### Organic geochemistry and palynology of Lower Cretaceous Züünbayan oil shales, Mongolia

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Masanobu YAMAMOTO, Delegiin BAT-ERDENE, Pureyiin ULZIIKHISHIG, Yoshio WATANABE, Noboru IMAI, Yoshiteru KAJIWARA, Nobuyori TAKEDA and Terumasa NAKAJIMA (1998) Organic geochemistry and palynology of Lower Cretaceous Züünbayan oil shales, Mongolia. *Bull. Geol. Surv. Japan*, vol. 49 (6), p. 257–274, 14 figs., 4 table.

**Abstract** : Biomarkers and spore-pollens were analyzed for twenty-six oil shales from the Züünbayan Group, Lower Cretaceous lacustrine sedimentary sequences in eastern Mongolia.

The distributions of n-alkane, steranes, hopanes, gammacerane and gammacer-2-ene indicate diversity in the contributions of an autotrophic prokaryote such as a cyanobacterium, nonmarine algae, terrestrial higher plants, heterotrophic bacteria and bacterivorous ciliates. The presence of thermally unstable compounds and low concentrations of diagenetically-generated compounds indicate that the samples are in an immature stage below the oil generation window.

Good correlations exist among organic carbon content, oil yield, bitumen content and n-heptadecane anomaly  $\{2 \times n - C_{17}/(n - C_{16} + n - C_{18})$  n-alkane ratio $\}$ . This indicates that the organic carbon content and oil yield were related to the contribution of a blooming autotrophic prokaryote which sourced the dominant n-heptadecane.

High C/S ratio of the samples and the low concentration of organic sulfur compounds indicate that the Züünbayan oil shales were deposited in a freshwater environment. A palynological analysis shows a common assemblage of the Neocomian sediments belonging to the Boreal palynofloral Province. The detailed assemblage suggests that the area where the Züünbayan oil shales were deposited was situated near the border between warm-humid and hot-arid climate zones. Although Mongolia was situated in midlatitude during early Cretaceous, the tropical-subtropical climate promoted thermal stratification and therefore bottom water anoxia in the freshwater lakes. The degree of development of bottom anoxia was likely controlled by nutrient supply from the surrounding area.

#### 1. Introduction

The Lower Cretaceous Züünbayan Group is distributed in the eastern Mongolian Mesozoic basins (Fig. 1) and is composed of lacustrine sedimentary sequences with thick oil shale horizons and coal measures (Bat-erdene and Enkhtugs, 1987). The oil shale of the Züünbayan Group (Züünbayan oil shale) is undoubtedly a petroleum source rock of waxy oil of the Züünbayan oil field (1941–1969) in the East-Gobi basin (*e.g.*, Petzet, 1990). The Züünbayan Group is correlated to the Lower Cretaceous lacustrine source beds distributed in Chinese territory.

The basins where the Züünbayan oil shales were deposited are developed in the accretional terrain on

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the southern margin of the Siberian craton, and were formed by rift and graben deformations initiated in late Jurassic time (Petzet, 1990). After the rift filling with conglomerates, breccias and volcanics during late Jurassic time (Sharilin Group), lacustrine sediments (Tsagaantsav and Züünbayan Groups) were deposited during early Cretaceous time (Fig. 2; Petzet, 1990). Based on the similarity of the timing and mechanisms of basin developments, the East Mongolian Province is regarded as the northern extension of the East China Petroleum Province defined by Zhai *et al.* (1988).

The geological and geochemical investigations on the Züünbayan oil shales had been conducted by some Mongolian and Estonian institutes; nevertheless the

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Keywords: organic geochemistry, palynology, early Cretaceous, the Züünbayan (Dsunbayan) Group, oil shale, Mongolia, paleoenvironment, biomarker

<sup>&</sup>quot;Züünbayan" was expressed as "Dsunbayan" in our previous papers (Yamamoto *et al.*, 1993; Yamamoto *et al.*, 1998)



Fig. 1 Map showing the distribution of Mesozoic basins and the sampling locations in the East Mongolia coal and oil shale province. Modified from Bat-erdene and Enkhtugs (1987). After Yamamoto *et al.* (1993).

System	Period	Stage	Stratigraphic unit						
SL		Albian		Barunbayan Formation					
ie0	<u>ب</u>	Aptian Barremian	Züünbayan Group	Khukhteg Formation					
etac	owe	Hauterivian	aloup	Shinekhudag Formation					
Cre		Valanginian Berriasian Tithonian	Tsagaantsav Group						
Issic	Upper	Tithonian Kimmeridgian	Sharilin Group						
Jura	Lower -Middle	Bathonian Lias	Kham	arkhoovor Group					

Fig. 2 Generalized stratigraphic column in eastern Mongolian Mesozoic basins. Modified from Petzet (1990) and Bat-erdene (1992). After Yamamoto *et al.* (1993).

results have not been published. Little published data is available about the geochemical aspects of the Züünbayan oil shales except for a few studies such as Yamamoto *et al.* (1993, 1998).

This paper reports the variations in the distribution of biomarkers and the compositions of spores and pollens in oil shales of the Züünbayan Group (Züünbayan oil shales) from the Bayan-Erkhit, Eidemt and Shawart-ovoo oil shale deposits, and discusses their geochemical characteristics and depositional environment. The oil shale samples provided for this study were taken by some of the authors (M. Y., D. B. and P. U.) during the field survey in August 1991.

#### 2. Samples and analytical methods

Twenty-six Züünbayan oil shales from the Shinekhudag Formation (four samples from the Bayan-Erkhit oil shale deposit, ten from the Eidemt deposit and twelve from the Shawart-ovoo deposit) were collected for this study (Fig. 3 and Table 1).

The rock samples were crushed and milled to a particle size of about 200 mesh. More than 1 kg of sample was crushed at the same time and homogenized to eliminate the centimeter and decimeter scale heterogeneity of the sample.

The powdered sample (c. 1-5 g) was extracted three times by ultrasonification with benzene/methanol (7/3 v/v) for 15 minutes. The solvent extract (bitumen) was chromatographed by thin layer chromatography with a silica gel plate (Whatman, PLKC 18 F 20  $\times$  20 cm, 1000  $\mu$ m) and hexane as a development solvent. The band of *Rf* 0.7-1.0 was scraped off from the plate and re-extracted with a mixture of benzene/methanol (1/1 v/v). This fraction is called "Hydrocarbon fraction."

