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Article

Evaluation of sedimentary processes of plant particles by gravity flow using biomarkers in plant fragment-concentrated sediments of a turbiditic sequence in the Miocene Kawabata Formation distributed along the Higashiyama-gawa River, Yubari, Hokkaido, Japan

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Abstract

Distinctive plant fragment-concentrated sandstones are found in a turbiditic sequence deposited under deep sea environment in the Miocene Kawabata Formation distributed along the Higashiyama-gawa River, Yubari, central Hokkaido, Japan. We observed microscopically the plant fragments and analyzed terrestrial higher plant biomarkers in the sediments to evaluate sedimentological and hydrodynamic behaviors of plant particles by gravity flow depositional processes. Biomarker compositions such as pristane / phytane and regular sterane ratios indicate a large contribution of terrestrial organic matter, especially woody fragments, in the sandstone layer. The relative abundances of terrestrial higher plant terpenoids (pentacyclic triterpenoids, des-A-triterpenoids and diterpenoids) are high in all parts of the sandstone layer, while long-chain *n*-alkane concentrations are remarkably higher only at the uppermost part. Also, leaf cuticle fragments are mainly found in the uppermost part. These results suggest that plant leaves are mainly deposited in the uppermost part of the sandstone layer. Thus, it is concluded that the variations in plant fragment types (tissues) deposited are thought to be resulted from various hydrodynamic behavior in gravity flow.

1. Introduction

Biomarker has been extensively used for reconstructing paleoclimate and paleoenvironment, and for assessing biogeochemical material-cycling and sedimentological systems representing transport of terrigenous materials in land-ocean interface from coastal to pelagic sediments. Gravity flows including turbidity and debris flows are known as main transport systems of terrigenous organic matter from land to abyssal plain (e.g. Treignier et al., 2006). The gravity flow produces sedimentary layers in which lithological and geochemical features are heterogeneous due to non-steady state deposition (Buckley and Cranstone, 1988; Meyers et al., 1996; Okano and Sawada, 2008). Sediments deposited by the gravity flow provide us multiple information for both marine and terrestrial environments because it contains the autochthonous matter derived from marine organisms and terrigenous matter transported from land areas. Also, organic geochemical studies in turbiditic sequence indicated that organic molecule (biomarker) compositions were clearly distinguishable between turbiditic and hemipelagic mudstone layers in the Bouma sequence (Okano and Sawada, 2008). Therefore, organic geochemical approach is useful for evaluating depositional system. In addition, several turbidite systems transported enormous terrestrial organic matter to the abyssal plain, so that, they are considered to be important oil and gas source rocks (Baudin et al., 2010). Thus, understanding of transport and depositional processes of terrigenous

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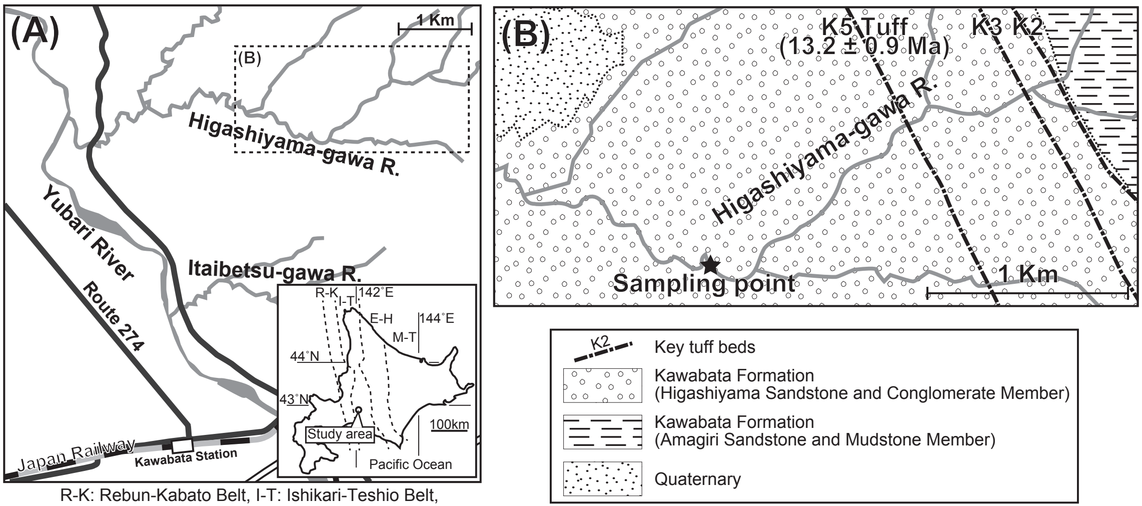

