Differential transportation and deposition of terrestrial biomarkers in middle Eocene fluvial to estuarine environments, Hokkaido, Japan

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Abstract

Higher plants constitute a significant portion of sedimentary organic matter in middle Eocene fluvial–floodplain–estuarine sedimentary rocks exposed in the Bibai region of central Hokkaido, Japan. The differential transportation and deposition of terrestrial biomarkers were studied in this area. The distribution of higher plant and fungal biomarkers in the Bibai non-marine sedimentary rocks was constrained by sedimentary facies and lithology. Claystones and siltstones lacking coaly fragments tended to be rich in angiosperm biomarkers, whereas coal and coaly mudstones were comparatively rich in gymnosperm biomarkers. Perylene, a possible fungal biomarker, was detected in fine-grained floodplain deposits. Facies and lithologic controls on terrestrial biomarker distribution can be attributed to the differential transportation and deposition of organic debris and degradation products derived from higher plants and fungi. Redox potential of the depositional environment is another important factor for the formation and preservation of terrestrial aromatic biomarkers. Reconstruction of land-based paleovegetation from terrestrial biomarkers in non-marine sediments requires careful consideration of the differential transportation and preservation of precursory terrestrial organic compounds.

Key words

aromatic biomarker, transportation, vegetation, diterpenoids, oleanoids, perylene

Introduction

Eocene coal-bearing strata are widely distributed between Sakhalin island, central Hokkaido, and just off the Sanriku coast (the northwest Pacific off northeast Japan) (Nishita et al., 1997; Takano and Waseda, 2003; Honda and Nishita, 2005). These strata contain coal resources as well as petroleum (oil and gas) sources. The Yufutsu oil and gas deposit in south-central Hokkaido is one of the largest petroleum deposits in Japan, producing oil and gas derived mainly from terrestrial higher plants of middle Eocene age (Nishita et al., 1997; Waseda and Nishita, 1998; Yessalina et al., 2006). Terrestrial sediments are rich in various types of higher plant biomarkers, which can provide paleoenvironmental information including clues to vegetation and climate changes on land (Simoneit, 1977; Richardson and Miller, 1982; Chaffee and Fookes, 1988; Ellis et al., 1996; Bastow et al., 2001; Bechtel et al., 2008). Biomarkers derived from fungi can also be present in sediments rich in terrestrial organic matter. Perylene, a possible fungal biomarker, is abundant in the middle Eocene terrestrial sediments from mid-latitude East Asia, suggesting a humid continental climate in which fungi flourished (Suzuki et al., 2010).

Terrestrial biomarkers have primarily been studied in sediment samples from lacustrine and marine environments, although a few studies have investigated the distribution of terrestrial biomarkers using samples from fluvial, floodplain, and paleosol deposits (e.g., Bechtel et al., 2004; Haberer et al., 2006). The distribution of terrestrial biomarkers in various sedimentary facies on land can provide information on the fractionation of terrestrial organic matter during transportation and deposition. Although an understanding of the differential transportation of terrestrial organic matter is critical for reconstructing vegetation and climatic changes on land, few studies have considered this aspect.

In the current study, we investigated the distribution of higher plant and possible fungal

biomarkers in the middle Eocene fluvial/floodplain to estuarine sedimentary rocks of the Ishikari Group exposed in the Bibai region of central Hokkaido, Japan, to understand the differential transportation and sedimentation of terrestrial biomarkers. In addition to the distribution of aromatic diterpenoids and oleanoids as biomarkers of gymnosperms and angiosperms, respectively, the distribution of perylene, a possible fungal biomarker, was examined to confirm its sedimentological origin.

2. Geologic and Stratigraphic Setting

2.1. Ishikari Group

Paleogene sedimentary rocks are widely distributed from north to south in the Ishikari sedimentary basin in central Hokkaido (Fig. 1). The Ishikari Group comprises the major stratigraphic sequence in the Ishikari sedimentary basin and was deposited during the middle to late middle Eocene (ca. 46 to 37 Ma) (Editorial Committee of Hokkaido (ed.), 1990; Tanai, 1990, 1994; Iijima, 1996). The Ishikari Group mainly consists of non-marine to littoral alternating beds of sandstone, mudstone, and coal seams. The abundant coal seams in the sedimentary basin have been exploited as the Ishikari Coal Field since the late 19th century. The Ishikari Group is divided into nine lithostratigraphic formations; in stratigraphically ascending order, these are the Noborikawa, Horokabetsu, Yubari, Wakanabe, Bibai, Akabira, Ikushunbetsu, Hiragishi, and Ashibetsu Formations (Fig. 1: Imai, 1924; Yabe and Aoki, 1924; Editorial Committee of Hokkaido (ed.), 1990). The detailed lithostratigraphy and sedimentary facies of these nine formations have been studied based on lithology, sedimentary structures, and biofacies (Takano et al., 1998; Takano and Waseda, 2003). Total thickness of the Ishikari Group is about 3000 m. According to the sequence stratigraphy, the Ishikari Group consists of third-order (4-million-year-old) depositional sequences with a combination of transgressions

and regressions resulting primarily from relative sea level changes (Takano et al., 1998; Takano and Waseda, 2003).

2.2. Bibai Formation

All sediment samples used for this study were taken from the middle Eocene Bibai Formation as exposed in the Sanbi Coal Mine, Bibai city, central Hokkaido (Figs. 1 and 2; Tanai, 1990; Takano and Waseda, 2003; Hasegawa et al., 2009). The Bibai Formation is composed of alternating beds of sandstone, siltstone, claystone, and coal seams. Major coal seams in this area developed at six horizons, numbered as No. 1 seam to No. 6 seam, in ascending order, respectively (Fig. 2). The No. 1 to No. 3 and No. 6 seams are intercalated with thick sandstones of fluvial channel origin (Figs. 2, 3B, and 3E), indicating deposition in the floodplain of a meandering river. In contrast, No. 4 and No. 5 seams are associated with several siderite nodule layers and are interbedded with siltstones and claystones with horizontal and rippled cross-laminations (Figs. 2, 3A, 3C, and 3D), suggesting deposition in a low-energy floodplain, swampy area, and/or estuarine environment.

The Bibai Formation includes two cycles of transgression and regression intervals, corresponding to third- or fourth-order sequence boundaries (Fig. 2; Takano and Waseda, 2003). Alternating beds of sandstone, mudstone, and coal in fluvial channel and floodplain deposits containing No. 1 and No. 2 seams are in the regressive interval, reflecting a change from the bay to estuary sedimentary facies of the underlying Wakanabe Formation into meandering fluvial and floodplain sedimentary facies. The sediments from the upper part of No. 2 seam to the upper part of No. 3 seam consist of thick and well-developed accretions of channel sandstones formed in braided to meandering fluvial systems. The channel sandstone in the upper part of No. 2 seam is the thickest and has a marked erosional surface, and is

therefore considered correlative with a third- or fourth-order sequence boundary. The sedimentary succession from No. 4 seam to the lower part of No. 5 seam is poor in coarse sandy layers and rich in coal seams interbedded with siltstone, claystone, and siderite nodules, suggesting deposition in a low-energy swamp, lake, or estuarine environment. The coal between No. 4 seam and the upper seam of No. 4 contains abundant pyrite, indicating a marine influence. These pyrite-rich coal seams correspond to the maximum flooding surface. Thus, the sedimentary succession from the upper part of No. 3 seam to the upper part of No. 4 seam corresponds to a transgressive interval (Fig. 2). The sedimentary succession from the upper part of No. 5 seam to No. 6 seam including the relatively thick channel sandstones suggests a transition into a meandering fluvial and floodplain environment due to the marine regression. The upper part of No. 5 seam, therefore, corresponds to a third- or fourth-order sequence boundary. The upper part of No. 6 seam is characterized by the alternation of siltstone, claystone, and coal and is overlain by the bay to estuary sedimentary facies of the Akabira Formation, suggesting the start of a marine transgression (Fig. 2).

Vitrinite reflectance (Ro) and other maturity parameters of coal seams in the study area (Amenomori et al., 1999) show comparatively immature levels prior to the main stages of oil generation: Ro = 0.44 to 0.59%, *n*-alkane CPI (C_{24} to C_{34}) = 1.5 to 1.8, and 20S/(20S + 20R) of C_{29} sterane = 0.20 to 0.35. Coals in the Bibai Formation can therefore be classified as subbituminous.

