Sedimentary and organic geochemical investigation of tertiary lacustrine oil shale in the central Tibetan plateau: Palaeolimnological and palaeoclimatic significances

Licheng Wang a,b, Chengshan Wang a,b,*, Yalin Li a,b, Lidong Zhu c, Yushuai Wei a,b

* State Key Laboratory of Geological Process and Mineral Resources, China University of Geosciences, Beijing 100083, China
a School of Earth Science and Resources, China University of Geosciences, Beijing 100083, China
b Institute of Sedimentary Geology, Chengdu University of Technology, Chengdu 610059, China

Abstract

The Zhuonai Lake and Lunpori oil shale, located in the central Tibetan Plateau, were deposited in a Tertiary lacustrine environment in the Hoh Xil and Lunpola Basins, respectively. A combined investigation of sedimentary, organic geochemistry, and organic carbon isotope was performed to determine the palaeoenvironment, and source of the organic matter. Three types of facies sequences are developed in the Zhuonai Lake section and oil shale mainly occurs in the oil shale-marl sequence. The oil shale-silty claystone and oil shale-marl facies sequences are developed in the Lunpori section. Both oil shales are finely stratified especially for the Lunpori oil shale with thickness of the laminae about 10 μm which contains abundant pyrite crystals and fossilized fish bones. Both the Zhuonai Lake and Lunpori oil shale contain high values of total organic matter (TOC), S2, and hydrogen index (HI), indicating the oil shales have good oil source rock potential. Tmax values show an immature stage of organic matter for the Zhuonai Lake oil shale and thermally marginally mature for the Lunpori oil shale because of difference in their burial history. Lunpori oil shale shows the characteristics of amorphous organic matter (AOM) dominance, odd-over-even predominance, maximum n-alkanes peak at nC25 or nC23, higher proportion of C29 sterane, light δ13Corg values (−30.0%, to −27.4%), high concentrations of phytane (Pr/Ph ratio ranging from 0.02 to 0.18), high values of gammacerane index (up to 25.26), and presence of β-carotane, which are consistent with a reducing, stratified, and hypersaline palaeo-lake with main contribution of algae and bacteria to the organic matter (OM). Oil shale samples from the lower and upper part of the Zhuonai Lake section are characterized by low H/C ratios and high O/C ratios, amorphous humic OM and vitrinite dominance, odd-over-even predominance with long-chain n-alkanes dominance, heavy organic carbon isotope, and C28–C27 sterane distribution, in agreement with a main contribution of land plant. The heavy organic carbon isotope suggests the expanding of C4 land plant during the early Miocene. While the most samples show characteristics of AOM dominance, maximum peak at nC29 or nC31, and high C27 sterane concentration, consistent with a main contribution from algae to the OM. The Pr/Ph ratio cannot be applied as a measure for redox conditions in the section because of maturity effects. Biomarker analysis indicates that the salinity during the deposition of the Zhuonai Lake oil shale was not enhanced. The Oligocene Lunpori oil shale and the Early Miocene Zhuonai Lake oil shale recorded the variation of palaeolimnological water chemistry. The development history of the palaeo-lakes from the Oligocene saline to the Early Miocene fresh water reflects the variation of palaeoclimate from dry to humid in the central Tibetan Plateau.

1. Introduction

China had imported about 179 million tons of crude oil in 2008 (Fu et al., 2010), nearly 50% of annual overall consumption. The consumption and sustainable development of energy are the main concerns with the rapid economic growth in China. Oil shale, one of the substantial unconventional fossil resources that could be produced and converted to liquid fuels (DASFRP, 2006), has received much attention. Oil shale deposits are widespread in many regions in China, the proved reserves amount to about 32 billion tons presenting a potential energy source (Qian et al., 2003). Fushun and Maoming oil shale is well known to international geologists (e.g. Brassell et al., 1986, 1988), but little information about oil shale in the Tibetan Plateau has been published yet. Recently, Fu et al. (2009a, b, 2010) reported a large marine oil shale deposit in northern Tibet. Although Xu (1984) mentioned the oil shale...
in the Lunpola Basin, lacustrine oil shale exposed in the several Tertiary sedimentary basins in central Tibet has not been discussed in detail.

Tertiary lacustrine oil shales are exposed at the Zhuonai Lake section of the Wudaoliang Group in northern Hoh Xil Basin and at the Lunpori section of the Dingqinghu Formation in southern Lunpola Basin. In this paper, the sedimentary and organic geochemical characteristics of selected oil shales of Zhuonai Lake and Lunpori sections from the Hoh Xil and Lunpola Basin are examined. Effects of palaeoclimatic changes on the source of organic matter and palaeoenvironment of the oil shales also are discussed.

2. Geological setting

The Hoh Xil Basin, with an area of 101,000 km² and an average elevation of over 5000 m, is the largest Cenozoic sedimentary basin in the hinterland of the Tibetan Plateau (Liu and Wang, 2001; Wang et al., 2002). It is situated in the middle part of the Songpan-Ganzi terrane and the northern part of the Qiangtang terrane, and it covers the Jinsha Suture zone (Liu and Wang, 2001; Liu et al., 2001) (Fig. 1). Over 5 km of sediments that can be divided into three lithostratigraphic units are exposed. The basal Fenghuoshan Group was deposited in the Early
Eocene to Early Oligocene and consists of fluvial and fan-delta cobble–pebble conglomerate, sandstone, and lacustrine bioclastic limestone, overlain by fluvial and playa sandstone, mudstone, marl, and gyspsum of the Yaxicuo Group (Early Oligocene) (Wang et al., 2008). The Wudaoliang Group consists mainly of lacustrine limestone and oil shale and uncomfortably overlies the Yaxicuo Group with deposition occurring 23.5–13.5 Ma (Wang et al., 2008; Wu et al., 2008).