Molecular distributions were determined using a Hewlett Packard 5890A+5970B gas chromatographymass spectrometry (GC/MS) system equipped with a fused silica capillary column coated (Ultra-1, length =25 m, i.d. =0.20 mm, film thickness=0.33  $\mu$ m thick). Hydrocarbon fraction was dissolved in benzene and then injected into the splitless injection system at 300 °C with helium carrier gas. The oven temperature was programmed from 60°C to 160°C at 20°C/min., from 160°C to 300°C at 4°C/min., and then isothermal at 300°C for 30 minutes. The mass spectrometer was



Fig. 3 Stratigraphic and lithologic sections of the Bayan-Erkit, Eidemt and Shawart-ovoo deposits. The numbers in the column indicate sampling positions and sample numbers. A=mudstone, B=calcareous mudstone/siltstone, C=fine grained sandstone, D=dolomite nodule, E=conglomerate, F=tuffaceous mudstone, G=tuff, H=gypsum. After Yamamoto *et al.* (1998).

run in the full scan ion monitoring mode  $(m/z \ 50-550)$  or in the selected ion monitoring mode (SIM;  $m/z \ 99, 125, 177, 191, 205, 217 \ and 231)$ , with an ionizingelectron energy of 70 eV. Assignment of peaks on the gas chromatograms was carried out by comparison with those of standards and in literature, *e.g.*, Philp (1985) and Peters and Moldowan (1993). Abundances of the compounds were represented by their peak areas in the specific fragmentograms, *i.e.*,  $m/z \ 99$  for n-alkanes,  $m/z \ 125$  for  $\beta$ -carotane,  $m/z \ 191$  for triterpanes and  $m/z \ 217$  for steranes. Relative abundances of biomarkers were calculated according to the formula in Appendix I.

The analysis of spores and pollens in three se-

lected samples was conducted by Palynosurvey Co. Ltd., Tokyo.

#### 3. Results and discussion

## 3.1 Biomarker distributions and sources of organic matter

The hydrocarbons extracted from the Züünbayan oil shales consist mainly of n-alkanes, isoprenoid alkanes, hopanes, hop-17(21)-enes, isohop-13(18)-enes, steranes, gammacerane, gammacer-2-ene and  $\beta$ -carotane (Fig. 4, Table 2). Little sulfur compound was detected. The relative abundances of each compound classes are shown in Table 3. The correlation coefficients (r)

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Sample name	Rock type	color	Bioturbation
	Bayan-Erkhit		·
no.5	mudstone	dark brownish gray	none
no.7	mudstone	dark brownish gray	none
no.8	mudstone	dark brownish gray	none
no.9	mudstone	dark brownish gray	none
	Eidemt		
no.1	mudstone	dark brownish gray	none
no.2	mudstone	dark brownish gray	none
no.3	mudstone	dark brownish gray	none
no.4	mudstone	dark brownish gray	none
no.5	calcareous mudstone	beige gray	none
no.6	mudstone	dark brownish gray	none
no.7	mudstone	dark brownish gray	none
no.8	mudstone	dark brownish gray	none
no.9	mudstone	dark brownish gray	none
no.10	mudstone	dark brownish gray	none
	Shawart-ovoo		
no.8	calcareous mudstone	bluish gray	none
no.9	calcareous mudstone	bluish gray	none
no.10	calcareous mudstone	bluish gray	none
no.11	calcareous mudstone	bluish gray	none
no.12	phosphatic calcareous	bluish gray	· bioturbated
	siltstone		
no.1	calcareous mudstone	bluish gray	none
no.2	calcareous mudstone	bluish gray	none
no.3	calcareous mudstone	bluish gray	none
no.4	calcareous mudstone	bluish gray	none
no.5	calcareous mudstone	bluish gray	none
no.6	calcareous mudstone	bluish gray	none
no.7	calcareous mudstone	bluish gray	none

Table 1 List of oil shale samples from the Shinekhudag Formation of the Lower Cretaceous Züünbayan Group

for Rock-Eval and biomarker parameters are shown in Table 4.

#### 3.1.1 Maturity

The presence of thermally unstable compounds, *e.g.*,  $5\beta$ (H),  $14\alpha$ (H),  $17\alpha$ (H)-steranes,  $17\beta$ (H),  $21\beta$ (H)-hopanes, hop-17(21)-enes, isohop-13(18)-enes and gammacer-2-ene and low concentrations of diagenetically-generated compounds, *e.g.*, 20 S-steranes and 22 S-hopanes in samples (Table 3) indicate that they are in an immature stage below the oil generation window.

The ratio of gammacer-2-ene to gammacerane is slightly higher in Shawart-ovoo samples than the others (Fig. 5). Since the gammacerane is thought to be formed from tetrahymanol *via* gammacer-2-ene (ten Haven *et al.*, 1989), the ratio of gammacer-2-ene to gammacerane must decrease with increasing maturity. Thus the higher ratios of the Shawart-ovoo samples indicate that they are less mature than the others.

 $\beta\beta$ -hopane (%) ( $\beta\beta/(\beta\beta+\beta\alpha+\beta\alpha)$  hopane × 100), often used as a maturity parameter (Seifert and Moldowan, 1980), varies largely among samples (Fig. 5). Interestingly, the samples with low  $\beta\beta$ -hopane (%) (Bayan-Erkhit no. 9, Eidemt no. 4, Shawart-ovoo nos. 2 and 3) have high hop-17(21)-enes/ $\beta\beta$ -hopane ratio (Fig. 5). Since hop-17(21)-ene yields abundant  $\beta\alpha$ - and  $\alpha\beta$ hopanes on hydrogenation during early diagenesis (ten Haven *et al.*, 1988), the hop-17(21)-ene might be a precursor of the abundant  $\beta\alpha$ - and  $\alpha\beta$ -hopane. It indicates that the  $\beta\beta$ -hopane (%) does not reflect maturity but source differences in these samples.

#### 3.1.2 Sources of organic matter

About half of samples show a dominant n-heptadecane (n-C<sub>17</sub> alkane) on n-alkane distribution. The n-heptadecane anomaly (expressed in  $2 \times C_{17}/(C_{16}+C_{18})$  n-alkane ratio) is extremely high in two samples (Eidemt nos. 3 and 4) (Fig. 5). Although the dominant n-heptadecane is often attributed to algal contribution (Tissot et al., 1978; Dean and Anders, 1991), its origin is still questionable. A dominance of C17 straight chain hydrocarbons has been reported in some photosynthetic and nonphotosynthetic bacteria as well as marine algae (compiled in Hunt, 1979). A good correlation exists between nheptadecane anomaly and isohop-13(18)-ene/ $\beta\beta$ -hopane ratio (r=0.72; Table 4), which suggests that both nheptadecane and isohop-13(18)-ene have a common origin (Fig. 6). Since hopanoids are biosynthesized mostly by prokaryotic microorganisms (Ourrison et al., 1979, 1984), the dominant n-heptadecane was most likely



Fig. 4 Total ion chromatogram (TIC; m/z 50-550) and mass fragmentograms of acyclic alkanes (m/z 99) triterpenoid hydrocarbons (m/z 191) and steranes (m/z 217) of hydrocarbon fraction from an oil shale sample (Eidemt no. 3). The numbers in the figure indicate the carbon number of n-alkanes. IS=internal standard (benzo (h) quinoline). The compounds identified are listed in Table 2.

derived from a specific blooming prokaryote which produced the precursor of isohop-13(18)-ene as well.