3. Materials and Methods

3.1. Samples

A total of 46 samples including claystones, siltstones, coaly mudstones, and coals of the Bibai Formation from the Sanbi Coal Mine were collected from outcrop. Depositional

environments were interpreted on the basis of lithofacies and sedimentary structures as discussed later in this paper. The rock samples were dried at room temperature, carefully cleaned with a grinder, and washed with dichloromethane/methanol (9:1) to remove contamination. The samples were then crushed and pulverized finer than 200 mesh. The powdered samples were used for elemental (C, N, and S) analysis and biomarker analysis.

3.2. Elemental Analysis

Total organic carbon (TOC), total inorganic carbon (TIC), total nitrogen (TN), and total sulfur (TS) contents were determined using an EA 3000 elemental analyzer (Euro Vector Co. Milan, Italy). The samples were weighed and placed in a silver capsule with drops of 1N HCl to remove carbonates. The sample was then dried at 120°C for 2 hours and placed in a tin capsule. TOC was determined on the carbonate-free samples. Total carbon, TN, and TS were determined on the samples that were not acid-treated. TIC was determined by difference between total carbon and TOC. L-Cystine was used as the standard. All elemental compositions in this paper are reported in dry weight. The C/N and S/C ratios in the present paper are the weight ratios of TOC to TN and TS to TOC, respectively. The errors of the analyses were ±3% for TOC and TN and ±5% for TS.

3.3. Biomarker Analysis

Each sample was extracted by ultrasonication (3 × 15 min each) with a mixture of CH_2Cl_2 and MeOH (v/v; 1/3, 1/1, and 1/0 respectively). The extracts were separated into aliphatic and aromatic hydrocarbon fractions using silica-gel column chromatography (Gel Q-23, Wako Co., Osaka, Japan). The isolated hydrocarbons were analyzed using gas chromatography (GC; Shimadzu GC-17A, Shimadzu Co., Kyoto, Japan) with a splitless

injection system, a flame ionization detector (FID), and a fused silica DB-5HT column (30 m × 0.25 mm i.d.) (J&W Scientific Inc., Folsom, CA, USA). Helium was used as the carrier gas (1.5 ml min^{-1}). The oven temperature was programmed for 2 min at 40°C, increased from 40 to 300°C at 4°C min^{-1}, and finally held for 20 min at 300°C. Gas chromatography-mass spectrometry (GC/MS) was conducted using an HP 6890 GC with a fused silica DB-5HT column (30 m × 0.25 mm i.d.) (J&W Scientific Inc., Folsom, CA, USA) and HP 5973 inert XL mass selective detector (MSD) (Hewlett-Packard, Palo Alto, CA, USA) operated at 70 eV with a mass range from m/z 50 to 550. Identification of compounds was based on comparison with mass spectral library data and data available in the literature. The same oven-temperature program was applied for the GC-MS analysis.

4. Results and Discussion

4.1. Depositional environment of the Bibai Formation

The Bibai Formation includes various types of terrestrial sedimentary rocks, ranging from fluvial to estuarine deposits. The TOC, TIC, TN, and TS elemental compositions of the samples showed significant variation (Table 1). The TOC concentration ranged from 0.94 to 79.5%. TOC concentration is primarily controlled by the abundance of coaly material. In this paper, sedimentary rock characterized by TOC concentrations >50% is considered coal, and that with concentrations <50% and >5% is considered coaly mudstone. The TN concentration generally increased with the increase in TOC concentration, ranging from 0 to 3.63%. The TS concentration ranged from 0.01 to 4.24%. The samples associated with No. 4 and No. 4 upper seams tended to be rich in sulfur, consistent with the abundant pyrite.

Coal and coaly mudstone samples from the Bibai Formation were primarily characterized by high C/N ratios (generally >10), whereas claystone and siltstone samples had

comparatively low C/N ratios (<10), with the exception of the No. 5 upper (5-u-L) and No. 3 (3-d) siltstone samples (Table 1). Marine organic matter is generally characterized by C/N ratios between 6 and 9, whereas terrestrial organic matter is generally characterized by C/N ratios >10 reflective of the generally higher C/N ratios of terrestrial higher plants (Krishnamurthy et al., 1986; Meyers and Ishiwatari, 1993). Thus, the comparatively higher C/N ratios in coal and coaly mudstone samples from the middle Eocene Bibai Formation indicate a significant organic matter contribution from terrestrial higher plants. The TOC and TN compositions are consistent with the interpreted lithology and depositional environments of sedimentary rocks from the Bibai Formation.

The Bibai rocks showed variable TS concentrations, ranging from 0 to 4.24%. The coal samples of No. 1 seam (1-a), No. 2 lower seam (2-l), No. 4 (4-2 and 4-5) seams, and the coaly mudstones of No.4 upper seams (4-uu-d to 4-uu-a) were characterized by higher TS contents >1% (Table 1). The significantly higher sulfur concentrations in No. 4 and No. 4 upper seams are consistent with the field observation that free sulfur, possibly liberated from sulfide minerals due to weathering, was often found at the surface outcrops of No. 4 seams and associated rocks. On the other hand, coal seams from No. 2, No. 3, and No. 5 seams are comparatively deficient in sulfur. TS contents of coals were generally higher than those of coaly mudstones, claystones, and siltstones. The S/C ratios of coal and coaly mudstones from the Bibai Formation were generally <0.5, with the exception of a claystone sample (4-uu-a, S/C=0.89) associated with No. 4 seam (Table 1). These S/C ratios of Bibai mudstones are close to the average S/C ratio of normal non-marine freshwater mudstones as shown in Fig. 4 (Berner, 1984; Raiswell and Berner, 1986). The S/C ratio is related to both oxic/anoxic conditions and salinity. The slightly higher S/C ratios of coaly mudstones associated with No. 4 seam suggest a brackish water and/or weakly oxic depositional environment. The pristane to

phytane ratio (pr/ph) is another geochemical indicator related to oxic/anoxic conditions in the water column and surface sediments (Powell and McKirdy, 1973; Didyk et al., 1978). All the samples from the Bibai Formation showed higher pr/ph ratios, ranging from 5.7 to 16.1 (Table 2), indicating overall oxic depositional conditions.

4.2. Distribution of higher plant biomarkers

Bibai terrigenous sedimentary rocks contained various aromatic biomarkers of gymnosperm, angiosperm, and fungal origin (Fig. 5). Aromatic diterpenoids such as simonellite, retene, and 2-methylretene that were present in many samples are typical gymnosperm-derived aromatic biomarkers (Simoneit, 1977; Ellis et al, 1996; Bastow et al., 2001). Typical angiosperm biomarkers such as trimethyl-tetrahydrochrysene, seco-oleanoid, pentamethyl-nonahydropicene, tetramethyl-octahydropicene, and trimethyl-tetrahydropicene (Spyckerelle et al., 1977; Chaffee and Fookes, 1988) were also present in many samples from the Bibai Formation. Perylene, a pentacyclic aromatic hydrocarbon, was present in significant amounts in some claystones and siltstones (Fig. 5 and Table 2). Contemporary Eocene coastal marine to non-marine sediments from the MITI Sanriku-oki borehole, also from within the Paleogene Ishikari basin, were remarkably abundant in perylene, which is suggested to be fungal in origin (Suzuki et al., 2010). However, the origin of perylene has been controversially discussed (Cameron et al., 1964; Thomson, 1971; De Riccardis et al., 1991; Wolkenstein et al., 2006; Grice et al., 2009). Cadalene and other alkylnaphthalenes were also common in most of the samples. Claystones and siltstones of the Bibai Formation tended to be rich in alkylnaphthalenes as compared to the coal. Cadalene is a diagenetic product of cadinene, which is the product of a sesquiterpenoid biosynthetic pathway and considered a generic vascular plant biomarker (Van Aarssen et al., 1990, 1992).

The distribution of higher plant biomarkers is closely related to the lithology and concentration of coaly material. Stratigraphic variation in terrestrial biomarkers in the sedimentary rocks of the Bibai Formation with S/C and pr/ph ratios is shown in Fig. 6. The relative abundances of angiosperm and gymnosperm plants were calculated using the ratio of typical biomarkers as described in the captions of Table 2 and Fig. 6. The abundance of coal seams increased in the marine transgressive interval, indicating that cycles of coastal transgression and regression played an important role in coal formation. Claystones and siltstones lacking coaly fragments tended to be rich in angiosperm biomarkers, whereas coal and coaly mudstones were comparatively rich in gymnosperm biomarkers (Figs. 5 and 6). This difference is clearly expressed in the relation between the abundance of terrestrial biomarkers and TOC content (Fig. 7). Clastic sedimentary rocks comparatively low in organic matter (TOC <5%) are characterized by higher relative abundance of angiosperm biomarkers. A higher abundance of gymnosperm biomarkers in coal and coaly mudstones is consistent with the occurrence of abundant gymnosperm fossils in the middle Eocene coals from the Ishikari sedimentary basin (Tanai, 1994).