Several Tertiary continental basins are located on the approximately east–west along the surface trace of the Bangong suture zone in the central Tibetan Plateau, including the Lunpola Basin and the Nima Basin (Fig.1). The Lunpola Basin, located in central Tibet, covers an area of 5000 km² and is bound to north and south by the Qiangtang and Lhasa terranes, respectively. The basin has been explored geophysically and through a series of wells (Rowley and Currie, 2006). In 1999, production tests at two wells were successful (Gu et al., 1999). Nearby to the west of the Lunpola Basin is the Tertiary Nima Basin. The Nima and Lunpola Basins are closely similar in terms of age, sedimentary fill and development history (Wang et al., 2011). The sedimentary succession is mainly composed of the Niubao Formation and the overlying Dingjinghu Formation in both basins. Previous study of the age of these formations suggested the Paleocene–Oligocene and Miocene–Pliocene, respectively (Tanner and Meyerhoff, 1990a, b; Xu, 1980), based mainly on fossil ostracodes and palynological assemblages. More recent investigation and geological mapping showed that the Niubao and Dingjinghu Formations are Paleocene–Eocene and Oligocene in age, respectively (DeCelles et al., 2007a; Xia and Liu, 1997). The Dingjinghu Formation, studied herein, mainly consists of dark mudstone, marl, oil shale, siltstone, and shale, and contains ostracodes and green algae according to exploration wells (Ma et al., 1996).

3. Materials and methods

A total of 26 outcrop oil shale samples from the Zhuonai Lake and Lunpori areas were collected from measured sections in the Hoh Xil and the Lunpola Basins, respectively. To minimize the effects of surface weathering, surface material was removed before sampling. Twenty-three samples were selected for total organic carbon (TOC), Rock-Eval pyrolysis, organic petrology, and stable carbon isotope analyses. Extracts from 23 samples were analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). TOC values were determined by a Leco CS-200 carbon-sulfur equipment. The crushed sample (about 100 mg, 120 meshes) was heated from ambient temperature to 1200 °C in an induction furnace after removing carbonate by hydrochloric acid (HCl). Rock-Eval pyrolysis data were performed on a Rock-Eval II instrument following guidelines established by Peters (1986).

Powdered samples were extracted with chloroform for 72 h in a Soxhlet apparatus. The extracts were separated by column chromatography into saturated hydrocarbons, aromatic hydrocarbons, and NSO compounds using a silica gel alumina column after the precipitation of asphaltenites (Petersen et al., 2005). GC of the saturated hydrocarbon fraction was performed on a Hewlett Packard 5890 with a DB-1 fused silica column (15 m × 0.22 mm ID × 0.2 μm film thickness). The oven temperature was initially set to rise from 80 °C to 320 °C at 10 °C/min and hold at 320 °C for 20 min (Fildani et al., 2005). The injector was set at 325 °C in the splitless and hydrogen was used as the carrier gas with a head pressure of 20 psi (Fildani et al., 2005). GC–MS of saturated hydrocarbon fractions were performed on a Finnigan SQQ-7000 instrument (fitted with a DB5-MS fused silica capillary column, 30 m length, 0.25 mm inner diameter and 0.25 μm film thickness). Helium was used as the carrier gas. The oven was held for 1 min at 35 °C, programmed from 35 °C to 120 °C at 10 °C/min, and then 120 °C to 300 °C at 3 °C/min with a final holding time of 30 min at 300 °C (Bu et al., 2009b). The selected ion monitoring capabilities of the data acquisition system permitted specific ions to be monitored, such as tricyclic terpanes and hopanes (m/z 191) and steranes (m/z 217) (Korkmaz and Gülbay, 2007).

To prepare kerogens, fragments of rock were leached in 12 N HCl for 12 h to remove carbonates, then washed several times with distilled water and treated with hydrofluoric acid (HF) for 12 h to remove silicates (Guthrie and Pratt, 1994). Samples were again washed several times with distilled water and again treated with 12 N HCl (Guthrie and Pratt, 1994). Visual estimation of the relative abundance of maceral content was determined using a Zeiss incident-light microscope and a Swift point counter (Petersen et al., 2005). Elemental analyses were performed on a FLASH EA-1112 Series elemental analyzer with a precision generally within 0.3% for carbon and 0.5% for nitrogen. 613C kerogen isotopic measurements were determined on a EA-Finnigan Delta plus XL mass spectrometer. Results of carbon isotope analysis are reported in the usual δ-notation relative to the PDB standard; the analytical precision by this method was better than ±0.2‰ (Bu et al., 2009b). All analyses were performed in the Organic Geochemistry Laboratory, Research Institute of Exploration and Development, Huabei Oilfield Branch Company of PetroChina.

4. Sedimentary characteristics

4.1. The wudaoliang group

The Wudaoliang Group in the Hoh Xil Basin is mainly comprised of lacustrine carbonate strata, including marl, calcarenite, algal lump limestone, bioclastic limestone, and crystalline limestone (Liu et al., 2001). The strata change from main carbonate deposits in the north–central part of the Tibetan Plateau to carbonate with progressively greater proportions of fine to coarse clastic material toward the southeast and northwest (Wu et al., 2008).

In the Zhuonai Lake section, the group has a thickness of ~160 m and consists of silty claystone, mudstone, calcareous shale, marl, and oil shale. The section forms a fining-upward sequence from silty claystone in the lower part to oil shale and marl in the upper part (Fig. 2). Three types of facies sequences are developed in the Zhuonai Lake section: oil shale–marl sequence, silty claystone–mudstone sequence, and mudstone–mudstone sequence. The oil shale–marl sequence contains 60% dark gray-black oil shale, 35% gray marl, and 5% gray mudstone. The total thickness of oil shale is about 45 m. The oil shales are finely stratified and the marls are massive (Fig. 3A and B). The silty claystone–mudstone sequence is at the base of the section and consists of purple-green silty claystone interbedded with gray mudstone containing plant fragments with no observation of rootlets. The mudstone–marl or shale–mudstone sequence is composed of green-gray shale and mudstone interbedded with light gray marl. The predominance of argillaceous rocks of the Zhuonai Lake section requires suspension and settling of finer sediments in a quiet low energy environment. The lithological features and plant fragments suggest a shallow lacustrine environment for the Wudaoliang Group (e.g. Carroll et al., 1992).

4.2. The Dingjinghu Formation

The lithological succession of the Dingjinghu Formation in the Lunpola Basin can be subdivided into three members from the lower to upper part (Ma et al., 1996) based on the data of several wells. The lower member mainly is comprised of gray mudstone, calcareous shale, oil shale, marl, and siltsstone with fluvial or fan delta deposits at the basin margin slope. The middle member is dominated by gray mudstone, calcareous shale interbedded with oil shale, siltsstone, and fine sandstone containing ostracodes and charophytes. The upper member is primarily composed of gray mudstone and interbedded calcareous shale, marl, siltsstone, and basal reddish brown mudstone.