A dominant n-heptadecane was also found in Green River oil shales (Tissot *et al.*, 1978; Dean and Anders 1991; Collister *et al.*, 1994). The  $\delta^{3}$ C of the n-heptadecane is 1-2 per mil lower than those of steroids and the other mid-chain length n-alkanes in Green River oil shales, which suggests that the dominant n-heptadecane derive mainly from prokaryotes such as cyanobacteria (Collister *et al.*, 1994).

and Watanabe, 1994). Three major types can be rec-ognized based on the variations in n-heptadecane sterane ratio reflects either the productivity of autot-01 anomaly and hopane/sterane ratio (Fig. 6). Type A is of hetrotrophic bacteria as decomposers (e.g., Yamamoto bacteria and chemoautrophic bacteria, or the activity rophic prokaryotes, *i.e.*, cyanobacteria, photosynthetic aquatic environment. Thus the variation of karyotes act as either producers or decomposers in ratio reflects the relative contribution of prokaryotes karyotes, while steroids by eukaryotes, hopane/sterane Since hopanoids are biosynthesized mostly by proeukaryotes (Seifert and Moldowan, 1978). hopane/ Pro-

(Fig. ratios, and covariation of the two indices. Type B is anomaly (above 2), a big scatter of the hopane/sterane sterane ratios. high activity of hetrotrophic bacteria samples are lacking in  $\beta$ -carotane, which suggests that algae as well as the autotrophic prokaryote. Type C bution of a blooming autotrophic prokaryote. hopane/sterane ratio resulted from the large of Type A samples was highly reducing and the high al., 1993). It indicates that the depositional environment and is easily degraded by aerobic bacteria (Adam et Type B samples, it is abundant in most Type A samples carotane is under detection limit in Type C and most is characterized by low n-heptadecane anomaly (below (from 1 to 2) and low hopane/sterane ratio. characterized by moderate n-heptadecane anomaly characterized by high values of the n-heptadecane oxygenated environment resulted in the high hopane/ low, which indicates the contribution of eukaryotic 1) and high hopane/sterane ratio (Fig. 6). B samples, 6). The precursor of  $\beta$ -carotane is the hopane/sterane ratios are relatively in relatively  $\beta$ -carotene, While Type C In Type contriβ

Gammacerane and gammacer-2-ene occur ubiqui-

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Peak name	Compound name
isop-C <sub>16</sub>	2,6,10-trimethyltridecane
isop-C <sub>18</sub>	2,6,10-trimethylpentadecane
Pr	pristane
Ph	phytane
PME	2,6,10,15,19-pentamethyleicosane
Sq	squalane
18α-C <sub>27</sub>	$18\alpha$ -22,29,30-trisnorneohopane
17α-C <sub>27</sub>	$17\alpha$ -22,29,30-trisnorhopane
$17\beta$ -C <sub>27</sub>	$17\beta$ -22,29,30-trisnorhopane
$\Delta^{13(18)}$ -C <sub>29</sub>	30-norisohop-13(18)-ene
$\Delta^{17(21)}$ -C <sub>29</sub>	30-norhop-17(21)-ene
$\alpha\beta$ -C <sub>29</sub>	$17\alpha$ ,21 $\beta$ -30-norhopane
$\Delta^{17(21)}$ -C <sub>30</sub>	hop-17(21)-ene
β <b>α-</b> C <sub>29</sub>	$17\beta$ ,21 $\alpha$ -30-norhopane
<b>αβ-</b> C <sub>30</sub>	17α,21β-hopane
$\Delta^{13(18)}$ -C <sub>30</sub>	isohop-13(18)-ene
<b>ββ-</b> C <sub>29</sub>	17β,21β-30-norhopane
βα-C <sub>30</sub>	$17\beta$ ,21 $\alpha$ -moretane(hopane)
$\Delta^{17(21)}$ -C <sub>31</sub>	22R-homohop-17(21)-ene
Gam:1	gammacer-2-ene
$\alpha\beta$ -C <sub>31</sub> S	22S-17α,21β-homohopane
$\alpha\beta$ -C <sub>31</sub> R	22R-17α,21β-homohopane
Gam	gammacerane
ββ-C <sub>30</sub>	17β,21β-hopane
$\beta \alpha$ -C <sub>31</sub> R	$22R-17\beta$ , $21\alpha$ -homohopane
$\Delta^{17(21)}$ -C <sub>32</sub>	22R-bishomohop-17(21)-ene
αβ-C <sub>32</sub> R	$22R-17\alpha$ , $21\beta$ -bishomohopane
$\Delta^{17(21)}$ -C <sub>33</sub>	22R-trishomohop-17(21)-ene
ββ-C <sub>31</sub>	17β,21β-homohopane
<b>ββ-</b> C <sub>32</sub>	17β,21β-bishomohopane
ββ-C <sub>33</sub>	$17\beta$ , $21\beta$ -trishomohopane
βaaC27R	$20R-5\beta$ , $14\alpha$ , $17\alpha$ (H)-cholestane
aaaC27R	$20R-5\alpha$ , $14\alpha$ , $17\alpha$ (H)-cholestane
aaaC28S	$20S-5\alpha$ , $14\alpha$ , $17\alpha$ (H)-24-methylcholestane
βααC28R	$20R-5\beta$ , $14\alpha$ , $17\alpha$ (H)-24-methylcholestane
$\alpha\alpha\alpha C_{28}R$	$20R-5\alpha$ , $14\alpha$ , $17\alpha$ (H)-24-methylcholestane
aaaC29S	$20S-5\alpha$ , $14\alpha$ , $17\alpha$ (H)-24-ethylcholestane
βααC29R	$20R-5\beta$ , $14\alpha$ , $17\alpha$ (H)-24-ethylcholestane
$\alpha \alpha \alpha C_{29}R$	$20R-5\alpha$ , $14\alpha$ , $17\alpha$ (H)-24-ethylcholestane

Table 2 List of identified compounds shown in Fig. 4

tously in samples (Table 3). They are thought to be formed from tetrahymanol (ten Haven *et al.*, 1989) which were reported in a fern (Zander *et al.*, 1969), photosynthetic sulfur bacteria (Kleeman *et al.*, 1990) and bacterivorous ciliates (Harvey and McManus, 1991). In lacustrine systems, gammacerane and gammacer-2ene are supposed to derive from bacterivorous ciliates that feed on prokaryotes based on stable carbon isotopic compositions (Sinninghe Damsté *et al.*, 1995). Gammacerane/n-alkane ratio is high in the Types A and B samples with high n-heptadecane anomaly, supporting that the gammacerane originates from bacterivorous ciliates.

Long chain n-alkanes (> $C_{23}$ ) occur as a dominant compound class in all samples. Long chain n-alkanes are biosynthesized mainly by higher plants (compiled in Hunt, 1979) and some species of nonmarine algae (Gelpi *et al.*, 1970). Long chain straight hydrocarbons ( $C_{13}$ - $C_{31}$ ) are also generated from resistant aliphatic biomacromolecules by pyrolysis and are common in matured rocks and crude oils (Tegelaar *et al.*, 1989). Higher plant n-alkanes show strong odd carbon number