Perylene was detected at significant levels in siltstones and claystones, similar to the distribution of angiosperm biomarkers (Fig. 6). These fine-grained sediments rich in perylene were associated with thick and coarse-grained sandstones located at stratigraphic levels 20–30 m, 40–45 m, and 80–85 m, respectively. These sandstones were deposited in meandering to braided fluvial channels. Fine-grained sediments with rippled and horizontal laminations indicate a floodplain environment, whereas similarly fine-grained sediments constituting the intercalation of coals and coaly mudstones were deposited in swamp environments. These fine-grained sediments are generally overlain by fluvial channel deposits. Perylene was relatively abundant in fine-grained floodplain deposits and rare in the organic-rich swamp

deposits. The fine-grained floodplain deposits are characterized by a S/C ratio >0.1 and a pr/ph ratio <10, suggesting a comparatively less oxic depositional environment (Fig. 6). The presence of perylene in the fine-grained floodplain deposits would be related to the depositional environment and the source of perylene.

4.3. Transportation and deposition of terrestrial biomarkers

Facies and lithological controls on the terrestrial biomarker distribution observed in the middle Eocene non-marine sedimentary environment are noteworthy. The relative abundance of angiosperm, gymnosperm, and possible fungal biomarkers in the fluvial/floodplain to estuarine sediments of the Bibai Formation showed significant lithofacies-dependent differences. As described above, fine clastic sediments low in coaly fragments tended to be rich in aromatic oleanoids (i.e., angiosperm biomarkers), whereas coal and coaly mudstones were comparatively rich in aromatic diterpenoids (i.e., gymnosperm biomarkers) (Figs. 6 and 7). The relative abundance of gymnosperm biomarkers positively correlates with TOC content.

Diterpenoid hydrocarbons such as retene and simonellite are mainly derived from gymnosperm resins (e.g., Noble et al., 1986; Simoneit, 1986; Alexander et al., 1988; Ellis et al., 1995). Natural plant resins occur as viscous and sticky exudates, interacting with the trunk, stem, and woody fragments. The Eocene Bibai coal is mainly composed of vitrinite group macerals derived from woody plant tissues (Amenomori et al., 1999). The higher relative abundance of aromatic diterpenoids in the coal and coaly mudstones coincides with the expected behavior of natural plant resins in the sedimentary environment.

In contrast, the relative abundance of oleanoids was higher in the clastic fine sediments than in the organic-rich coal and coaly mudstones, suggesting that organic matter rich in

oleanoid precursors was transported on clastic particles and/or as organic debris. Most of the samples in the present study contained oleanane-type and ursane-type triterpenoids as angiosperm biomarkers, which are derived from oxygenated triterpenoids such as β- and α-amyrins, oleanolic acids, and ursolic acids in angiosperm leaves, flowers, and fruits (Peters et al., 2005). Significant levels of oleanoid precursors in the trunk and stem have not been reported so far. Leaves, petals, and fruits rich in oleanoid precursors are easily broken down by biological and chemical degradation on and within soils. These degradation products that are rich in oleanoid precursors can be transported with soil particles and/or as organic debris by wind, rainfall, runoff, and flood. Abundant distribution of oleanoid biomarkers in fine-grained clastic sediments associated with channel and floodplain deposits is thus closely related to the origin of oleanoids.

4.4 Formation and preservation of perylene

Numerous studies indicate that perylene is formed through diagenetic alteration of natural precursors under anaerobic conditions (Orr and Grady, 1967; Aizenshtat, 1973; Hites et al., 1977; Garrigues et al., 1988; Silliman et al., 1998). A possible precursor includes perylene quinones derived from black pigments in plants, insects, fungi, and crinoids (Blumer, 1960; Cameron et al., 1964; Thomson, 1971; Britton, 1983; Hardil et al., 1989; Stierle et al., 1989; Wu et al., 1989; De Riccardis et al., 1991; Hashimoto et al., 1994; Wolkenstein et al., 2006). Recent studies of hydrogen and carbon isotope compositions of perylene in Quaternary and Paleogene sediments have strongly suggested a fungal origin for perylene (Grice et al., 2009; Suzuki et al., 2010). Floodplain deposits are mainly composed of allochthonous sediments derived from soil and highly weathered rocks. Soil is normally rich in organic

matter derived from fungi. If the major perylene precursor is derived from fungi, the detection of perylene in fine-grained sediments from floodplain depositional environments is consistent with the proposed source of perylene.

The relative abundance of perylene in Eocene terrestrial sediments from the MITI Sanriku-oki borehole is remarkably high, and perylene is often the most abundant aromatic biomarker in the aromatic hydrocarbon fraction (Suzuki et al., 2010). However, perylene in the terrestrial sediments from the Bibai Formation is less abundant compared to the gymnosperm and angiosperm biomarkers (Fig. 5 and Table 2). In the current study, perylene generally accounted for <15% of total aromatic biomarker content (Fig. 6). The pr/ph ratios of the samples from the Sanbi coal mine were generally >7, except for one sample at 5.7; many of the samples had values >10 (Table 2). In contrast, the pr/ph ratios of the Eocene estuarine to coastal marine sediments from MITI Sanriku-oki are generally <3, showing overall less oxic conditions during and after sedimentation.

Redox potential is an important factor for the formation and preservation of perylene. The different perylene abundances in the samples from outcrops of the Bibai Formation and MITI Sanriku-oki borehole could be attributable to the different overall redox potential during the early stages of diagenesis, suggesting that perylene formation proceeds more efficiently in estuarine to coastal marine settings than in floodplain environments. The aromatization of unsaturated diterpenoids and triterpenoids by oxidative dehydrogenation is critical for the formation of aromatic biomarkers in the terrestrial sedimentary environment (Otto et al., 2005; Simoneit, 2005; Charrié-Duhaut et al., 2009). Oxic/anoxic conditions are therefore also related to the abundance of aromatic biomarkers derived from angiosperm and gymnosperm plants.

4.5 Differential transportation of terrestrial biomarkers

Understanding the fractionation and selective preservation of terrestrial biomarkers during sedimentation processes is essential for the reconstruction of terrestrial paleovegetation. Terrestrial biomarkers such as diterpenoids and oleanoids were detected at significant levels in sediments deposited in lacustrine, estuarine, deltaic, and coastal environments. Hemi-pelagic sediments are generally very poor in diterpenoids and oleanoids. However, long chain *n*-alkanes derived from higher plant wax are often detected in pelagic sediments (e.g., Aizenshtat et al., 1973; Westerhausen et al.; 1993; Ratnayake et al., 2006). As noted above, diterpenoids in higher plant resins are difficult to transport far from land because their adherent nature causes them to be transported in association with phytoclasts and clastic particles. Oleanane and other angiosperm biomarkers are generally poor in the saturated hydrocarbon fraction from non-marine oils and sedimentary rocks, suggesting that oleananes in sedimentary rocks are not quantitatively related to the land plant input (Murray et al., 1994; 1997). Oleanoid compounds in fruits and leaves could be more easily degraded during transportation and deposition compared to other terrestrial biomarkers. On the other hand, long chain *n*-alkanes can be transported long distances because they are found in fine plant cuticles that are resistant to biological and chemical degradation (Eglinton and Hamilton, 1967; Baker and Hunt, 1987). Considerations of the differential transportation of biomarkers derived from C3 and C4 plants might be also necessary. C4 plants are predominantly herbaceous, whereas C3 plants are woody. Therefore, biomarkers derived from C4 plants are expected to be more dispersed than those from C3 plants. This expectation is also true for biomarkers derived from angiosperms and gymnosperms. Angiosperms are more dispersive than gymnosperms because many angiosperms, including C4 plants, are herbaceous. Understanding the differential transportation and preservation of terrestrial biomarkers during

sedimentation is critical for the reconstruction of terrestrial paleovegetation and climatic change.

The distribution of terrestrial biomarkers in the sedimentary rocks of the Bibai Formation is closely related to sedimentary facies and lithology. Clastic fine sediments poor in coaly fragments are comparatively rich in perylene and aromatic oleanoids, whereas coal and coaly mudstones are rich in aromatic diterpenoids. Facies and lithological controls on the distribution of terrestrial biomarkers can be attributed to the differential transportation and preservation of organic matter derived from higher plants and fungi as discussed above. The present study suggests that reconstruction of paleovegetation based on terrestrial biomarkers requires data set obtained from lithologically similar sedimentary rocks formed in the similar depositional environment.