R-K: Rebun-Kabato Belt, I-T: Ishikari-Teshio Belt,
E-H: Esashi-Hidaka Belt, M-T: Monbetsu-Tokachi Belt

Fig. 1. Index map showing (A) location of the Higashiyama-gawa River of Yubari area, central Hokkaido, Japan, and (B) a sampling location in the Higashiyama-gawa River (modified from Kawakami et al., 2002).

organic matter by gravity flow will provide new insight for sedimetological study and petroleum geological exploration in deep sea systems.

Remains of terrestrial plant fragments found in deep sea sediment can be obvious evidence for efficient transport of terrigenous matter from land to abyssal plain (Nakajima, 2006; Zavala et al., 2012). Several studies focused on palynofacies analytical results of insoluble organic matter (kerogen) in turbidite sediments, and discussed the sedimentary processes associated with transport of the terrigenous matter (Omura and Hoyanagi, 2004; Sawada, 2006; Yoshida et al., 2009). Moreover, molecular geochemical approach such as biomarker analysis of turbidites in deep sea sediments have been carried out for evaluating sedimentary processes (Hoefs et al., 2002; Treignier et al., 2006; Okano and Sawada, 2008).

In this study, we found distinctive plant fragment-concentrated sediments from a turbiditic sequence in the Miocene Kawabata Formation distributed along the Higashiyama-gawa River, Yubari, central Hokkaido, Japan. We observed microscopically the plant fragments and analyzed terrestrial higher plant biomarkers in the sediments to evaluate sedimentological and hydrodynamic behaviors of plant particles by gravity flow depositional processes in the deep sea.

2. Geological setting of the Kawabata Formation

Studied area (Yubari, central Hokkaido) is located in the Neogene sedimentary basin in the Ishikari-Teshio Belt, where is characterized by N-S trending foreland basins developed along the western side of the Hidaka Mountain during the middle to late Miocene (Fig. 1; Hoyanagi, 1989; Kawakami, 2013). The Ishikari basin is filled with thick and coarse-grained sediments of the Kawabata Formation constituting a very thick turbiditic succession about 3500 m thick (Kawakami et al., 2002; Kawakami, 2013). The Kawabata Formation is subdivided into two members of the Amagiri sandstone and mudstone Member of the lower and the Higashiyama sandstone and conglomerate Member of the upper stratigraphic level. The Amagiri sandstone and mudstone Member is characterized by mudstone dominated mud-sand alternations deposited by basinal turbidite system, and the Higashiyama sandstone and conglomerate Member is characterized by sandstone dominated alternations and thick conglomerate layers deposited by slope-apron turbidite system. There are five key beds of acidic tuff (K1 - K5 tuffs), and the age of the K5 tuff in the Higashiyama Member shows an age of 13.2 ± 0.9 Ma by fission-track dating (Fig. 1; Kawakami et al., 2002). Diatom biostratigraphy suggests that a relatively mud-dominated interval above the K5 tuff bed corresponds to *Crucidenticula nicobarica* to *Denticulopsis praedimorpha* Zones (13.1 – 11.5 Ma; Kawakami et al., 2002). These results indicate the Kawabata Formation was deposited during the middle to late Miocene. Paleo-water depth of depositional environment of the Kawabata Formation is estimated to be deeper than 1000 m water depth by the presence of microfossil species inhabiting lower middle bathyal marine zone (e.g. benthic foraminifera *Uvigerina proboscidea*: Tsubakihara et al., 1990). Some of turbiditic sand layers in the Higashiyama Member contain plant fragments at their upper part, which might be corresponding to Tb - Td units of the