Sample	Bitumen	R	elative ab	undances	o n-alkanes			1	1-Alkane		
name	wt%	Isop.alkanes	Steranes	Hopanes	β-Carotane	gammacerane	Hopane/sterane	C29/C19	CPI	n-C17 anomaly	Pr/Ph
						Bayan-Erkhit				and the state of t	
no.5	0.47	0.25	0.95	0.17	0.0052	0.049	0.17	1.33	6.40	1.43	0.11
no.7	0.35	0.03	0.04	0.06	0.0000	0.004	1.42	1.06	11.14	1.16	0.10
no.8	0.35	0.15	0.17	0.42	0.0000	0.059	2.51	2.23	4.97	1.48	0.09
no.9	0.48	0.17	0.21	0.46	0.0000	0.133	2.21	2.24	4.52	1.18	0.08
no.1	0.31	0.09	0.14	0.08	0.0000	0.005	0.58	0.87	5.43	1.22	0.17
no.2	0.70	0.10	0.13	0.43	0.0010	0.061	3.35	1.65	4.37	1.25	0.24
no.3	3.12	0.17	0.03	0.23	0.0042	0.096	6.62	0.69	6.43	5.71	0.33
no.4	2.63	0.19	0.06	0.17	0.0031	0.023	3.03	0.87	4.63	6.26	0.26
no.5	0.92	0.04	0.03	0.03	0.0000	0.001	0.94	0.64	5.39	1.50	0.23
no.6	1.93	0.11	0.06	0.12	0.0215	0.011	1.97	0.46	4.58	2.78	0.23
no.7	0.21	0.10	0.04	0.08	0.0019	0.010	1.99	0.50	5.17	3.02	0.28
no.8	0.91	0.09	0.18	0.09	0.0059	0.011	0.51	1.19	8.29	1.46	0.13
no.9	1.22	0.07	0.09	0.10	0.0032	0.009	1.12	0.64	8.10	2.46	0.13
no.10	. 0.71	0.17	0.07	0.13	0.0039	0.025	1.95	0.39	4.56	2.03	0.14
						Shawart-ovoo					
no.8	0.23	0.03	0.02	0.08	0.0001	0.001	3.80	3.68	2.84	0.76	0.00
no.9	0.28	0.03	0.02	0.10	0.0000	0.001	6.18	3.14	2.89	0.65	0.00
no.10	0.25	0.03	0.01	0.06	0.0000	0.001	7.81	2.16	2.99	0.68	0.00
no.11	0.26	0.04	0.03	0.11	0.0000	0.001	4.16	2.45	3.41	0.81	0.00
no.12	0.04	0.05	0.02	0.04	0.0000	0.000	2.01	1.08	3.35	1.35	0.65
no.1	1.23	0.01	0.02	0.05	0.0000	0.002	2.00	6.96	4.46	1.20	0.00
no.2	1.87	0.09	0.03	0.24	0.0000	0.009	6.75	3.06	4.38	4.59	0.07
no.3	0.85	0.06	0.03	0.11	0.0000	0.005	3.92	2.99	4.47	3.22	0.06
no.4	0.73	0.03	0.03	0.07	0.0000	0.003	2.66	3.57	4.43	1.31	0.00
no.5	0.26	0.01	0.01	0.06	0.0000	0.001	5.00	3.69	3.73	0.65	0.00
no.6	0.52	0.04	0.01	0.03	0.0001	0.001	5.75	1.33	1.98	0.93	0.07
no.7	0.90	0.05	0.01	0.07	0.0000	0.001	5.60	2.81	3.15	1.93	0.05

 $\frac{1}{1000} \frac{1}{1000} \frac{1}{1000$ 

Table 3 continued

Sample		Hopane		Homohopane Bi	Homohopane Bishomohopane Hopanes				Relative abundances to I				
name	ββ (%)	βα (%)	αβ (%)	22S/22R	22S/22R	C27/C30	C29/C30	Σ(C31-C35)/C30	Hop-17(21)-ene	Isohop-13(18)-ene			
					Ba	yan-Erkh	it		and a second	an a			
no.5	9.89	13.44	76.66	0.12	0.00	2.18	1.53	1.64	0.12	0.08			
no.7	28.10	20.96	50.94	0.09	0.00	1.59	0.76	2.93	0.36	0.12			
no.8	25.49	24.58	49.93	0.10	0.58	0.94	0.65	1.86	0.69	0.11			
no.9	20.59	27.72	51.68	0.10	0.41	2.07	1.26	3.71	1.07	0.17			
no.1	21.03	27.35	51.63	0.14	0.21	2.25	1.17	0.76	0.04	0.23			
no.2	30.70	23.42	45.88	0.33	0.69	0.91	0.73	0.91	0.09	0.24			
no.3	19.81	28.72	51.48	0.30	0.71	0.96	0.65	1.66	0.06	0.36			
no.4	17.54	27.72	54.74	0.22	0.76	3.29	1.06	1.35	1.16	0.44			
no.5	33.31	25.03	41.65	0.10	0.00	1.36	0.81	0.95	0.00	0.08			
no.6	23.58	25.00	51.42	0.16	0.00	1.70	0.68	1.85	0.05	0.23			
no.7	19.73	26.67	53.60	0.20	0.76	2.15	0.72	1.86	0.12	0.27			
no.8	22.46	20.86	56.68	0.17	0.53	1.99	0.95	0.92	0.05	0.35			
no.9	21.56	24.59	53.86	0.31	0.49	1.30	1.04	0.59	0.13	0.44			
no.10	17.07	27.71	55.23	0.22	0.48	1.93	1.06	0.79	0.11	0.16			
					Sh	awart-ovo	00						
no.8	28.03	48.57	23.40	0.11	0.27	4.24	1.08	2.83	0.05	0.19			
no.9	39.48	41.57	18.95	0.10	0.17	2.14	0.75	3.20	0.02	0.10			
no.10	44.42	34.43	21.14	0.09	0.31	1.86	0.73	1.64	0.02	0.09			
no.11	29.70	53.94	16.36	0.07	0.32	1.84	0.75	2.76	0.05	0.15			
no.12	24.75	29.31	45.94	0.41	0.56	1.53	0.42	1.31	0.16	0.10			
no.1	7.82	62.60	29.59	0.09	0.00	4.00	2.09	4.56	0.31	0.22			
no.2	11.43	65.53	23.04	0.35	0.00	3.28	4.52	2.42	2.16	0.48			
no.3	11.00	59.72	29.28	0.17	0.37	2.83	2.43	2.58	1.08	0.15			
no.4	17.55	56.82	25.63	0.14	0.15	2.92	1.20	3.51	0.06	0.05			
no.5	33.93	39.20	26.87	0.09	0.36	2.61	0.93	3.42	0.04	0.11			
no.6	40.09	41.04	18.87	0.15	0.40	2.44	0.89	2.74	0.04	0.10			
no.7	33.99	47.35	18.66	0.11	0.08	2.97	1.12	1.82	0.06	0.14			