In the Lunpori section, the formation is about 960 m and consists mainly of silty claystone, marl, and oil shale. Two types of facies sequences are developed in the section, oil shale–silty claystone and oil shale–marl (Fig. 2). Dark-black oil shale interbedded with gray marl forms several cycles in the upper part of the section. The upper oil shale
sequence contains a higher proportion of oil shale and is finer grain than the lower oil shale sequence. The upper oil shale is finely stratified with thickness of the laminae about 10 μm (Fig. 3C). Laminae are primary and formed by organic-rich layers. Fossilized fish skeleton (Fig. 3D) and ostracodes remain. Disseminated pyrite crystal grains are distributed in the surface of laminae. The lower oil shale-silty claystone sequence forms a rhythmic layer containing spores and pollen grains. The basal of the section is ~50 m of calcareous siltstone. The dark gray-black fine particles of argillaceous rocks with abundance of spores and pollen grains, fish skeleton and ostracodes of the Lunpori section are interpreted to be formed in a basinal lacustrine environment (e.g. Carroll et al., 1992; Gibling et al., 1985).

5. Organic geochemistry

5.1. TOC and Rock-Eval

Rock-Eval and TOC data are summarized in Table 1. The TOC content of the Zhuonai Lake oil shale samples is in the range 0.48–14.49 wt.%, averaging 7.53%, with most samples >7 wt.%. Rock-Eval S₁ and S₂ are 0.26–19.03 and 0.78–127.37 mg HC/g rock, respectively. The hydrogen index (HI) is variable, ranging from 163 to 942 mg HC/g TOC. $T_{\text{max}}$ values vary from 370 to 420 °C (average 402 °C) indicating a thermally immature stage. All samples have production indices (PI) ($\text{PI} = S_1/[S_1 + S_2]$) ranging from 0.08 to 0.47. The PI reaches about 0.4 at the bottom of the oil window and decreases to 0.1 at the top of the oil window (Peters, 1986). The maturity suggested by $T_{\text{max}}$ and PI are not consistent, probably attributed to weathering that can affect Rock-Eval pyrolysis data (Lo and Cardott, 1995). The Lunpori oil shale samples have TOC contents ranging from 0.91 to 13 wt.%, averaging 5.92%, variations being related to lithology. Marls (n = 3) have TOC contents in the range of 0.23–0.97 wt.%, and oil shale samples have comparatively higher TOC contents, averaging 7.28 wt.% (n = 12). This assessment is consistent with the $S_2$ values which are much higher in oil shales than in marls. The $S_2$ values in oil shale samples are in the range of 4.67–115.68 mg HC/g rock, compared to 0.20–1.63 mg HC/g rock for the marl samples. The HI is consistently high in oil shale samples ranging from 331 to 1043 mg HC/g TOC. $T_{\text{max}}$ values for all the samples mostly fall within the range 430–440 °C, averaging 432 °C, indicating that the samples are marginally mature and at the onset of hydrocarbon generation. Difference in thermal maturity between these two oil shales is likely related to burial history.
According to Tissot and Welte (1984), high S2 and HI values indicate that the Zhuonai Lake and Lunpori oil shale are potentially good oil source rock.

5.2. Element and maceral analysis of kerogen

Elemental analysis provides a measure of the bulk chemical properties of isolated kerogen (Katz, 1988). The elemental analysis data are listed in Table 2. Greater variability is observed in the Zhuonai Lake oil shale data. H/C ratios range from 1.07 to 1.76 and O/C ratios from 0.04 to 0.15 (Table 2). Samples from the lower part (sample ZL-1 and ZL-2) and the upper part of the section (sample ZL-11) have lower H/C ratios (1.34, 1.29; 1.07, respectively) and higher O/C ratios (0.15, 0.15; 0.15) than the samples from the middle part, having H/C ratios (1.20–1.76) and O/C ratios (0.04–0.11). These data form a large scatter cloud about the type II reference curve suggesting significant contributions of allochthonous organic matter (OM) (e.g. Katz, 1988) (Fig. 4). The variation tendency in the stratigraphic section is also supported by the maceral composition of kerogen. The amorphous organic matter (AOM) consist of 45–50% kerogen assemblages, along with 25–30% amorphous humic OM, 23–25% vitrinite, and 1–2% inertinite for the sample ZL-1 and ZL-2 (Table 2). The amole ZL-11 is composed of 30% AOM, 2% sporinite, 52% vitrinite, and 16% inertinite. The samples from middle part of the section were dominated by 65–90% AOM, followed by 1–17% vitrinite, and 6–20% inertinite. According to Styan and Bustin (1983), amorphous humic materials were formed by biodegradation of land plants. AOM is generally related to in situ production of algal or bacterial phytoplanktonic sources at the surface of lacustrine waters (Schnyder et al., 2009; Tyson, 1995). Taking the H/C and O/C ratios into account, a higher terrestrial OM contribution in the lower and upper section could be indicated, while a higher algae or bacteria input in the middle section could be inferred.

The Lunpori oil shale can be classified as Type I (except for sample LBR-2 and LBR-6) and marls can be classified as Type II (Fig. 4). The H/C ratios are greater than 1.3 (most samples with the ratios > 1.5) with O/C ratios < 0.16. Type I kerogens of lacustrine origin are dominated by planktonic green algae, or of AOM (Talbot, 1988). Hydrogen-rich AOM was dominated (95–96%) in the samples, with minor vitrinite and inertinite (Table 2), consistent with the interpretation of type I kerogen. The high HI values (> 750) in most samples also support the algal or bacterial contribution to the OM (Talbot and Livingstone, 1989).