5. Conclusions

The middle Eocene Bibai Formation is composed of a wide variety of non-marine sedimentary facies representing depositional environments including braided to meandering fluvial systems, floodplains, swamps, and estuarine environments. The distribution of aromatic biomarkers derived from angiosperms, gymnosperms, and fungi in the sediments of the Bibai Formation were controlled by sedimentary facies and lithology. The fine-grained sediments associated with the fluvial channel and floodplain deposits were rich in aromatic oleanoids of angiosperm origin. Aromatic diterpenoids derived from gymnosperm resins were abundant in the coals and coaly mudstones. Perylene, a possible fungal biomarker, tended to be abundant in the fine-grained floodplain deposits and scarce in the organic-rich swamp deposits. Facies and lithological controls on biomarker distribution resulted from the differential transportation and preservation of precursory organic components such as resins,

trunks, stems, leaves, petals, and fruits. The redox potential of the depositional environment is another important factor controlling the abundance of aromatic terrestrial biomarkers. Reconstruction of paleovegetation on land based on terrestrial biomarkers requires careful consideration of their fractionation during the sedimentation process.

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1

2

Figure captions

Fig. 1. Distribution of Eocene sedimentary basins and coal-bearing strata, and locations of the Sanbi Coal Mine in Bibai and the Yufutsu Oil and Gas Field, central Hokkaido (left). Generalized lithostratigraphy and depositional system of the middle Eocene Ishikari Group (right).

Fig. 2. Columnar section of the coal-bearing succession of the Bibai Formation in the Sanbi Coal Mine. Coal seams in the mine are numbered from No. 1L (No. 1 Lower) to No. 6U (No. 6 Upper) in stratigraphically ascending order. Depositional system and environment were determined by field observations.

Fig. 3. Outcrop photographs of the Bibai Formation: A) Coal-bearing succession in the Sanbi Coal Mine with coal seams and various clastic rocks such as claystone, siltstone, and channel sandstone (ss); B) No. 5U① and No. 6L seams and intercalated horizontal and lenticular channel sandstone (ss) with lateral accretion structures; C) No. 5L seam and underlying siderite nodules, which are mainly composed of siderite and dolomite; D) No. 4U① and No. 4U② seams and intercalated tuff.; E) No. 2 seam and overlying lenticular channel sandstones (ss) with coaly mudstone deposited in floodplain environment.

Fig. 4. Relationship between the concentrations of total sulfur (TS) and total organic carbon (TOC) in coals, coaly mudstones, and mudstones of the Bibai Formation. The boundary line between marine and freshwater environments follows Berner (1984).

Fig. 5. Representative total ion chromatograms (TIC) showing the distribution of perylene

and higher plant biomarkers in siltstone, claystone, and coal of the Eocene Bibai Formation. A is simonellite, B is retene, C is 2-methylretene, D is trimethyl-tetrahydrochrysene, E is perylene, F is 8, 14-seco-oleanoid, G is 2, 2, 4a, 6a, 9-pentamethyl-1, 3, 4, 5, 6, 13, 14, 14a, 14b-nonahydropicene, H is 1, 2, 4a, 9-tetramethyl-1, 2, 3, 4, 4a, 5, 6, 14b-octahydropicene, I is hexamethyl-nonahydropicene, J is 1, 2, 9-trimethyl-1, 2, 3, 4-tetrahydropicene, K is 2, 9-dimethylpicene, and L is 1, 2, 9-trimethylpicene.

Fig. 6. Stratigraphic variation in C/N ratios, S/C ratios, pristane to phytane (pr/ph) ratios, and terrestrial biomarker concentrations in coals, coaly mudstones, and mudstones of the Bibai Formation. Relative abundances of angiosperm biomarkers, gymnosperm biomarkers, and perylene were calculated by the same equations as shown in Table 2.

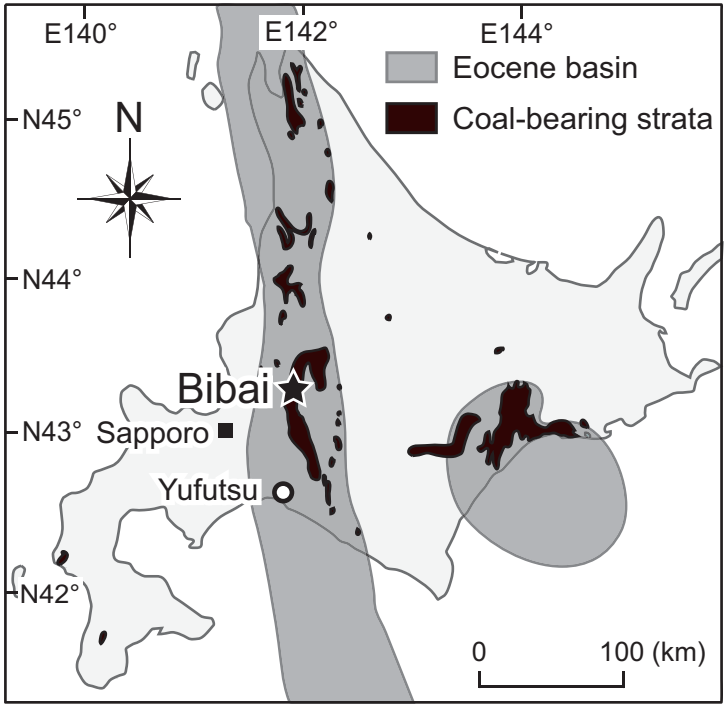
Fig. 7. Relationship between relative abundances of angiosperm biomarkers, gymnosperm biomarkers, and perylene and TOC concentrations in coals, coaly mudstones, and mudstones from the Sanbi Coal Mine. Relative abundances of angiosperm biomarkers, gymnosperm biomarkers, and perylene concentrations were calculated by the same equations as shown in Table 2.

Table Captions:

Table 1. Concentrations of total nitrogen (TN), total organic carbon (TOC), total inorganic carbon (TIC), total sulfur (TS), total sulfur/total organic carbon (S/C), total organic carbon/total nitrogen (C/N), and pristane to phytane (pr/ph) ratios for coals, coaly mudstones, and mudstones of the Bibai Formation.

Table 2. Concentrations and relative abundances of typical terrestrial biomarkers commonly present in coals, coaly mudstones, and mudstones of the Bibai Formation. Relative abundances of angiosperm biomarkers, gymnosperm biomarkers, and perylene were calculated by the following equations. Angiosperm abundance = (F+G+I+J) / {(A+B+C) + E + (F+G+I+J)}; Gymnosperm abundance = (A+B+C) / {(A+B+C) + E + (F+G+I+J)}; and perylene abundance = E / {(A+B+C) + E + (F+G+I+J)}, where A is simonellite, B is retene, C is 2-methylretene, D is trimethyl-tetrahydrochrysene, E is perylene, F is 8, 14-seco-oleanoid, G is 2, 2, 4a, 6a, 9-pentamethyl-1, 3, 4, 5, 6, 13, 14, 14a, 14b-nonahydropicene, H is 1, 2, 4a, 9-tetramethyl-1, 2, 3, 4, 4a, 5, 6, 14b-octahydropicene, I is hexamethyl-nonahydropicene, J is 1, 2, 9-trimethyl-1, 2, 3, 4-tetrahydropicene, K is 2, 9-dimethylpicene, and L is 1, 2, 9-trimethylpicene.

Fig.1 (Inoue et al.)



Geologic age		Lithostratigraphic division		Lithologic facies	Depositional system
middle Eocene	36.7 Ma (FT)	ISHIKARI Group	Ashibetsu Fm (200m)		Meandering fluvial
			Hiragishi Fm (200m)		Bay-Estuarine
			Ikushunbetsu Fm (400m)		Braided and meandering fluvial
			Akabira Fm (200m)		Bay-Estuarine
			Bibai Fm (180m)		Meandering fluvial to estuarine
	41.6 Ma (FT)		Wakanabe Fm (150m)		Bay-Estuarine
			Yubari Fm (250m)		Braided and meandering fluvial
	44.0 Ma (FT)		Horokabetsu Fm (100m)		Lacustrine
			Noborikawa Fm (250m)		Meandering fluvial

conglomerate sandstone mudstone coal

Fig.2 (Inoue et al.)