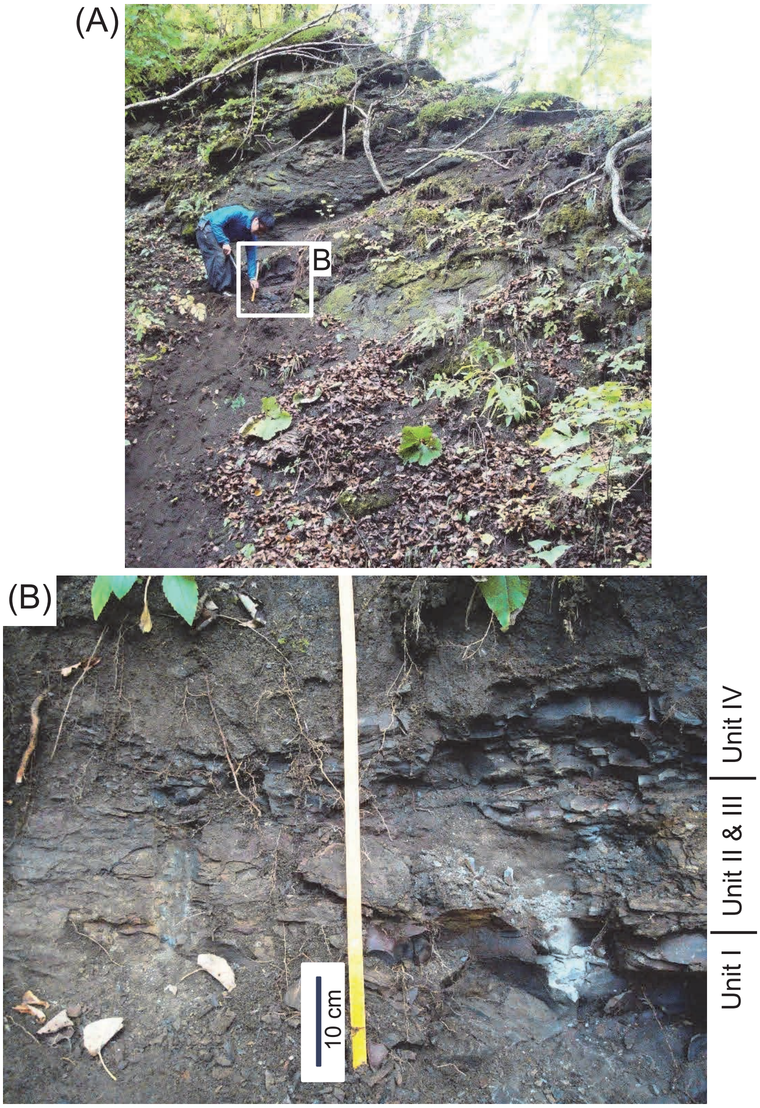

Fig. 2. The outcrop of the turbiditic sequence containing the plant fragment-concentrated (PFC) sandstone layer: (A) whole view and (B) a turbiditic sequence.

Bouma sequence (Bouma, 1962). On the other hand, a few sandstone layers contain a large amount of plant fragments in whole part of the sandstone layer, called 'plant fragment-concentrated (PFC) sandstone layer' in this study.

3. Materials and methods

3.1. Sample collection and preparation

A PFC sandstone layer is observed in the Higashiyama Member of the Kawabata Formation along the Higashiyama-gawa River (Fig. 2). The thickness of the PFC sandstone layer is about 17 cm. The depositional age of the PFC sandstone layer is estimated to be about 9 Ma based on the stratigraphic data in Kawakami et al. (2002), and a stratigraphic horizon of the layer is roughly same as a HG-21 sample in Furota et al. (unpublished data). The part of the Kawabata Formation around the HG-21 horizon (50 m below and above) is composed of mud-rich and even mud-sand alternations with intercalations of some pebbly sandstone layers. Sedimentary rock samples were collected from an outcrop (about 5 m width) in the Higashiyama-gawa River (Fig. 2). The studied interval is divided into the following four units: massive mudstone layers below and above the PFC sandstone (Units I and IV), a fine sandstone layer containing large plant fragments and mud clasts (Unit II), and a fine to very fine sandstone layer containing much minute and thin plant fragments and showing distinct fining upward grading (Unit III) (Fig. 3). The PFC sandstone layer (Units II and III) is very fine grained 17 cm thick sand layer bounded by sharp contact with underlying mudstone at its base (Units I and II) and distinct fining-upward at the uppermost part (Units III and IV; Fig. 3). Relatively large size of plant (woody) fragments and a few mud clasts are contained (concentrated) at basal to the lower part of the Unit II. Small plant fragments are abundant at middle to upper parts of the Unit II. Small and thin plant fragments appear in the Unit III. Remains of mudclast clearly indicate that the PFC sandstone layer was deposited by gravity flow sedimentary process. There are no erosional surface in the Units II and III, so that these units were deposited by the single sedimentary process.