5.3. Molecular geochemistry of organic matter

5.3.1. n-Alkanes and acyclic isoprenoids

Selected C15+ gas chromatograms of saturated hydrocarbons from the Zhuonai Lake and Lunpori oil shale are showed in Fig. 5. The n-alkanes patterns of oil shales from both areas are dominated by long-chain n-alkanes with a marked odd over even preference in the nC23 to nC31 range (most samples having CPI > 3; Bray and Evans, 1961). Long-chain n-alkanes (n-C27 to n-C31) are known as biomarkers for higher terrestrial plants waxes (e.g. Eglinton and Hamilton, 1967; Meyers, 1997; Tissot and Welte, 1984). The dominance of long-chain n-alkanes for the samples ZL-1, ZL-2, and ZL-11, therefore, reflects the major contribution of terrestrial plants, which is consistent with the observation from the petrographic data and H/C and O/C ratios. Long-chain n-alkanes are also dominated in the samples from the middle part of the Zhuonai Lake section and from the Lunpori section. However, contribution from terrestrial plants is not dominant in the kerogens according to petrographic observation. Riboulleau et al. (2007) indicated that non-marine algae could be a source of long-chain n-alkanes. Although there is no palynofacies evidence of non-marine algae, algae is probably responsible for the long chain odd n-alkanes predominance.
The \( n \)-alkanes of intermediate molecular weight (\( n \)-C\(_{21} \) to \( n \)-C\(_{25} \)), which are reported to have been originated from \textit{Sphagnum} (Nott et al., 2000) or aquatic macrophytes (high contents of \( n \)-C\(_{23} \) and \( n \)-C\(_{25} \); Bechtel et al., 2007; Ficken et al., 2000; Sachsenhofer et al., 2006), are found in relative proportions in the samples ZL1, ZL-2, and ZL-11. Because the origin in a mire or peat bog can be excluded, input of OM

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Lithology</th>
<th>TOC(^a) (wt.%)</th>
<th>( T_{\text{max}})(^b) (°C)</th>
<th>( S_1)(^c) (mg HC(^b)/g)</th>
<th>( S_2)(^d) (mg HC/g)</th>
<th>( P_Y) (S(_1) + S(_2)) (mg HC/g)</th>
<th>HI(^e) (% HC/g TOC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ZL-1 )</td>
<td>Shale</td>
<td>9.90</td>
<td>419</td>
<td>3.66</td>
<td>45.05</td>
<td>48.71</td>
<td>455</td>
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<tr>
<td>( ZL-2 )</td>
<td>Shale</td>
<td>13.30</td>
<td>415</td>
<td>5.82</td>
<td>58.31</td>
<td>64.13</td>
<td>438</td>
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<tr>
<td>( ZL-3 )</td>
<td>Shale</td>
<td>1.88</td>
<td>413</td>
<td>1.75</td>
<td>7.43</td>
<td>9.17</td>
<td>395</td>
</tr>
<tr>
<td>( ZL-4 )</td>
<td>Shale</td>
<td>1.65</td>
<td>412</td>
<td>1.35</td>
<td>7.31</td>
<td>8.66</td>
<td>443</td>
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<tr>
<td>( ZL-5 )</td>
<td>Shale</td>
<td>7.46</td>
<td>370</td>
<td>9.69</td>
<td>70.27</td>
<td>75.95</td>
<td>942</td>
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<tr>
<td>( ZL-6 )</td>
<td>Shale</td>
<td>14.00</td>
<td>379</td>
<td>13.34</td>
<td>127.37</td>
<td>140.71</td>
<td>910</td>
</tr>
<tr>
<td>( ZL-7 )</td>
<td>Shale</td>
<td>0.48</td>
<td>400</td>
<td>0.26</td>
<td>0.78</td>
<td>1.04</td>
<td>163</td>
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<tr>
<td>( ZP-8 )</td>
<td>Shale</td>
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<td>386</td>
<td>19.03</td>
<td>47.70</td>
<td>66.73</td>
<td>548</td>
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<tr>
<td>( ZP-9 )</td>
<td>Shale</td>
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<td>9.00</td>
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<td>( ZP-10 )</td>
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<td>15.79</td>
<td>54.84</td>
<td>70.63</td>
<td>378</td>
</tr>
</tbody>
</table>

**Table 1**

Results of Rock-Eval and TOC analysis and calculated parameters.

The \( n \)-alkanes of intermediate molecular weight (\( n \)-C\(_{21} \) to \( n \)-C\(_{25} \)), which are reported to have been originated from \textit{Sphagnum} (Nott et al., 2000) or aquatic macrophytes (high contents of \( n \)-C\(_{23} \) and \( n \)-C\(_{25} \); Bechtel et al., 2007; Ficken et al., 2000; Sachsenhofer et al., 2006), are found in relative proportions in the samples ZL1, ZL-2, and ZL-11. Because the origin in a mire or peat bog can be excluded, input of OM

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>H/C</th>
<th>O/C</th>
<th>( \delta^{13}C ) (‰)</th>
<th>AOM(^a)</th>
<th>Sporinite</th>
<th>Amorphous humic OM</th>
<th>Vitrinite</th>
<th>Inertinite</th>
</tr>
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<tr>
<td>( ZL-1 )</td>
<td>1.34</td>
<td>0.15</td>
<td>-18.4</td>
<td>45</td>
<td>n.d.</td>
<td>30</td>
<td>24</td>
<td>2</td>
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<tr>
<td>( ZL-2 )</td>
<td>1.29</td>
<td>0.15</td>
<td>-18.2</td>
<td>50</td>
<td>n.d.</td>
<td>25</td>
<td>25</td>
<td>1</td>
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<tr>
<td>( ZL-3 )</td>
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<td>0.1</td>
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<td>65</td>
<td>4</td>
<td>n.d.</td>
<td>17</td>
<td>14</td>
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<tr>
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<td>88</td>
<td>n.d.</td>
<td>2</td>
<td>10</td>
<td>10</td>
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<tr>
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<td>-27.8</td>
<td>90</td>
<td>n.d.</td>
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<td>9</td>
<td>2</td>
</tr>
<tr>
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<td>70</td>
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<td>n.d.</td>
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<td>20</td>
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<tr>
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<td>n.d.</td>
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<td>20</td>
<td>6</td>
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<td>80</td>
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<td>n.d.</td>
<td>5</td>
<td>6</td>
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<tr>
<td>( ZL-11 )</td>
<td>1.07</td>
<td>0.15</td>
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<td>30</td>
<td>2</td>
<td>n.d.</td>
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<tr>
<td>( LBR-1 )</td>
<td>1.36</td>
<td>0.16</td>
<td>-28.0</td>
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<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
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<tr>
<td>( LBR-2 )</td>
<td>1.38</td>
<td>0.14</td>
<td>-29.8</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
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<tr>
<td>( LBR-3 )</td>
<td>1.31</td>
<td>0.16</td>
<td>-27.9</td>
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<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
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<tr>
<td>( LBR-4 )</td>
<td>1.21</td>
<td>0.16</td>
<td>-26.4</td>
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<td>n.a.</td>
<td>n.a.</td>
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<td>n.a.</td>
</tr>
<tr>
<td>( LBR-5 )</td>
<td>1.60</td>
<td>0.13</td>
<td>-30.0</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>( LBR-6 )</td>
<td>1.37</td>
<td>0.15</td>
<td>-28.9</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>( LBR-7 )</td>
<td>1.51</td>
<td>0.12</td>
<td>-27.6</td>
<td>95</td>
<td>n.d.</td>
<td>1</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>( LBR-7-2 )</td>
<td>1.53</td>
<td>0.13</td>
<td>-27.4</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>( LBR-8 )</td>
<td>1.64</td>
<td>0.13</td>
<td>-28.6</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>( LBR-9 )</td>
<td>1.56</td>
<td>0.14</td>
<td>-29.8</td>
<td>95</td>
<td>1</td>
<td>n.d.</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>( LBR-10 )</td>
<td>1.57</td>
<td>0.13</td>
<td>-28.4</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>( LBR-11 )</td>
<td>1.58</td>
<td>0.13</td>
<td>-28.0</td>
<td>94</td>
<td>1</td>
<td>n.d.</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>( LBR-11-2 )</td>
<td>1.58</td>
<td>0.13</td>
<td>-28.0</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>( LBR-12 )</td>
<td>1.61</td>
<td>0.13</td>
<td>-29.2</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>( LBR-12-2 )</td>
<td>1.61</td>
<td>0.13</td>
<td>-29.0</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