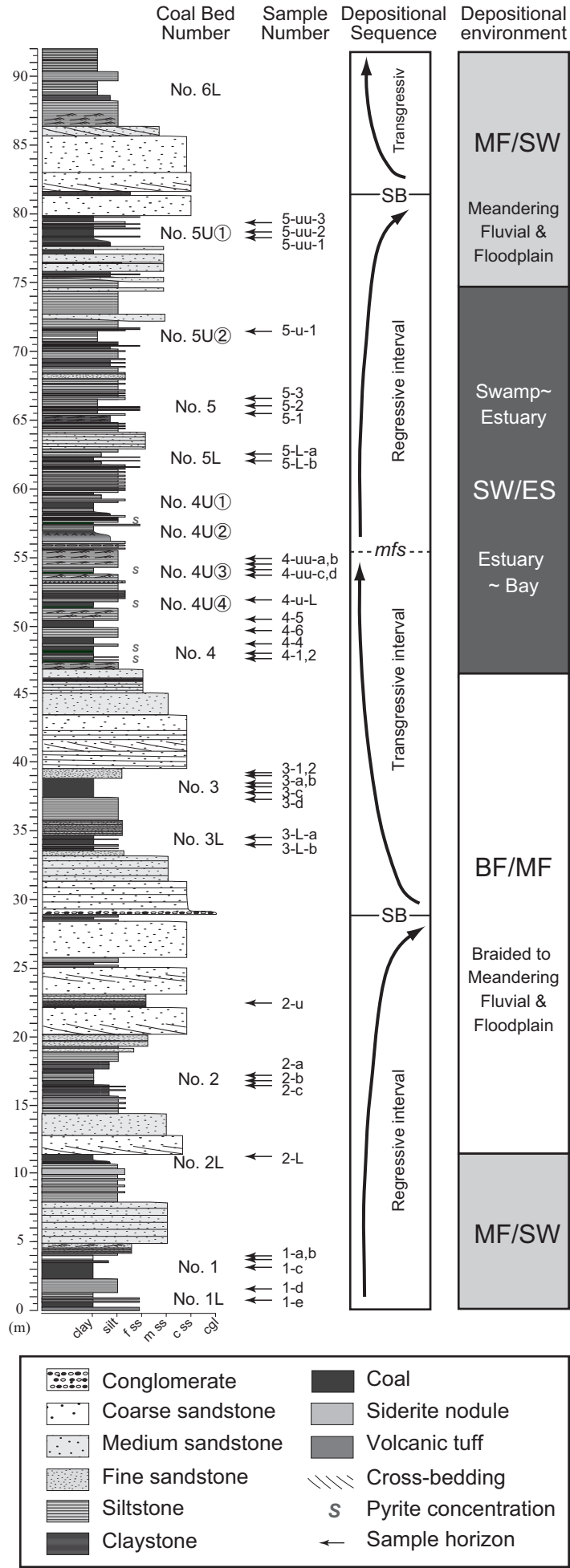
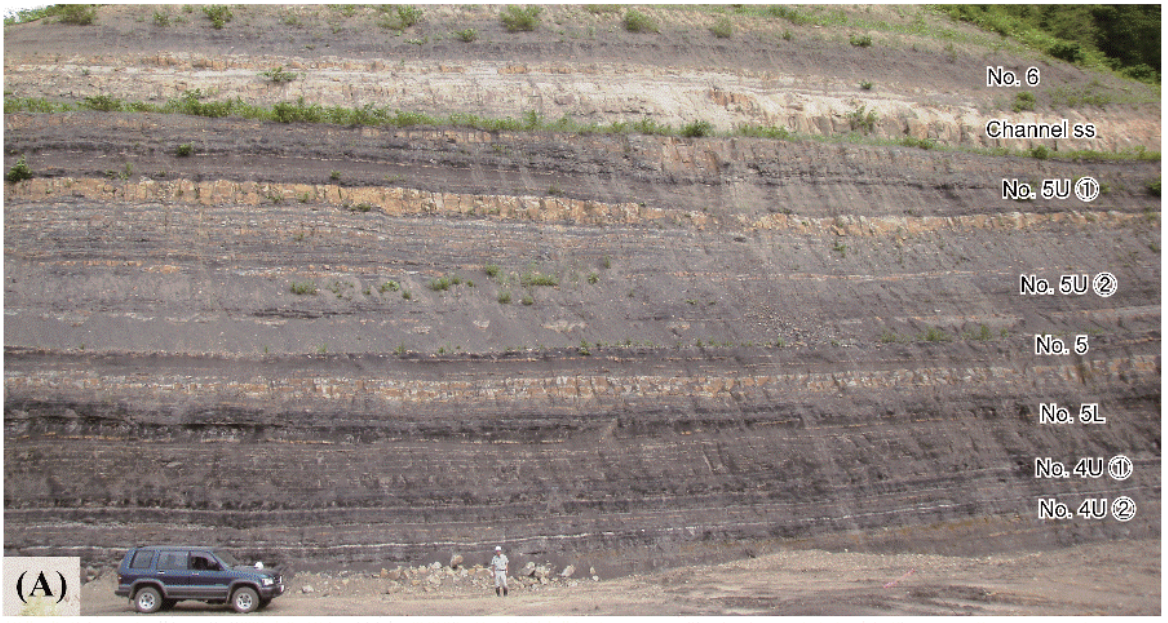
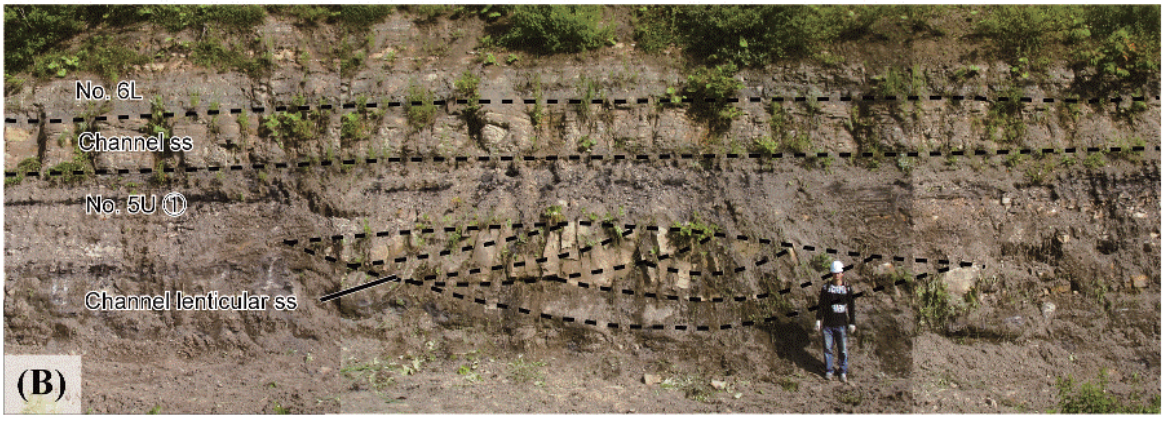
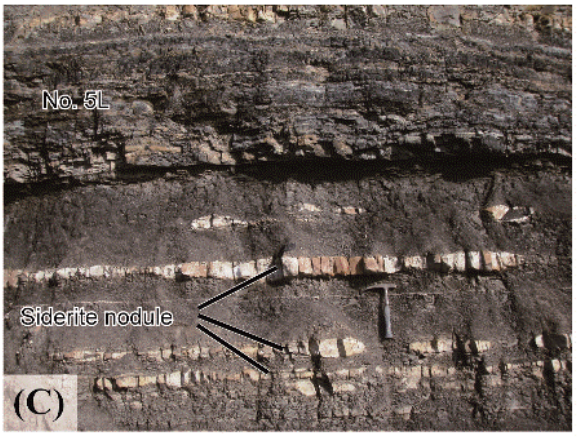
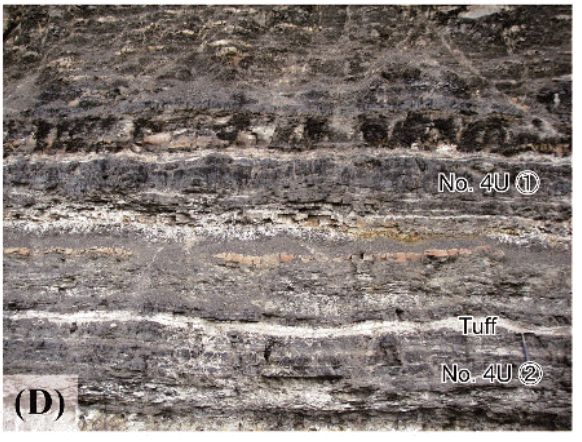


Fig.3 (Inoue et al.)