Sample	energy of the second	Gammacer-2-ene	C29 Sterane		Steranes	Steranes	Туре			
name	Gam. index	/gammacerane	βαα/ααα	20S/20R	20S/20R	C27(%)	C28(%)	C29(%)	C27/C29	
			B	ayan-Erkhit	·			and the second secon		
no.5	18.59	0.15	0.39	0.08	0.12	25.9	32.6	41.5	0.62	В
no.7	13.16	0.87	0.55	0.02	0.04	15.0	39.0	45.9	0.33	В
no.8	16.15	0.73	0.53	0.06	0.03	40.8	26.9	32.3	1.27	В
no.9	48.24	0.62	0.72	0.06	0.08	44.6	26.9	28.6	1.56	В
no.1	6.19	0.99	0.36	0.03	0.04	26.8	33.2	40.0	0.67	В
no.2	15.44	0.84	0.36	0.38	0.03	28.6	21.3	50.1	0.57	в
no.3	35.50	1.01	0.61	0.09	0.00	34.6	23.8	41.6	0.83	Α
no.4	15.91	0.65	0.47	0.07	0.06	42.1	22.0	35.9	1.18	Α
no.5	3.06	1.41	0.34	0.03	0.02	22.7	40.2	37.2	0.61	В
no.6	11.52	0.88	0.50	0.05	0.04	41.0	28.8	30.2	1.36	Α
no.7	15.03	0.93	0.64	0.04	0.06	44.8	25.8	29.4	1.52	Α
no.8	12.93	0.73	0.37	0.05	0.04	41.7	21.4	37.0	1.13	В
no.9	7.42	0.98	0.36	0.03	0.05	18.2	34.7	47.1	0.39	А
no.10	15.61	0.64	0.38	0.34	0.03	19.3	43.3	37.4	0.52	А
			S	hawart-ovoo	ı.					
no.8	3.48	1.37	0.65	0.04	0.19	35.3	32.1	32.6	1.08	С
no.9	3.90	1.13	0.58	0.05	0.16	34.4	26.6	39.0	0.88	С
no.10	3.01	2.35	0.45	0.00	0.08	44.3	19.0	36.6	1.21	С
no.11	2.51	1.68	0.57	0.00	0.17	37.4	24.8	37.8	0.99	С
no.12	0.00	n.d.	0.61	0.00	0.19	28.3	31.9	39.8	0.71	В
no.1	4.93	0.89	0.87	0.00	0.17	42.4	17.8	39.7	1.07	?
no.2	5.06	1.39	0.91	0.00	0.00	47.9	19.4	32.7	1.46	Α
no.3	4.13	1.26	0.68	0.00	0.15	35.6	12.9	51.5	0.69	Α
no.4	7.08	0.78	0.76	0.00	0.08	41.2	18.6	40.2	1.03	В
no.5	5.43	0.85	0.77	0.05	0.08	34.0	25.1	40.9	0.83	С
no.6	5.67	1.18	0.51	0.00	0.14	50.4	22.7	26.9	1.87	С
no.7	3.67	1.26	0.73	0.04	0.16	42.9	26.8	30.4	1.41	?

Table 3 continued

Gam.index = gammacerane index.

preference, while resistant biomacromolecule-derived n-alkanes show no odd carbon number preference (Tegelaar *et al.*, 1989). The long chain n-alkanes of the Züünbayan oil shales have strong odd carbon number preference, which indicates that the long-chain n-alkanes were derived mainly from terrestrial higher plants.

 $C_{27}$ - $C_{28}$ - $C_{29}$  Sterane distribution (Fig. 7) shows that most samples have sterane compositions close to those of petroleum of nonmarine algal origin (Area N in Fig. 7, Moldowan *et al.*, 1985), while some samples have intermediate compositions of petroleums between nonmarine algal (Area N) and higher plant (Area L) origins. This suggests that the steranes were derived mainly from nonmarine algae and partly from higher plants.

As shown in Fig. 8, a negative correlation exists between  $C_{27}/C_{29}$  sterane ratio and odd carbon number preference (Carbon Preference Index : CPI) of long chain n-alkanes ( $C_{24}$ - $C_{34}$ ). Since  $C_{27}$  steroids are abundant in algae, while  $C_{29}$  steroids are dominant in higher plants (Huang and Meinschein, 1979),  $C_{27}/C_{29}$  sterane ratio is used as a parameter indicating the relative contribution of algae and higher plants. On the other hands, CPI of long chain n-alkanes are high in higher plant waxes (Eglinton *et al.*, 1962). Thus the negative correlation between  $C_{27}/C_{29}$  sterane ratio and the CPI of long chain n-alkanes most likely resulted from the variation in the contribution of higher plants in each sample.

# 3.2 Pollen-spore compositions and the climate of the environment where Züünbayan oil shales were deposited

The pollen-spore compositions for three selected samples are shown in Fig. 9. Fern spores and gymnosperm pollens are recognized, while no angiosperm pollen is recognized. Gymnosperm pollens predominate over fern spores (Fig. 9). The spore-pollen compositions show a common assemblage of the Neocomian sediments belonging to the Boreal palynofloral Province (Herngreen and Chlonova, 1981) that covered present eastern Europe and northern Asia.

Herngreen and Chlonova (1981) recognized the differences on the palynoflora between Siberian and Chinese areas in the eastern part of the Boreal palynofloral Province, and divided it into the two types ; the Boreal-Siberian subprovince which is characterized by the presence of *Pilosisporites*, *Impardecispora*, Aequitriradites, and the southern adjacent subprovince ("Chinese subprovince" called tentatively here) which is characterized by a dominant Classopollis. A comparison between these palynofloral subprovinces and the floral provinces proposed by Kimura (1979, 1980) indicates that the palynoflora of the Boreal-Siberian subprovince reflects the "Tetori" type flora indicating a warm-humid climate, while that of the "Chinese subprovince" reflects the "Ryoseki" type flora indicating a hot-arid climate. The presence of *Classopollis* (but not dominant) and the absence of Pilosisporites, Impardecispora, Aequitriradites in the Züünbayan oil shales