\( ^a \) AOM = amorphous organic matter; n.d. not detected; n.a. not analyzed.
from *Sphagnum* could be ruled out and a contribution of macrophytes may be responsible for the \( n \)-alkanes patterns. The values \( P_{aq} \) of Ficken et al. (2000), where \( P_{aq} = \frac{(C_{23} + C_{25})}{(C_{23} + C_{25} + C_{29} + C_{31})} \), obtained from these three samples (averaging 0.55) are consistent with the data measured in submerged/ floating macrophytes (Ficken et al., 2000).

Phytane usually is the dominant acyclic isoprenoid in Lunpori oil shale samples and has a higher peak than \( n \)-alkanes in the samples (Fig. 5). The pristane/phytane (Pr/Ph) ratio is a commonly-used parameter for the study of oxic/anoxic conditions (Montero-Serrano et al., 2010). The Pr/Ph ratios (Table 3) are very low for the Lunpori oil shale samples ranging from 0.02 to 0.18. According to Didyk et al. (1978), Pr/Ph < 1.0 indicates anoxic source-rock deposition, while Pr/Ph > 1.0 indicates an oxic deposition. However, several factors, such as thermal maturity (Koopmans et al., 1999) and variable source input (Peters et al., 2005), must be taken into account when Pr/Ph ratios are considered. ten Haven et al. (1987) suggested that it is virtually impossible to draw valid conclusions from Pr/Ph ratio with respect to the oxicity of the environment of deposition. However, Peters et al. (2005) still recommended that Pr/Ph < 0.6 indicates anoxic, commonly hypersaline or carbonate environments, while Pr/Ph > 3.0 typify terrigenous OM input under oxic conditions for rocks within the oil-generative window. Maturity variations within the studied Lunpori samples can be excluded. In present case, for the Lunpori oil shale studied, the Pr/Ph ratios are interpreted to reflect an anoxic deposited condition, which is supported by the abundant pyrite crystals found in the Lunpori oil shale. Syngenic pyrite in coal and oil shales indicates an anoxic sedimentary environment (Dai et al., 2002; Fu et al., 2010). Taking into account the very low abundance of the acyclic isoprenoids in the Zhunai Lake oil shale samples, the Pr/Ph ratios must be interpreted with care. The Zhunai Lake oil shale samples are thermally immature, the Pr/Ph ratios cannot be interpreted to reflect redox conditions although the ratios are low (< 1.0).

\( \beta \)-carotane is the most prominent compound of the carotenoid carbon skeleton preserved in sediments under highly reducing conditions (Peters et al., 2005). The presence of \( \beta \)-carotane is associated primarily with anoxic, saline lacustrine, or highly restricted marine settings (Fu et al., 1990; Jiang and Fowler, 1986; Peters et al., 2005). \( \beta \)-carotane occurs in several samples from the Lunpori oil shale (Fig. 6, Table 3), indicating an anoxic and saline lacustrine environment. This compound is also reported in Green River shale (Murphy et al., 1967), Junggar Permian oil shale (Carroll et al., 1992), and Jianghan oil shale (Brassell et al., 1988).

5.3.2. Hopanes and steranes

The gammacerane/C\(_{31}\) hopane ((22S + 22R)/2) ratio varies between 1.36 to 25.26 through the Lunpori section and shows a stratigraphic trend that a high value at the base increases to highest value in the middle and then decreases to the lowest value at the top. The ratios vary from 0.58 at the base to 5.38 in the middle, and decreases to 0.3 at the top of the Zhunai Lake section (Table 3, Fig. 7). Large amounts of gammacerane indicate highly reducing, hypersaline conditions during deposition of the contributing OM (Fu et al., 1986; Moldowan et al., 1985). Sinninghe Damsté et al. (1995) argued that Gammacerane indicates a stratified water column in marine and non-marine source-
rock depositional environments, commonly resulting from hypersalinity at depth. Clearly, since the water columns in hypersaline depositional environments are often density stratified, it can be understood why the compound is abundant in saline lacustrine deposits (Sinninghe Damsté et al., 1995). Commonly, very low Pr/Ph ratios of <0.5 have been associated with hypersaline conditions (ten Haven et al., 1985, 1987). The supporting relationship between Pr/Ph ratios and gammacerane indices for the Lunpori oil shale reinforces the inferred salinity relationship (Fig. 8). The Lunpori oil shale was therefore probably deposited in a highly saline lacustrine environment, which is also supported by the presence of β-carotane. The discovery of gypsum in the Dingqingu Formation in the Nima Basin (DeCelles et al., 2007b) also supports the interpretation. The high salinity was accompanied by water-column density stratification and resulted in an anoxic state in bottom water. It is possible that the salinity in the water column remained the same and water-column stratification are constant in most of the time when the Lunpori oil shale deposited, which is supported by the high TOC and HI values of Lunpori oil shales (e.g. Talbot, 1988; Talbot and Livingstone, 1989). Although samples of the middle part of the Zhuonai Lake section have relative abundance of gammacerane, other biomarkers (e.g. β-carotane; very low Pr/Ph ratio; high abundance of C25 isoprenoid) showed no values indicative of enhanced salinity and indicator compounds were not present. This implied that the salinity during the deposition of the Zhuonai Lake oil shale was not enhanced.