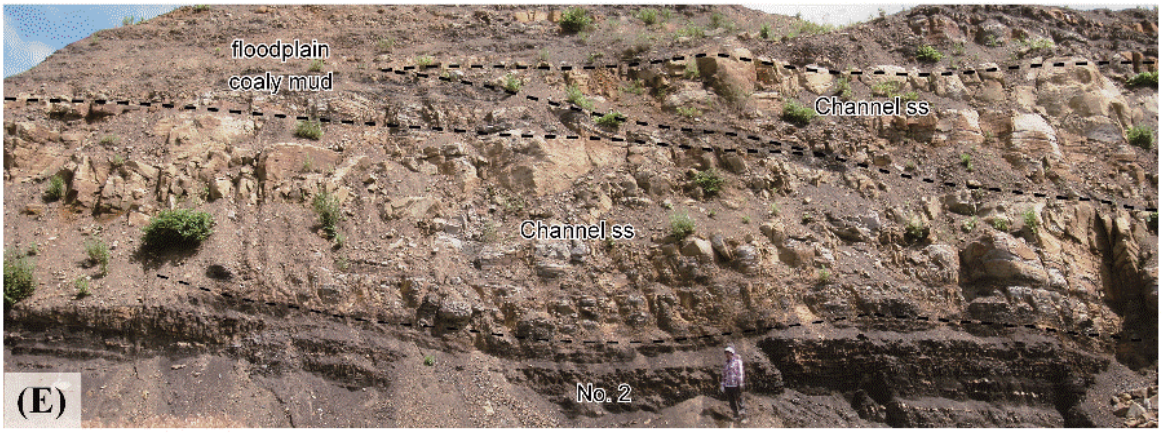


Fig.4 (Inoue et al.)

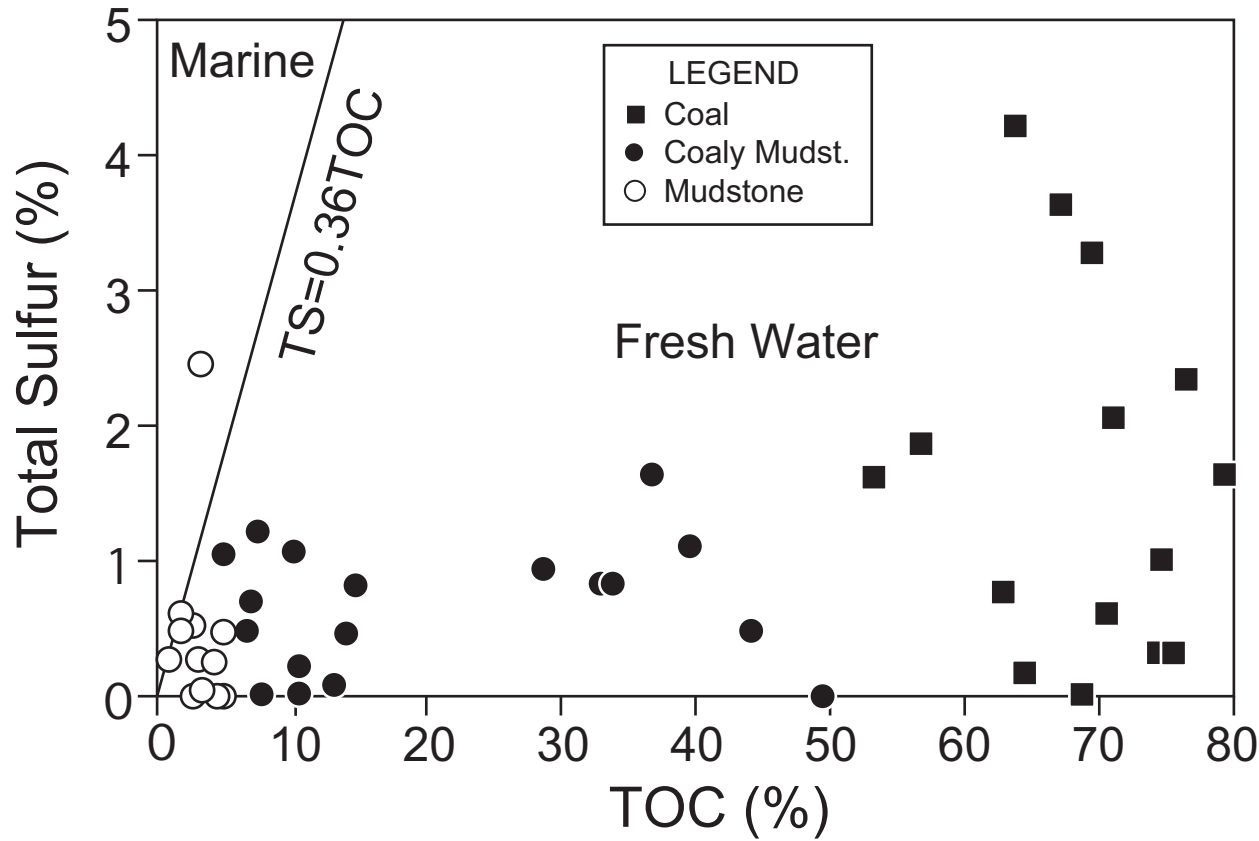


Fig. 5 (Inoue et al.)

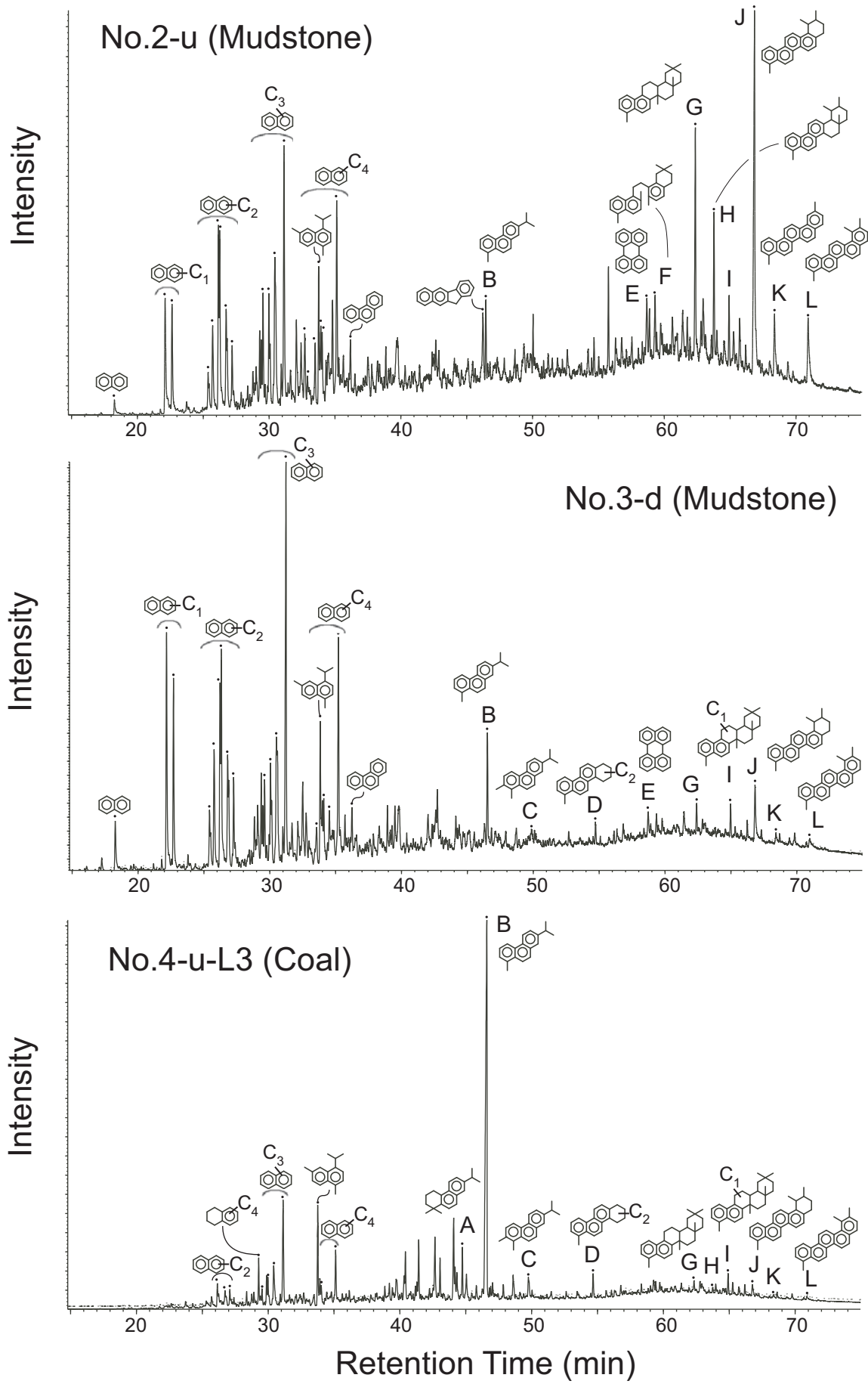


Fig.6 (Inoue et al.)