		org. C	C/S	Tmax	<b>S</b> 1	S2	<b>S</b> 3	H.I.	O.I.	P.I.	S2/S3	EOM	I/N A	S/NA	H/NA	3-C/NA (	Jam/NA	H/S	C29/C19 NA	CPI	C17 NA	Pr/Ph	HH/H &	17(21)H/H	Δ13(18	)H/H C	Jam.I.
C/S		0.43																									
Tmax		-0.59	-0.30																								
<b>S</b> 1		0.80	0.39	-0.87																							
S2		0.99	0.40	-0.59	0.80																						
S3		0.93	0.33	-0.58	0.76	0.92																					
H.I.		0.53	-0.08	-0.22	0.38	0.60	0.51																•				
O.I.		-0.13	-0.28	0.09	-0.09	-0.12	0.19	0.15																			
P.I.		0.36	0.24	-0.70	0.78	0.33	0.37	0.08	0.02																		
S2/S3		0.23	0.08	-0.12	0.14	0.28	-0.06	0.36	-0.80	-0.11																	
Bitumen content	EOM	0.59	0.32	-0.86	0.80	0.56	0.63	0.28	0.05	0.66	0.58																
Isoprenoid/normal alkane	I/N A	0.57	0.23	-0.35	0.52	0.53	0.55	0.08	0.02	0.24	-0.02	0.39															
Sterane/n-alkane	S/NA	0.67	0.06	0.22	-0.10	0.03	-0.01	-0.04	-0.08	-0.20	0.07	-0.10	0.66														
Hopane/n-alkane	H/NA	0.07	-0.07	-0.07	0.14	0.01	0.19	-0.19	0.35	0.21	-0.40	0.16	0.58	0.26													
β-Carotane/n-alkane	β-C/NA	0.44	0.44	-0.16	0.22	0.42	0.48	0.18	-0.01	0.05	0.02	0.43	0.35	0.18	0.00												
gammacerane/n-alkane	Gam/NA	0.17	-0.08	-0.26	0.23	0.13	0.23	-0.08	0.22	0.11	-0.23	0.26	0.69	0.36	0.84	0.06											
Hopane/sterane	H/S	-0.17	-0.03	-0.27	0.21	-0.15	-0.12	0.11	0.07	0.49	-0.02	0.17	-0.28	-0.43	0.01	-0.25	-0.05										
C29/C19 n-alkane	C29/C19 NA	-0.51	-0.52	0.11	-0.29	-0.50	-0.39	-0.04	0.03	0.10	-0.23	-0.15	-0.48	-0.17	-0.06	-0.39	-0.18	0.29	F								
CPI		0.26	0.13	-0.02	0.12	0.19	0.17	-0.03	-0.09	-0.03	0.01	0.18	0.22	0.26	0.03	0.17	0.14	-0.55	-0.37								
n-heptadecane anomaly	C17 NA	0.69	0.36	-0.85	0.89	0.65	0.65	0.17	-0.10	0.76	0.07	0.87	0.49	-0.09	0.18	0.26	0.23	0.15	-0.29	0.17							
Pr/Ph		0.29	0.52	-0.36	0.25	0.27	0.18	-0.40	-0.52	0.00	0.24	0.22	0.29	-0.01	0.04	0.23	0.16	-0.28	-0.58	0.13	0.36						
Σ(C31-C35)/C30 hopane	HH/H	-0.46	-0.53	0.15	-0.29	-0.44	-0.37	0.02	0.27	-0.03	-0.14	-0.16	-0.39	-0.17	-0.04	-0.26	-0.01	0.28	0.78	-0.25	-0.26	-0.54					
Hop-17(21)-ene/hopane	∆17(21)H/H	0.08	-0.18	-0.26	0.35	0.02	0.11	-0.20	0.05	0.60	-0.20	0.34	0.26	-0.02	0.44	-0.15	0.23	0.17	0.16	0.01	0.53	-0.06	0.18				
Isohop-13(18)-ene/hopane	Δ13(18)H/H	0.60	0.48	-0.63	0.70	0.55	0.55	0.17	-0.11	0.69	0.05	0.69	0.29	-0.12	0.20	0.23	0.13	0.01	-0.19	0.30	0.72	0.20	-0.32	0.46	<b>;</b> ,		
Gammacerane index	Gam.I.	0.34	-0.04	-0.32	0.33	0.30	0.38	0.09	0.20	0.12	-0.14	0.32	0.70	0.32	0.69	0.17	0.94	-0.13	-0.27	0.29	0.30	0.14	0.03	0.20	)	0.21	
C27/C29 sterane	C27/C29 S	-0.03	-0.04	-0.11	0.03	0.01	0.09	0.19	0.33	0.14	-0.17	0.08	0.00	-0.18	0.13	0.08	0.09	0.39	0.18	-0.50	0.10	-0.18	0.33	0.27		0.08	0.13
Note: hold value means the	correlation cooff	iniant (m	\ halou	0.50 0	nd abox	0 0 50	within	00% 00	nfidano	aintor	(10	1040 B 1040 C 0		Contraction of the second	A Charles and a charles of the					and the second							

Table 4 Correlation coefficients (r) for Rock-Eval parameters and the relative abundances of biomarkers in Züünbayan oil shales

Note: bold value means the correlation coefficient (r) below -0.50 and above 0.50 (within 99% confidence interval).



Fig. 5 Stratigraphic variations in hopane/sterane ratio, hop-17(21)-ene/ $\beta\beta$ -hopane ratio, hop-13(18)-ene/ $\beta\beta$ -hopane ratio, the relative abundances of  $\beta\beta$ -,  $\beta\alpha$ - and  $\alpha\beta$ -hopanes, n-heptadecane anomaly (n-C<sub>17</sub> anomaly), gammacer-2-ene/gammacerane ratio and Pr/Ph ratio in Züünbayan oil shales.

(Table 4; Fig. 9) indicate that they have an intermediate palynofloral composition between the Boreal-Siberian and the Chinese subprovinces. It suggests that this area was situated near the border between warm-humid and hot-arid climate zones.

## 3.3 Rock-Eval pyrolysis and source rock characteristics

The results of Rock-Eval pyrolysis are listed in Yamamoto *et al.* (1993). The stratigraphic variations of the parameters are shown in Fig. 10.

Hydrogen Index-Oxygen Index (H.I.-O.I.) diagram shows that most samples are plotted in the region of Type II kerogens (Fig. 11). In contrast,  $T_{max}$ -H.I. diagram shows that they are plotted in the region of Type I kerogens (Fig. 11). Since the combination of constantly high  $T_{max}$  and high H.I. is typical in Type I kerogens, the kerogens of the samples are classified into Type I kerogens (lacustrine oil shale type). Although the O. I. values of the samples are slightly higher than that of typical Type I kerogen, it can be explained by the weathering at the outcrop surface.

Most samples show an almost identical  $T_{max}$  value

around 450°C, and Production Index (P.I. =  $S_1/(S_1 + S_2)$ S<sub>2</sub>)) below 0.05. Exceptionally, Eidemt nos. 3 and 4 samples show significantly lower T<sub>max</sub> values (ca. 420 -430°C) and higher P.I. values (above 0.05) than the others. T<sub>max</sub> and P.I. generally increase with increasing thermal maturity, and are often used as maturity indices (Bordenave et al., 1993). In this case, however, the  $T_{max}$  and P.I. of both samples are different from those of the other samples located very closely in stratigraphic column (Fig. 3), which is a negative evidence for the maturity control. A high P.I. is also often attributed to the contamination of migrated matured oil (Bordenave et al., 1993). Yet, biomarker distribution of both samples indicates that the bitumens are immature. In this case, both samples contain significantly high amount of bitumen (Table 3), and good correlations exist among  $T_{max}$ , P.I. and bitumen content (Fig. 12). This suggests that the anomalous P.I. value is attributed to the abundant indigenous bitumen in the samples. It is also possible that the anomalous  $T_{max}$  value is attributed to the contribution of heavy fraction of the bitumen to  $S_2$  peak, because the  $S_2$  peak



Fig. 6 Plots of isohop-13(18)-ene/ $\beta\beta$ -hopane, hopane/sterane,  $\beta$ -carotane/n-alkane and gammacerane/n-alkane ratios against n-heptadecane anomaly (n-C<sub>17</sub> anomaly) in Züünbayan oil shales.

represents partly the heavy hydrocarbons, resins and asphaltenes vaporized (Bordenave, 1993).

The Hydrogen Index (H.I., defined as  $S_2/org$ . C) of most samples ranges from c. 500 to c. 800 mgHC/gC (Fig. 10). The range indicates that the samples are in immature and/or early mature stages (Bordenave *et al.*, 1993). Exceptionally, Shawart-ovoo no. 12 sample shows a rather lower H.I. value (235 mgHC/gC) than the others. The bioturbated sedimentary structure of the sample (Table 1) suggests that the lower H.I. resulted from the degradation of organic matter in the oxic depositional environment.

Interestingly, n-heptadecane anomaly seems to be related to the petroleum source rock potentiality of the Züünbayan oil shales. The n-heptadecane anomaly has good correlations with organic carbon contents (r=0.69), oil yields (r=0.40), bitumen content (r=0.87) and P.I. (r=0.76) and a negative correlation with  $T_{max}$  (r=-0.85) (Fig. 13, Table 4). It means that the Type A oil shales with the highest n-heptadecane ratio are most excellent as a source rock. This suggests that the potentiality was controlled by primary production.