The distribution of the regular steranes in the m/z 217 mass chromatograms (Fig. 7) shows variable peaks in the extracts from both the Lunpori and Zhuonai Lake oil shales. The samples from middle part of the Zhuonai Lake section show a higher proportion of C29 sterane (46%–76%) compared to C27 sterane (20%–46%), while some samples (ZL-1, ZL-2, and ZL-11) having C29 > C27 sterols distribution (Table 3). The Lunpori oil shale is dominated by C29 sterols, which are found in bacterial membranes (Ourisson and Albrecht, 1992; Ourisson and Rohmer, 1992; Riboulleau et al., 2007) and haloalkaliphilic bacteria can be important sources of C29 sterols. In the present case, the predominance of C29 sterols in the lower and upper part of the Zhuonai Lake section indicates a main contribution of terrestrial plant, while the C27 sterols dominant in the middle part of the section could be interpreted to reflect a main contribution of algae, which are consistent with petrographic observation and n-alkanes distribution. For the samples in the Lunpori section, the interpretation from the dominant C29 sterols contradicts with the previous. A bacterial contribution is indicated by way of the presence of hopanoids (Riboulleau et al., 2007) and hopanes in the m/z 191 mass chromatograms (López-Díaz et al., 2010). Archaeobacteria and haloalkaliphilic bacteria can be important sources of phytane (Volkman, 1988) and thus the abundance of phytane in the Lunpori oil shale samples also may represent a main contribution of bacteria. Hopanes are pentacyclic triterpanes found in sediments and petroleum and are readily identified in the m/z 191 mass chromatograms (López-Díaz et al., 2010). Hopanes derive mainly from hopane polys which are found in bacterial membranes and cyano bacteria (Ourisson and Albrecht, 1992; Ourisson and Rohmer, 1992; Riboulleau et al., 2007). As mentioned above, the abundance of phytane probably

Table 3
Organic geochemical data for extracts of samples from the Zhuonai Lake and Lunpori oil shale.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>CPI</th>
<th>Pr/Ph</th>
<th>Pr/nC17</th>
<th>Ph/nC18</th>
<th>Gammacerane indexb</th>
<th>β-carotane</th>
<th>C27%c</th>
<th>C29%d</th>
<th>C29%E</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZL-1</td>
<td>4.7</td>
<td>0.17</td>
<td>0.22</td>
<td>0.92</td>
<td>0.58</td>
<td>n.d.</td>
<td>40</td>
<td>11</td>
<td>49</td>
</tr>
<tr>
<td>ZL-2</td>
<td>5.24</td>
<td>0.47</td>
<td>0.72</td>
<td>1.61</td>
<td>0.78</td>
<td>n.d.</td>
<td>43</td>
<td>10</td>
<td>47</td>
</tr>
<tr>
<td>ZL-3</td>
<td>5.41</td>
<td>0.49</td>
<td>0.78</td>
<td>1.94</td>
<td>3</td>
<td>n.d.</td>
<td>76</td>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>ZL-4</td>
<td>7.09</td>
<td>0.15</td>
<td>0.37</td>
<td>2.89</td>
<td>5.38</td>
<td>n.d.</td>
<td>46</td>
<td>7</td>
<td>46</td>
</tr>
<tr>
<td>ZL-5</td>
<td>3.57</td>
<td>0.27</td>
<td>0.61</td>
<td>2.58</td>
<td>4.81</td>
<td>n.d.</td>
<td>62</td>
<td>10</td>
<td>28</td>
</tr>
<tr>
<td>ZL-6</td>
<td>5.43</td>
<td>0.97</td>
<td>1.67</td>
<td>1.41</td>
<td>2.7</td>
<td>n.d.</td>
<td>59</td>
<td>9</td>
<td>32</td>
</tr>
<tr>
<td>ZL-7</td>
<td>4.60</td>
<td>0.91</td>
<td>0.47</td>
<td>4.54</td>
<td>5.38</td>
<td>n.d.</td>
<td>13</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>ZL-11</td>
<td>4.53</td>
<td>0.31</td>
<td>1.06</td>
<td>1.34</td>
<td>0.3</td>
<td>n.d.</td>
<td>28</td>
<td>15</td>
<td>57</td>
</tr>
<tr>
<td>LBR-1</td>
<td>3.55</td>
<td>0.06</td>
<td>0.82</td>
<td>26.96</td>
<td>11.73</td>
<td>n.d.</td>
<td>32</td>
<td>16</td>
<td>52</td>
</tr>
<tr>
<td>LBR-2</td>
<td>4.8</td>
<td>0.11</td>
<td>0.9</td>
<td>12.33</td>
<td>8.41</td>
<td>n.d.</td>
<td>38</td>
<td>17</td>
<td>45</td>
</tr>
<tr>
<td>LBR-3</td>
<td>2.83</td>
<td>0.11</td>
<td>1.55</td>
<td>15.56</td>
<td>8.13</td>
<td>presence</td>
<td>24</td>
<td>13</td>
<td>63</td>
</tr>
<tr>
<td>LBR-4</td>
<td>3.77</td>
<td>0.18</td>
<td>1.26</td>
<td>7.54</td>
<td>5.75</td>
<td>presence</td>
<td>26</td>
<td>15</td>
<td>59</td>
</tr>
<tr>
<td>LBR-5</td>
<td>3.95</td>
<td>0.04</td>
<td>1.07</td>
<td>59.93</td>
<td>25.26</td>
<td>presence</td>
<td>33</td>
<td>15</td>
<td>52</td>
</tr>
<tr>
<td>LBR-6</td>
<td>4.62</td>
<td>0.05</td>
<td>1.25</td>
<td>33.47</td>
<td>17.39</td>
<td>n.d.</td>
<td>49</td>
<td>22</td>
<td>29</td>
</tr>
<tr>
<td>LBR-7</td>
<td>4.65</td>
<td>0.04</td>
<td>1.42</td>
<td>52.96</td>
<td>15.36</td>
<td>n.d.</td>
<td>37</td>
<td>17</td>
<td>46</td>
</tr>
<tr>
<td>LBR-7-2</td>
<td>8.6</td>
<td>0.02</td>
<td>1.51</td>
<td>85.19</td>
<td>3.91</td>
<td>n.d.</td>
<td>38</td>
<td>21</td>
<td>41</td>
</tr>
<tr>
<td>LBR-8</td>
<td>2.6</td>
<td>0.05</td>
<td>1.1</td>
<td>42.82</td>
<td>11.28</td>
<td>n.d.</td>
<td>42</td>
<td>18</td>
<td>40</td>
</tr>
<tr>
<td>LBR-9</td>
<td>5.11</td>
<td>0.03</td>
<td>1.26</td>
<td>90.22</td>
<td>10.83</td>
<td>n.d.</td>
<td>29</td>
<td>21</td>
<td>50</td>
</tr>
<tr>
<td>LBR-10</td>
<td>7.32</td>
<td>0.03</td>
<td>0.91</td>
<td>58.24</td>
<td>5.05</td>
<td>n.d.</td>
<td>28</td>
<td>21</td>
<td>52</td>
</tr>
<tr>
<td>LBR-11</td>
<td>3.11</td>
<td>0.05</td>
<td>1.38</td>
<td>37.02</td>
<td>13.87</td>
<td>n.d.</td>
<td>12</td>
<td>20</td>
<td>68</td>
</tr>
<tr>
<td>LBR-11-2</td>
<td>3.8</td>
<td>0.05</td>
<td>2.17</td>
<td>59.74</td>
<td>2.01</td>
<td>n.d.</td>
<td>9</td>
<td>15</td>
<td>76</td>
</tr>
<tr>
<td>LBR-12</td>
<td>4.73</td>
<td>0.12</td>
<td>1.19</td>
<td>15.63</td>
<td>3.91</td>
<td>n.d.</td>
<td>46</td>
<td>22</td>
<td>32</td>
</tr>
<tr>
<td>LBR-12-2</td>
<td>5.04</td>
<td>0.07</td>
<td>1.08</td>
<td>19.82</td>
<td>1.36</td>
<td>n.d.</td>
<td>40</td>
<td>18</td>
<td>42</td>
</tr>
</tbody>
</table>