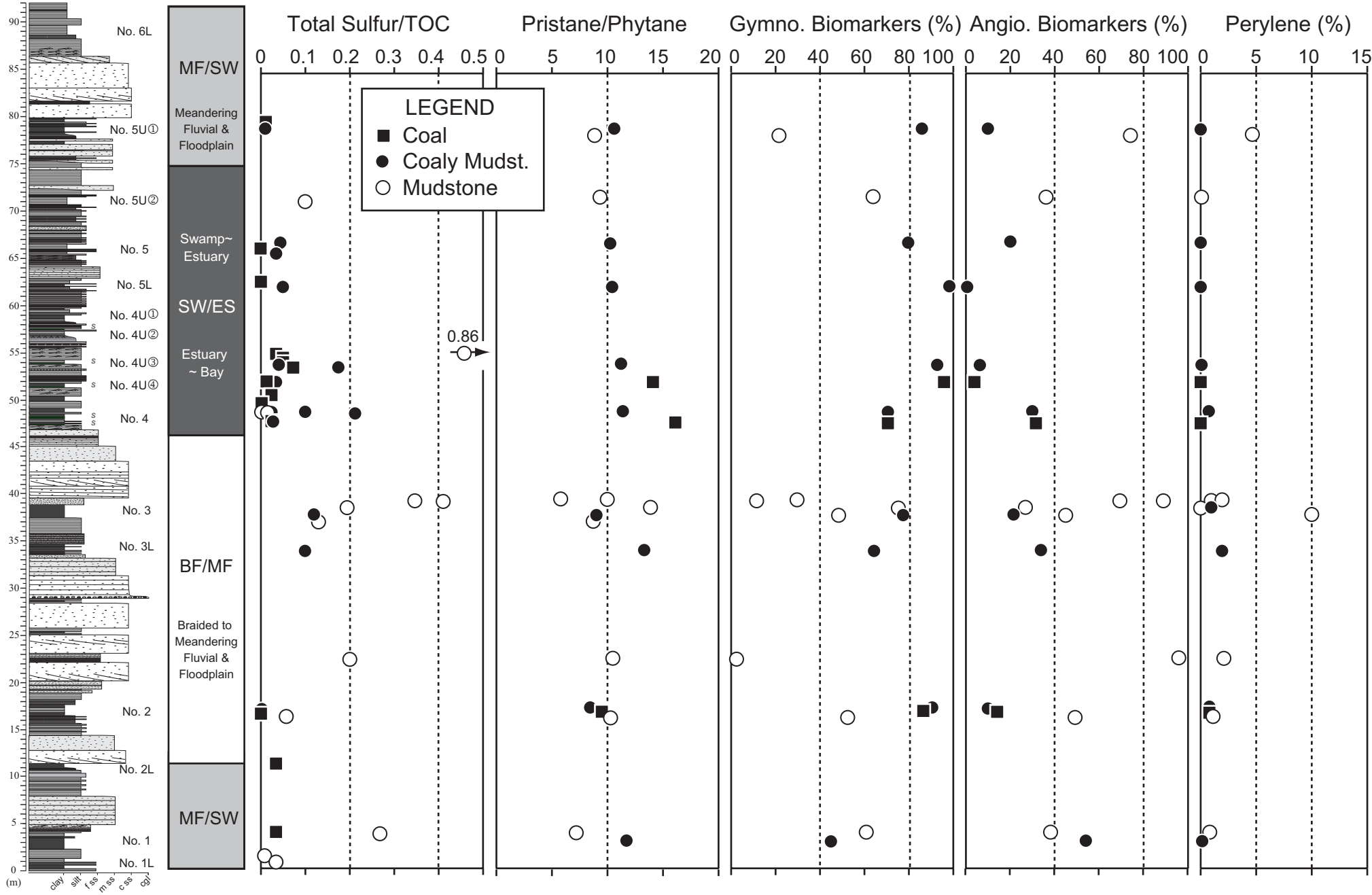


Fig. 7 (Inoue et al.)

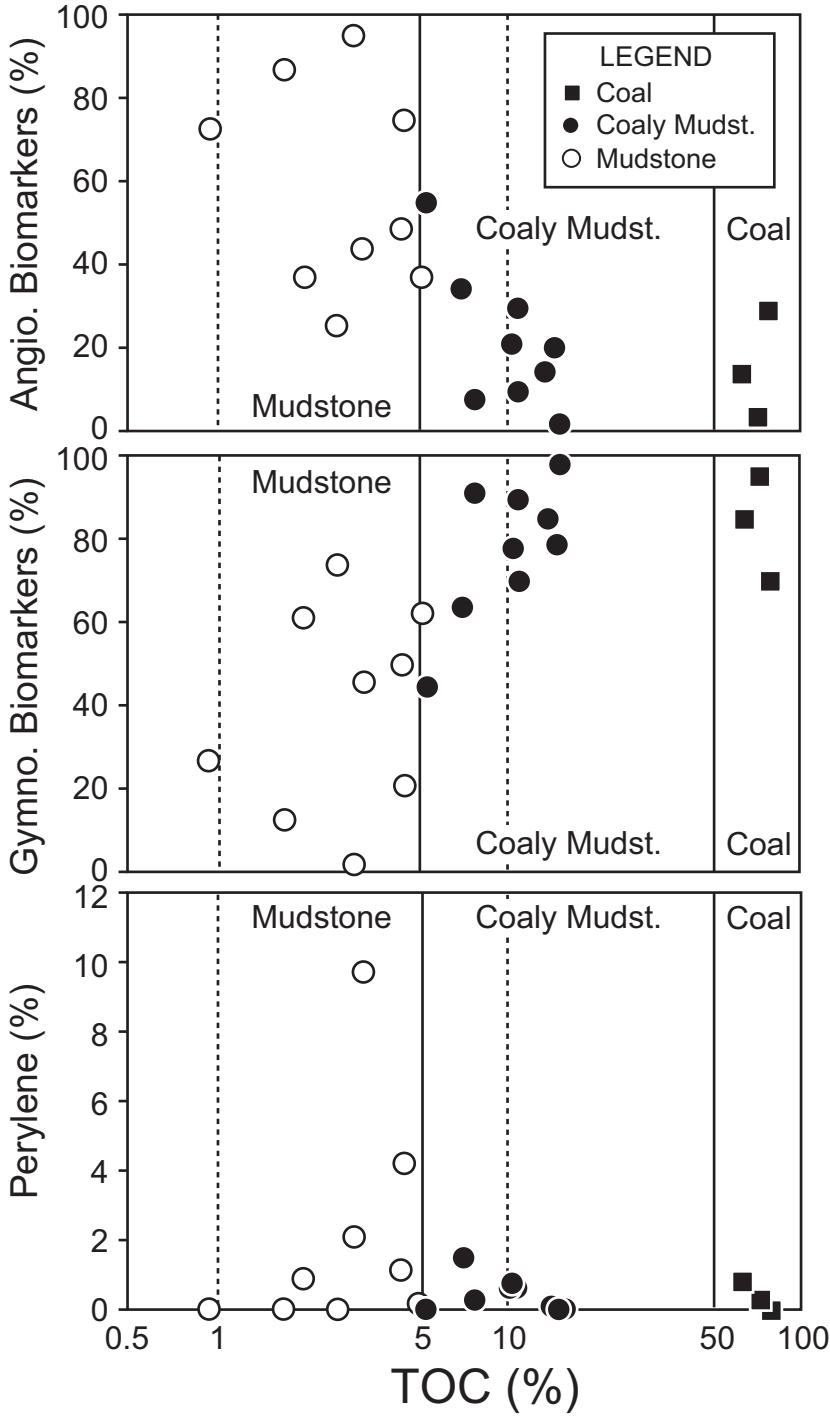


Table 1 (Inoue et al.)