#### 3.4 Depositional environment of Züünbayan oil shales

An organic carbon-total sulfur diagram (Fig. 14) shows that the Züünbayan oil shales are distributed in the region of freshwater environment (Berner and Raiswell, 1984). Also, the low concentration of organic

sulfur compounds in the samples is a characteristic of freshwater sediments (de Leeuw and Sinninghe Damsté, 1990). These results along with the occurrence of freshwater benthic fauna (Bat-erdene, 1992) indicate that the Züünbayan oil shales were deposited in a freshwater environment.

All but one samples have a well laminated texture with no significant bioturbation, which indicates a reducing bottom water environment (Savdra and Bottjer, 1991). Pristane over phytane ratios (Pr/Ph ratios) of all samples are below 0.65 (Fig. 5). Since the Pr/Ph ratio below 0.6 is common in the sediments deposited in anoxic environments (Peters and Moldowan, 1993), an anoxic depositional environment is also suggested. Shawart-ovoo no. 12 sample shows relatively high Pr/ Ph ratio (Pr/Ph=0.65). Since only this sample has bioturbated structure (Table 1), the relatively high Pr/Ph ratio most likely reflects the relatively oxygenated environment. The occurrence of the gammacerane and gammacer-2-ene which originate from anaerobic ciliates and/or bacteria also indicates the presence of anoxic water mass (Schoell et al., 1994; Sinninghe Damsté et al., 1995).

Permanent stratification promotes the development of anoxic bottom water in the large, deep lake with more than 100 meter depth (Demaison and Moore, 1980). Lake Malawi and Lake Tanganyika are examples of the recent freshwater lakes where permanent stratification promotes stagnant anoxic bottom water Bulletin of the Geological Survey of Japan, Vol. 49, No. 6, 1998



Fig. 7 C<sub>27</sub>-C<sub>28</sub>-C<sub>29</sub> Sterane (5  $\alpha$ , 14  $\alpha$ , 17  $\alpha$ , 20 R-isomer) distribution for Züünbayan oil shales. Areas N and L refer to petroleums sourced mainly from nonmarine algal and higher plant organic matters, respectively (Moldowan *et al.*, 1985). After Yamamoto *et al.* (1998).



Fig. 8 Carbon number preference (CPI) of  $C_{24}\text{-}C_{34}$  n-alkanes versus  $C_{27}/C_{29}$  sterane ratio in Züünbayan oil shales.



Fig. 9 Relative abundances of fern spores and gymnosperm pollens identified in Bayan-Erkhit no. 7, Eidemt no. 2 and Shawart-ovoo no. 2 oil shale samples.

and organic-rich bottom sediments (Degens *et al.*, 1971; Demaison and Moore, 1980; Talbot, 1988). In these tropical lakes, little seasonal temperature change and moderate to high rainfall, year round, tend to promote permanent water column stratification and therefore anoxia. On the other hands, in cold and temperate climates, seasonal overturning of water, the high capacity of cold water to dissolve oxygen, and density underflows of cold river waters all enhance oxic conditions in bottom waters (Demaison and Moore, 1980). Early Cretaceous Mongolia was situated at midlatitude (35° N to 40° N) (Smith and Briden, 1977). Nevertheless, as discussed in previous section, the palynoflora of the Züünbayan oil shales suggests hotarid to warm-humid climate. Also, tropical-subtropical flora was distributed in early Cretaceous Mongolia, and the southern limit of temperate flora was 50° N. (Vakhrameev, 1964). Crocodile fossils found in Creta-



Fig. 10 Stratigraphic variations of Rock-Eval parameters in Züünbayan oil shales.



Fig. 11 Hydrogen Index-Oxygen Index (H.I.-O.I.) and H.I.-T<sub>max</sub> diagrams for Züünbayan oil shales. After Yamamoto *et al.* (1998).



Fig. 12 Plots of T<sub>max</sub> and Production Index (P.I.) against bitumen content for Züünbayan oil shales.



Fig. 13 Plots of organic carbon content (org. C), oil yield, bitumen (EOM),  $T_{max}$  and Production Index (P.I.) against n-heptadecane anomaly (n- $C_{17}$  anomaly) in Züünbayan oil shales.



Fig. 14 Distribution of organic carbon and sulfur contents in Züünbayan oil shales. Areas of normal marine and freshwater sediments refer to Berner and Raiswell (1984). After Yamamoto *et al.* (1998).

ceous sediments in Mongolia also suggests tropicalsubtropical climate (Lefield, 1971). It is therefore possible that the temperature in winter season was rather high in the early Cretaceous Mongolia, and permanent stratification was maintained year round.

Variation in the abundance of  $\beta$ -carotane suggests the changes in the degree of development of bottom water anoxia (Table 3). In the case of tropical freshwater lakes, organic-rich sediments occur in early Holocene horizon (Talbot, 1988). The formation of organic-rich beds probably resulted from enhanced primary productivity caused by the nutrient supply promoted by chemical weathering in the densely vegetated area around the lake (Talbot, 1988).

On the analogy of the modern cases, it is possible that the Type A of the Züünbayan oil shales represents eutrophic environment, while the Type C represents oligotrophic environment. The depositional environment of each type oil shale was supposed as follows. In the Type A deposition, the massive supply of nutrient in a humid climate enhanced the productivity of a blooming autotrophic prokaryote such as a cyanobacterium, and formed highly reducing stagnant bottom-water below thermocline. In the Type B deposition, the decreased supply of nutrient in a relatively dry climate reduced the primary productivity, and the algae succeeded the blooming prokaryote. As the result, the bottom-water anoxia was weaker than that of Type A. In the Type C deposition, the little supply of nutrient in dry climate resulted in low primary productivity and relatively oxygenated bottom water. The organic matter was degraded by heterotrophic bacteria, and consequently relatively organic-lean sediments were deposited.

#### 4. Conclusions

Biomarker distribution indicates (1) the ubiquitous contributions of a blooming autotrophic prokaryote such as a cyanobacterium, nonmarine algae, terrestrial higher plants, heterotrophic bacteria and bacterivorous ciliates, (2) low maturity of organic matter in samples, (3) freshwater depositional environment and (4) the development of bottom water anoxia.

The palynoflora shows a common assemblage of the Neocomian sediments belonging to the Boreal palynofloral Province, and suggests that the area where the Zuunbayan oil shales were deposited was situated near the border between warm-humid and hot-arid climate zones.

Good correlations among organic carbon content, oil yield, bitumen content and n-heptadecane anomaly suggests that the degree of bottom water anoxia controlled organic carbon content and oil yield, and was related to the contribution of a blooming autotrophic prokaryote which sourced dominant n-heptadecane.

The tropical-subtropical climate promoted thermal stratification and therefore bottom water anoxia in the freshwater lakes. The degree of development of bottom anoxia was likely controlled by nutrient supply from the surrounding area.