n.d. not detected

\[ \text{Pr/Ph} = \text{pristane/phytane ratio.} \]

\[ \text{Gammacerane index} = \text{Gammacerane/(C}_{27}(22S + 22R)/2). \]

\[ \text{pristane/phytane ratio.} \]

\[ \text{C}_{27} \text{ steranes.} \]

\[ \text{C}_{29} \text{ sterols derived from hopane and phytane.} \]

\[ \text{C}_{29} \text{ sterols derived from hopane and phytane.} \]

\[ \text{C}_{29} \text{ sterols derived from hopane and phytane.} \]

\[ \text{C}_{29} \text{ sterols derived from hopane and phytane.} \]

Fig. 6. m/z 125 ion fragmentograms of the saturated fractions showing the presence of β-carotane in the extracts of the Lunpori oil shale.
indicated a main contribution of bacteria. The 4-methylsteranes in petroleum probably originate from 4α-methylsterols in living freshwater dinoflagellates (Peters et al., 2005; Wolff et al., 1986). However, Volkman et al. (1990) showed that 4α-methylsterols also occurred in microalgae of the genus *Pavlova*. Steranes of the 4-methyl are found in Lunpori oil shale samples in minor concentration except sample LBR-7 (Fig. 7). These observations, together with the fact that petrographic observation and n-alkanes distribution indicate a low terrestrial contribution to the OM of Lunpori oil shale samples, suggests that the predominance of C29 steroids derive from bacteria and microalgae.

5.4. Stable carbon isotopic composition

Carbon isotopic ratios are useful to distinguish between marine and continental plant sources of sedimentary organic matter and to identify organic matter from different types of land plants (Meyers, 1997). The composition of stable carbon isotopes in kerogen of Zhuonai Lake oil shale varies in the range from −27.8‰ to −17.8‰ (Table 2). The samples from the lowermost and top of the section (ZL-1, ZL-2, and ZL-11) have notably positive shift with δ13Corg values about −18‰. The carbon isotope distribution is similar to those of the Tertiary lacustrine Duatinga oil shale in Australia (Boreham et al., 1994). These differences in stable carbon isotope compositions could result from regional organic facies variations caused by bioassemblage input or significant climatic fluctuation (Talbot and Livingstone, 1989), or water column productivity variation (Curiale and Gibling, 1994; Fu et al., 2009b; Schouten et al., 2001). Organic matter produced from atmospheric CO2 by land plant using the C3 pathway show isotopic values ranging from −34‰ to −24‰, averaging −27‰ and by those using the C4 pathway show isotopic values ranging from −19‰ to −6‰, averaging −14‰ (Lichtfouse et al., 1994; Meyers, 1994,1997; Meyers and Ishiwatari, 1993; O'Leary, 1988). Some samples (ZL-1, ZL-2, and ZL-11) show a heavy C isotopic composition within C4 plant range. The OM of sample ZL-1, ZL-2, and ZL-11 has significant contribution from land plant based on kerogen maceral observation, n-alkanes and regular steranes

![Fig. 7. m/z 191 and m/z 217 ion fragmentograms of the saturated fractions showing the distribution of the terpanes and steranes for selected samples from the Zhuonai Lake and Lunpori oil shale.](image-url)
distribution, indicating terrestrial plants are associated with the positive δ13C value. This suggests that these terrestrial plants probably used the C4 photosynthetic pathway. The low δ13Corg values for oil shale samples in the middle part of Zhuonai Lake section mimic modern C3 land plants range. However, previous results indicate that the OM in these samples is derived from algae and bacteria. That is common for the lacustrine OM. Meyers (1997, 2003) reported that δ13Corg values of typical lake algae in fresh water is ranging from −30‰ to −25‰. Therefore, lake-derived OM that is produced by algae usually is isotopically indistinguishable from OM produced by C3 plants in the surrounding watershed (Meyers, 2003). Although δ13Corg values for the samples are within the range of the values typical of C3 land plants, the lake algae make a significant contribution to the OM of oil shale as already noted.

