian to Lower Paleozoic in southeastern margin of Sichuan basin. *Geol. Rev.* 57 (2), 285–299 (in Chinese with English abstract).
- Jia, W.L., Wang, Q.L., Peng, P.A., 2011. Carbon isotope evolution of hydrocarbon later generated from marine source rocks. In: *Proceedings of the 13th National Meeting on Organic Geochemistry in China* 43–44 (in Chinese).
- Liao, Z.W., Geng, A.S., 2002. Characterization of *n*C<sub>7</sub>-soluble fractions of the products from mild oxidation of asphaltenes. *Org. Geochem.* 33 (12), 1477–1486.
- Liao, Z.W., Zhou, H.G., Graciaa, A., Chrostowska, A., Creux, P., Geng, A.S., 2005. Adsorption/occlusion characteristics of asphaltenes: some implications for asphaltene structural features. *Energy Fuels* 19 (1), 180–186.
- Liao, Z.W., Geng, A.S., Graciaa, A., Creux, P., Chrostowska, A., Zhang, Y.X., 2006a. Different adsorption-occlusion properties of asphaltenes associated with their secondary evolution processes in oil reservoirs. *Energy Fuels* 20 (3), 1131–1136.
- Liao, Z.W., Graciaa, A., Geng, A.S., Chrostowska, A., Creux, P., 2006b. A new low-interference characterization method for hydrocarbons occluded inside asphaltene structures. *Appl. Geochem.* 21 (5), 833–838.
- Liao, Z.W., Geng, A.S., Graciaa, A., Creux, P., Chrostowska, A., Zhang, Y.X., 2006c. Saturated hydrocarbons occluded inside asphaltene structures and their geochemical significance, as exemplified by two Venezuelan oils. *Org. Geochem.* 37 (3), 291–303.
- Liu, S.G., Ma, Y.S., Cai, X.Y., Xu, G.S., Wang, G.Z., Yong, Z.Q., Sun, W., Yuan, H.F., Pan, C.L., 2009. Characteristic and accumulation process of the natural gas from Sinian to Lower Paleozoic in Sichuan basin. China. *J. Chengdu Univ. Technol. (Sci. Technol. Ed.)* 36 (4), 345–353 (in Chinese with English abstract).
- Liu, S.G., Qin, C., Sun, W., Wang, G.Z., Xu, G.S., Yuan, H.F., Zhang, C.J., Zhang, Z.J., 2012. The coupling formation process of four centers of hydrocarbon in Sinian Dengying Formation of Sichuan Basin. *Acta Pet. Sin.* 28 (3), 879–888 (in Chinese with English abstract).
- Mathis, P., Schenck, C.C., 1982. The functions of carotenoids in photosynthesis. In: Britton, G., Goodwin, T.W. (Eds.), *Carotenoid Chemistry and Biochemistry*. Pergamon Press, pp. 339–351.
- Tang, Y.C., Huang, Y.S., Ellis, G.S., Wang, Y., Kralert, P.G., Gillaizeau, B., Ma, Q.S., Hwang, R., 2005. A kinetic model for thermally induced hydrogen and carbon isotope fractionation of individual *n*-alkanes in crude oil. *Geochim. Cosmochim. Acta* 68 (18), 4505–4520.
- Tian, X.W., Hu, G.Y., Li, W., Li, X.Q., Su, G.P., Xu, Y.R., Cai, H.P., 2013. Geochemical characteristics and significance of Sinian reservoir bitumen in Leshan-Longnusi Paleo-uplift area, Sichuan basin. *Nat. Gas Geosci* 24 (5), 982–990 (in Chinese with English abstract).
- Tian, Y.K., Zhao, J., Yang, C.P., Liao, Z.W., Zhang, L.H., Zhang, H.Z., 2012a. Multiple-sourced features of marine oils in the Tarim Basin, NW China—geochemical evidence from occluded hydrocarbons inside asphaltenes. *J. Asian Earth Sci.* 54–55, 174–181.
- Tian, Y.K., Yang, C.P., Liao, Z.W., Zhang, H.Z., 2012b. Geochemical quantification of mixed marine oils from Tazhong area of Tarim Basin, NW China. *J. Pet. Sci. Eng.* 90–91, 96–106.
- Xu, G.S., Xu, Y.L., Yuan, H.F., Mang, Y.S., Cui, J.W., 2007a. Geochemical characteristics of source rocks and reservoir bitumen of Sinian-Lower Palaeozoic in the middle-southwest of Sichuan basin. *J. Oil Gas Technol.* 29 (4), 45–50 (in Chinese with English abstract).
- Xu, G.S., Yuan, H.F., Mang, Y.S., Liu, S.G., Mang, Y.S., Wang, G.Z., Pan, C.L., 2007b. The source of Sinian and Lower-Palaeozoic bitumen and hydrocarbon evolution in the middle and southeast of the Sichuan basin. *Acta Geol. Sin.* 81 (8), 1143–1151 (in Chinese with English abstract).
- Yuan, H.F., Xu, G.S., Wang, G.Z., Mao, M., Liang, J.J., 2009. Phase evolution during hydrocarbon accumulation and exploration prospect for Sinian reservoirs in central Sichuan basin, China. *J. Chengdu Univ. Technol. (Sci. Technol. Ed.)* 36 (6), 662–668 (in Chinese with English abstract).
- Zhao, J., Liao, Z.W., Zhang, L.H., Creux, P., Yang, C.P., Chrostowska, A., Zhang, H.Z., Graciaa, A., 2010. Comparative studies on compounds occluded inside asphaltenes hierarchically released by increasing amounts of H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>COOH. *Appl. Geochem.* 25, 1330–1338.
- Zhang, L., Wei, G.Q., Li, X.Z., Wang, Z.C., Xiao, X.M., 2007. The thermal history of Sinian-Lower Palaeozoic high/over mature source rock in Sichuan basin. *Nat. Gas Geosci* 18 (5), 726–731 (in Chinese with English abstract).