Acknowledgments: This research was financially supported by the program "Institute for Transfer of Industrial Technology (ITIT)" of AIST, MITI. We thank Mr. C. Khurtz and Dr. J. Byamber, former directors of Institute of Geology and Mineral Resources of Mongolia, (IGMR) for their contributions to this ITIT project. Special thanks are due to Messrs. T. Tseden, T. Battor, IGMR, Dr. B. Tumenbayar, Mongolian Academy of Science, Dr. M. Enomoto, National Institute for Resources and Environments, Drs. S. Murao, S. Terashima, M. Terashima, N. Kaneko, Y. Suzuki and M. Yamamuro, Geological Survey of Japan (GSJ), for their helpful discussions and assistance for experiments. A constructive review of Dr. S. Sakata of GSJ is gratefully acknowledged.

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Appendix I

- Isoprenoid/n-alkane ratio =(2,6,10-trimethyltridecane + 2,6,10-trimethylpentadecane + pristane + phytane + 2,6,10,15,19-pentamethyleicosane + squalane) (m/z 99)/ $C_{14}$ - $C_{35}$  n-alkanes (m/z 99).
- Sterane/n-alkane ratio =  $C_{27}$ - $C_{29}$  5  $\alpha$ , 14  $\alpha$ , 17  $\alpha$ , 20 R-steranes (m/z 217)/ $C_{14}$ - $C_{35}$  n-alkanes (m/z 99).
- Hopane/n-alkane ratio = $(17 \ \beta C_{27} + C_{29} C_{35} \ 17 \ \beta, \ 21 \ \beta)$ -hopanes  $(m/z \ 191)/C_{14} C_{35}$  n-alkanes  $(m/z \ 99)$ .
- $\beta$ -Carotane/n-alkane ratio =  $\beta$ -carotane (m/z 125)/C<sub>14</sub>-C<sub>35</sub> n-alkanes (m/z 99).
- Gammacerane/n-alkane ratio=gammacerane  $(m/z 191)/C_{14}-C_{35}$  n-alkanes (m/z 99).
- Hopane/sterane ratio= $(17 \ \beta$ -C<sub>27</sub>+C<sub>29</sub>-C<sub>35</sub> 17  $\beta$ , 21  $\beta$ )hopanes  $(m/z \ 191)/C_{27}$ -C<sub>29</sub> 5  $\alpha$ , 14  $\alpha$ , 17  $\alpha$ , 20 Rsteranes  $(m/z \ 217)$ .
- $C_{29}/C_{19}$  n-Alkane ratio =  $C_{29}/C_{19}$  n-alkanes (*m*/*z* 99).
- $$\begin{split} \text{CPI} = & 1/2\{(C_{25} + C_{27} + C_{29} + C_{31} + C_{33})/(C_{24} + C_{26} + C_{28} + C_{30} \\ &+ C_{32}\} + (C_{25} + C_{27} + C_{29} + C_{31} + C_{33})/(C_{26} + C_{28} + C_{30} + C_{32} \\ &+ C_{34}\} \text{ n-alkanes } (m/z \text{ 99}). \end{split}$$
- n-Heptadecane anomaly= $2 \times C_{17}/(C_{16}+C_{18})$  n-alkanes (m/z 99).
- Pristane/phytane ratio=pristane (m/z 99)/phytane (m/z 99).
- $\beta\beta$ -Hopane (%)=17  $\beta$ , 21  $\beta$ -hopane (m/z 191)/(17  $\beta$ , 21  $\beta$ -+17  $\beta$ , 21  $\alpha$ -+17  $\alpha$ , 21  $\beta$ -)hopanes (m/z 191) × 100.
- $\beta \alpha$ -Hopane (%)=17  $\beta$ , 21  $\alpha$ -hopane (m/z 191)/(17  $\beta$ , 21  $\beta$ -+17  $\beta$ , 21  $\alpha$ -+17  $\alpha$ , 21  $\beta$ -)hopanes (m/z 191)× 100.
- $\alpha\beta$ -Hopane (%)=17  $\alpha$ , 21  $\beta$ -hopane (m/z 191)/(17  $\beta$ , 21  $\beta$ -+17  $\beta$ , 21  $\alpha$ -+17  $\alpha$ , 21  $\beta$ -)hopanes (m/z 191)×

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Received January 14, 1998 Accepted March 18, 1998

100.

- 22.S/22 R Homohopane ratio = 22 S/22 R 17  $\alpha$ , 21  $\beta$ -C<sub>31</sub> hopanes (m/z 191).
- 22 S/22 R Bishomohopane ratio = 22 S/22 R 17  $\alpha$ , 21  $\beta$  -C<sub>32</sub> hopanes (m/z 191).
- C<sub>27</sub>/C<sub>30</sub> Hopane ratio=17 β-22, 29, 30-trisnorhopane (*m*/*z* 191)/17 β, 21 β-hopane (*m*/*z* 191).
- C<sub>29</sub>/C<sub>30</sub> Hopane ratio = 17  $\beta$ , 21  $\beta$ -30-norhopane (m/z 191)/17  $\beta$ , 21  $\beta$ -hopane (m/z 191).
- $\Sigma(C_{31}-C_{35})/C_{30}$  Hopane ratio =  $(C_{31}-C_{35})/C_{30}$  17  $\beta$ , 21  $\beta$ -hopanes (m/z 191).
- Hop-17(21)-ene/hopane ratio = hop-17(21)-ene  $(m/z \ 191)/$ 17  $\beta$ , 21  $\beta$ -hopane  $(m/z \ 191)$ .
- Isohop-13(18)-ene/hopane ratio=isohop-13(18)-ene (m/z 191)/17  $\beta$ , 21  $\beta$ -hopane (m/z 191).
- Gammacerane index = gammacerane  $(m/z \ 191)/(17 \beta, 21 \beta +17 \beta, 21 \alpha +17 \alpha, 21 \beta -)$ hopanes  $(m/z \ 191)$ .
- Gammacerane/n-alkane ratio=gammacerane  $(m/z 191)/C_{14}-C_{35}$  n-alkanes (m/z 99).
- Gammacer-2-ene/gammacerane ratio=gammacer-2ene  $(m/z \ 191)$ /gammacerane  $(m/z \ 191)$ .
- $\beta \alpha \alpha / \alpha \alpha \alpha C_{29}$  Sterane ratio = 5  $\beta / 5 \alpha 14 \alpha$ , 17  $\alpha$ , 20 R-C<sub>29</sub> steranes (m/z 217).
- 20 S/20 R C<sub>28</sub> Sterane ratio = 20 S/20 R 5  $\alpha$ , 14  $\alpha$ , 17  $\alpha$ -C<sub>28</sub> steranes (m/z 217).
- 20 S/20 R C<sub>29</sub> Sterane ratio = 20 S/20 R 5  $\alpha$ , 14  $\alpha$ , 17  $\alpha$ -C<sub>29</sub> steranes (m/z 217).
- C<sub>n</sub> Sterane (%)=C<sub>n</sub>/C<sub>27</sub>-C<sub>29</sub> 5  $\alpha$ , 14  $\alpha$ , 17  $\alpha$ , 20 R-sterane (m/z 217) ×100. n=27, 28 and 29.
- $C_{27}/C_{29}$  Sterane ratio= $C_{27}/C_{29}$  5  $\alpha$ , 14  $\alpha$ , 17  $\alpha$ , 20 R-steranes (m/z 217).