For the Lunpori oil shale samples, the kerogen δ13C values fall between −30.0‰ and −27.4‰, within the l-amoerphous kerogens range (Lewan, 1986). Lewan (1986) suggested that phytoplankton residing in environments that are dominated by organic-derived CO2 result in l-amoerphous kerogens, which are expected to occur in restricted basins that are overlain by stratified shallow (~200 m) water. The Lunpori palaeo-lake was a stratified and shallow water lake. In present case, we infer that lacustrine algae are considered to be the precursors for the amorphous kerogens and the isotopically light carbon isotopic values are attributed to lacustrine algae.

6. Palaeoecological and palaeoclimatic significances

Both climatic and tectonic factors govern the distribution of lakes and influence lake productivity and preservation of organic matter (Barron, 1990). Palaeoclimate and palaeogeography not only play major roles in controlling distribution of lake bodies but also influence water chemistry (Katz, 1990). Saline lakes develop when evaporation exceeds precipitation and fresh-water lakes develop when precipitation exceeds evaporation (Katz, 1990).

Major variations between the Oligocene Lunpori oil shale and the Early Miocene Zhuonai Lake oil shale on sedimentary and geochemical characteristics reflect the change of water chemistry of palaeo-lakes. As mentioned above, Lunpori oil shale deposited in a highly saline lacustrine environment and the Zhuonai Lake oil shale deposited in a fresh-water lake. Change from the Oligocene saline to the Early Miocene fresh water of the palaeo-lakes is controlled by palaeoclimatic variation from dry to humid. The climate change is supported by other evidences. Regional uplift in central Tibet at about 40 Ma contributed to an abrupt global cooling and dramatic aridification (Dupont-Nivet et al., 2007, 2008; Harris, 2006; Raymo and Ruddiman, 1992). Climate in the Tibetan Plateau became dry after Eocene/Oligocene transition. DeCelles et al. (2007b) indicated that considerable lake evaporation and low soil respiration rates existed in the Oligocene of the Nima area based on the oxygen isotope values in palaeo-lacustrine carbonates and carbon isotope values from palaeosol carbonates, which is indicative of an arid climate. Sedimentology and clay-mineral composition (Liu et al., 2003), fossilized vegetation (Wu et al., 2008), and trace element analysis (Yi et al., 2009) indicated a dry climate in the Oligocene Yaxico Group of the Wudaoliang area. All data probably support a conclusion that the saline palaeo-lakes were well developed in the central Tibetan Plateau in the Oligocene and the climate was dry. In the Early Miocene, regional climate in the central Tibetan Plateau became humid. The isolated Oligocene small lakes were connected to form two vast Miocene lakes represented by the Wudaoliang Group in the central Tibet (Wu et al., 2008). Wu et al. (2008) argued that the climate changed from warm and dry climate in the Oligocene to cool and wet with a forest dominated by coniferous trees in the Early Miocene in the Hoh Xil Basin. Yi et al. (2009) indicated that the Early Miocene palaeo-lake in Hoh Xil Basin was at a humid and low salinity status based on boron concentrations of mudstone. New results of carbon and oxygen isotopes in drill core of the Wudaoliang Group indicated a warm and humid condition in the Early Miocene (Wu et al., 2009). These data suggest that a humid condition presented in the Early Miocene. In summary, the development history of the palaeo-lakes from the Oligocene saline to the Early Miocene fresh water reflects the variation of palaeoclimate from dry to humid in the central Tibetan Plateau.

7. Conclusions

The sedimentary and geochemical features of the Oligocene Lunpori oil shale and the Early Miocene Zhuonai Lake oil shale in the central Tibetan Plateau were demonstrated. The following conclusions can be drawn.

(1) Three types of facies sequences are developed in the Zhuonai Lake section and oil shale occurs in the oil shale-marl sequence with plant fragments. Two types of facies sequences are developed in the Lunpori section: oil shale-silty claystone and oil shale-marl. Both oil shales are finely stratified especially for the Lunpori oil shale with laminae 10 um thick which contains abundant pyrite crystals and fossilized fish bones. The sedimentary characteristics of two types of oil shale suggest a lacustrine deposition.

(2) Both the Zhuonai Lake and Lunpori oil shale contain high values of TOC, S2, and HI, indicating that the oil shales have good oil source rock potential. Tmax values show an immature stage of organic matter for the Zhuonai Lake oil shale and marginally mature for the Lunpori oil shale because of difference in their burial history.

(3) Lunpori oil shale shows characteristics of AOM dominance, odd-over-even predominance, maximum n-alkanes peak at nC25 or nC23, higher proportion of C29 sterane, light δ13Corg values, high concentrations of phytane (low Pr/Ph ratio), high values of gammacerane index, and presence of β-carotane, which is consistent with a reducing, stratiﬁed, and hypersaline palaeo-lake with main contribution of algae and bacteria to the OM.

(4) Oil shale samples from the lower and upper part of the Zhuonai Lake section are characterized by low H/C ratios and high O/C ratios, amorphous humic OM and vitrinite dominance, odd-over-even predominance with long-chain n-alkanes dominance, heavy organic carbon isotope and C29> C27 sterane distribution, which is consistent with a main contribution of land plant. The heavy organic carbon isotope suggests the expanding of C3 land plant during the early Miocene. While the
most samples show characteristics of AOM dominance, odd-over-even predominance with maxima at nC_{29} or nC_{31} and high C_{27} sterane concentration, which is consistent with a main contribution from algae to the OM. Because of maturity effects, the Pr/Ph ratio cannot be applied as a measure for redox conditions in the section. Biomarker analysis indicates that the salinity during the deposition of the Zhuonai Lake oil shale was not enhanced.

(5) Major variations between the Oligocene Lunpori oil shale and the Early Miocene ZhuoNai Lake oil shale on the sedimentary and geochemical characteristics reflect the change of water chemistry of palaeo-lake. The development history of the palaeo-lakes from the Oligocene saline to the Early Miocene fresh water reflects the variation of palaeoclimate from dry to humid in the central Tibetan Plateau.

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