Stratigraphic Level (m)	Sample Name	Lithology	TOC (%)	TIC (%)	TN (%)	TS (%)	S/C	C/N
79.75	5-uu-3	Coal	74.8	0.63	1.55	0.98	0.01	48.3
78.75	5-uu-2	Coaly Mudst.	13.4	0.00	0.33	0.07	0.01	40.6
78.5	5-uu-1	Mudstone	4.35	0.00	0.11	<0.01	0.00	39.5
71.5	5-u-L	Mudstone	5.00	0.00	0.31	0.47	0.09	16.1
66.5	5-3	Coaly Mudst.	14.3	0.00	0.52	0.47	0.03	27.5
66	5-2	Coal	75.4	0.15	1.62	0.32	0.00	46.5
65.5	5-1	Coaly Mudst.	39.7	0.00	1.30	1.12	0.03	30.5
62.5	5-L-a	Coal	64.5	0.00	1.45	0.18	0.00	44.5
62	5-L-b	Coaly Mudst.	14.9	0.67	0.67	0.82	0.06	22.2
54.75	4-uu-a	Mudstone	2.76	0.00	0.33	2.45	0.89	8.4
54.55	4-uu-b1	Coal	71.3	0.00	1.14	2.06	0.03	62.5
54.5	4-uu-b2	Coal	67.3	0.00	1.81	3.63	0.05	37.2
54.5	4-uu-b3	Coal	69.4	0.04	1.20	3.28	0.05	57.8
54.25	4-uu-c1	Coaly Mudst.	37.0	0.00	0.96	1.64	0.04	38.5
54.25	4-uu-c2	Coal	63.9	0.74	2.03	4.24	0.07	31.5
54	4-uu-d	Coaly Mudst.	7.54	0.00	0.37	1.22	0.16	20.4
51.75	4-u-L1	Coaly Mudst.	28.8	0.00	1.11	0.94	0.03	25.9
51.75	4-u-L2	Coaly Mudst.	49.6	0.00	0.96	<0.01	0.00	51.7
51.7	4-u-L3	Coal	70.7	3.68	1.76	0.61	0.01	40.2
50.25	4--5	Coal	79.5	0.00	2.20	1.64	0.02	36.1
50	4--6	Coal	74.7	0.00	1.78	0.32	0.00	42.0
49.35	4-4-1	Mudstone	2.83	0.40	0.10	0.01	0.00	28.3
49.3	4-4-2	Coaly Mudst.	5.00	0.00	0.42	1.07	0.21	11.9
49.3	4-4-3	Coaly Mudst.	10.7	1.07	0.32	0.2	0.02	33.4
49.3	4-4-4	Mudstone	3.54	0.62	0.11	0.03	0.01	32.2
49.25	4-4-5	Coaly Mudst.	7.04	0.00	0.39	0.69	0.10	18.1
49.25	4-4-6	Coaly Mudst.	7.80	0.89	0.24	<0.01	0.00	32.5
48.75	4--2	Coal	76.7	0.00	2.72	2.34	0.03	28.2
47.5	4--1	Coaly Mudst.	33.1	0.00	1.18	0.82	0.02	28.1
39.45	3--1	Mudstone	0.94	0.00	0.16	0.28	0.30	5.9
39.4	3--2	Mudstone	1.69	0.00	0.26	0.49	0.29	6.5
38.75	3-a	Mudstone	2.56	0.00	0.28	0.47	0.18	9.1
37.75	3-c	Coaly Mudst.	10.2	0.00	0.55	1.07	0.10	18.5
37.25	3-d	Mudstone	3.13	0.00	0.08	0.28	0.09	39.1
34.25	3-L-a	Coal	68.8	0.00	1.49	<0.01	0.00	46.2
33.75	3-L-b	Coaly Mudst.	6.84	0.00	0.34	0.48	0.07	20.1
22.5	2-u	Mudstone	2.92	0.00	0.29	0.5	0.17	10.1
17	2-a	Coaly Mudst.	10.6	0.00	0.32	0.02	0.00	33.1
16.5	2-b	Coal	62.9	2.73	1.79	0.76	0.01	35.1
16.25	2-c	Mudstone	4.26	0.04	0.25	0.26	0.06	17.0
11.25	2-L	Coal	56.8	0.00	1.95	1.87	0.03	29.1
3.75	1-a	Coal	53.3	0.00	1.77	1.61	0.03	30.1
3.5	1-b	Mudstone	1.96	0.30	0.33	0.62	0.32	5.9
3	1-c	Coaly Mudst.	5.19	0.00	0.17	<0.01	0.00	30.5
1.25	1-d	Coaly Mudst.	44.3	0.00	1.50	0.49	0.01	29.5
0.5	1-e	Coaly Mudst.	33.8	0.00	1.16	0.82	0.02	29.1

Table 2 (Inoue et al.)

Sample Name	Stratigraphic Level (m)	Lithology	TOC (%)	Pr/Ph	Aromatic Biomarkers (μg/gRock)									Gymno. (%)	Angio. (%)	Perylene (%)
					A	B	C	D	E	F	G	I	J			
5-uu-2	78.75	Coaly mudst.	13.4	10.6	44.5	65.5	2.68	5.47	0.15	1.66	4.18	5.34	8.15	85.3	14.6	0.1
5-uu-1	78.50	Mudstone	4.35	8.5	0.02	0.07	0.01	0.07	0.02	0.03	0.13	0.10	0.09	21.3	74.5	4.3
5-u-L	71.50	Mudstone	5.00	9.4	0.00	8.45	0.00	0.87	0.03	0.46	0.66	0.50	3.38	62.7	37.1	0.2
5-3	66.50	Coaly mudst.	14.3	10.4	1.08	15.1	0.00	2.48	0.00	0.79	1.41	0.00	1.98	79.4	20.6	0.0
5-L-b	62.00	Coaly mudst.	14.9	10.6	7.83	48.9	1.38	0.60	0.00	0.00	0.00	0.57	0.35	98.4	1.6	0.0
4-uu-d	54.00	Coaly mudst.	7.54	11.4	3.93	14.3	0.00	0.00	0.07	0.00	0.38	0.69	0.43	92.1	7.6	0.4
4-u-L3	51.70	Coal	70.7	14.0	22.6	344	0.00	8.65	1.18	7.69	0.00	7.21	0.00	95.8	3.9	0.3
4-4-3	49.30	Coaly mudst.	10.7	11.5	0.71	4.78	0.00	0.00	0.05	0.77	0.60	0.32	0.57	70.4	29.0	0.6
4-2	48.75	Coal	76.7	16.1	29.1	144	0.00	14.3	0.00	20.0	0.00	15.8	37.0	70.4	29.6	0.0
3-1	39.45	Mudstone	0.94	5.7	0.00	0.02	0.01	<0.01	<0.01	0.00	0.02	0.00	0.06	27.3	72.7	0.0
3-2	39.40	Mudstone	1.69	10.0	0.00	0.02	0.01	0.00	<0.01	0.02	0.01	<0.01	0.17	13.0	87.0	0.0
3-a	38.75	Mudstone	2.56	13.9	0.00	1.55	0.07	0.00	0.00	0.09	0.07	0.07	0.33	74.3	25.7	0.0
3-c	37.75	Coaly mudst.	10.2	8.5	0.00	15.4	0.66	0.68	0.14	3.01	0.52	0.00	0.77	78.3	21.0	0.7
3-d	37.25	Mudstone	3.13	8.1	0.00	0.18	0.01	0.03	0.04	0.00	0.04	0.04	0.10	46.3	43.9	9.8
3-L-b	33.75	Coaly mudst.	6.84	13.1	0.00	4.72	0.35	0.47	0.12	0.61	0.39	1.00	0.71	64.2	34.3	1.5
2-u	22.50	Mudstone	2.92	10.5	0.00	0.06	0.00	0.00	0.05	0.12	0.27	0.07	1.70	2.6	95.2	2.2
2-a	17.00	Coaly mudst.	10.6	7.9	0.00	34.1	0.00	0.69	0.29	0.51	0.86	1.07	1.19	89.7	9.6	0.8
2-b	16.50	Coal	62.9	9.3	0.00	126	50.9	14.0	1.74	10.2	0.00	7.04	11.4	85.4	13.8	0.8
2-c	16.25	Mudstone	4.26	10.3	0.00	0.43	0.00	0.00	0.01	0.05	0.08	0.09	0.19	50.6	48.2	1.2
1-b	3.50	Mudstone	1.96	7.3	0.00	1.75	0.24	0.60	0.03	0.24	0.00	0.00	0.97	61.6	37.5	0.9
1-c	3.00	Coaly mudst.	5.19	11.7	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.07	0.04	45.0	55.0	0.0