We collected 1 to 4 samples from individual units for organic geochemical analysis. All samples were collected from 10 cm below surface of outcrop to minimize the effect of weathering. Therefore, we could collect only 3 samples from the PFC sandstone layer. Before organic geochemical analyses, whole rock samples were cleaned, and any weathered surface was removed by a penknife. The samples were then crushed to a fine powder in an agate mortar.

3.2. Grain size analysis and microscopic observation of plant fragments

Thin sections of the PFC sandstone layer were made by Faculty of Science, Hokkaido University. The thin sections are ca. 30 μm thick slice of rock attached to a glass slide with epoxy. Grain size measurement in the thin sections was performed under transmitted light microscope. Number and size distribution of grains were measured by point-counting more than 300 long-axis of grains in a given area, and the mean grain size was calculated. Observation of the type of plant fragments in the PFC sandstone layer was conducted under the transmitted light microscope and an Olympus BX41 reflected light fluorescent microscope with an Olympus ULH100HG mercury lamp, a DM4000 dichroic mirror containing a 330−385-nm excitation filter; and 420-nm-long pass barrier filter. Fluorescent light microscopic observation was mainly used to differentiate of plant fragments, because fluorescent characteristics of plant fragments are different between plant tissues (wood: no fluorescence; cuticle: strong fluorescence yellow to white color; resin: strong fluorescence orange color; Sawada et al., 2012).

3.3. Total organic carbon content

Powdered sediment samples were acidified with 3 M HCl to remove carbonate. After this treatment, these samples were dried on hot plate for 6 hours. Dry samples were analyzed for total organic carbon (TOC) content by a J-Science Micro Corder JM10 at the Instrumental Analysis Division, Equipment Management Center, Creative Research Institution, Hokkaido University.

3.4. Lipid extraction and separation

Lipids were extracted from sediment samples with dichloromethane (DCM) and methanol (MeOH) as described by Sawada et al. (1996) and Sawada (2006). Free organic molecule compounds were extracted with MeOH, MeOH / DCM (1 / 1, v / v) and DCM. d_{62}-Triacontane was added to extraction as internal standard for quantifying biomarkers. The extracts were dried in a rotary evaporator and redissolved in hexane. The hexane extract was passed through a silica gel column (95% activated), and aliphatic hydrocarbon fraction was collected. This fraction was analyzed by gas chromatography-mass spectrometry (GC-MS).

3.5. Gas chromatography-mass spectrometry (GC-MS)

Identification and quantification of the lipid fraction was carried out by GC-MS. The GC-MS was conducted with a Hewlett Packard 6890 attached to a DB-5HT column (30 m × 0.25 mm i.d., J&W Scientific) directly coupled to Hewlett Packard XL MSD quadrupole mass spectrometer (electon voltage, 70 eV; emission current, 350 μA; mass range, *m/z* 50−550 in 2.91 s). The GC oven was programmed at 4ºC / min from 50ºC (4 min) to 310ºC (held 17.50 min). Individual compound was identified on the basis of mass spectra and relative retention times in comparison with previous literature (ten Haven et al., 1992; Woolhouse et al., 1992; Logan and Eglington, 1994; Killops et al., 1995; Hautevelle et al., 2007; Jacob et al., 2007; Okano and Sawada., 2008; Nakamura et al., 2010; Sawada et al., 2013). Quantification of the compounds was made from the individual base peaks (e.g. *m/z* 57 for *n*-alkanes) determined from the authentic standards and previous literatures.

4. Results and discussion

4.1. Mean grain sizes and microscopic features of the plant fragment-concentrated sandstone layer

Mean grain sizes of the PFC sand stone layer gradually decrease from basal to middle part of the Unit II, and subsequently increase from middle to upper parts of the Unit II. These results indicate that Unit II is composed of lower fining upward layer and upper coarsening upward layer. Mean grain sizes

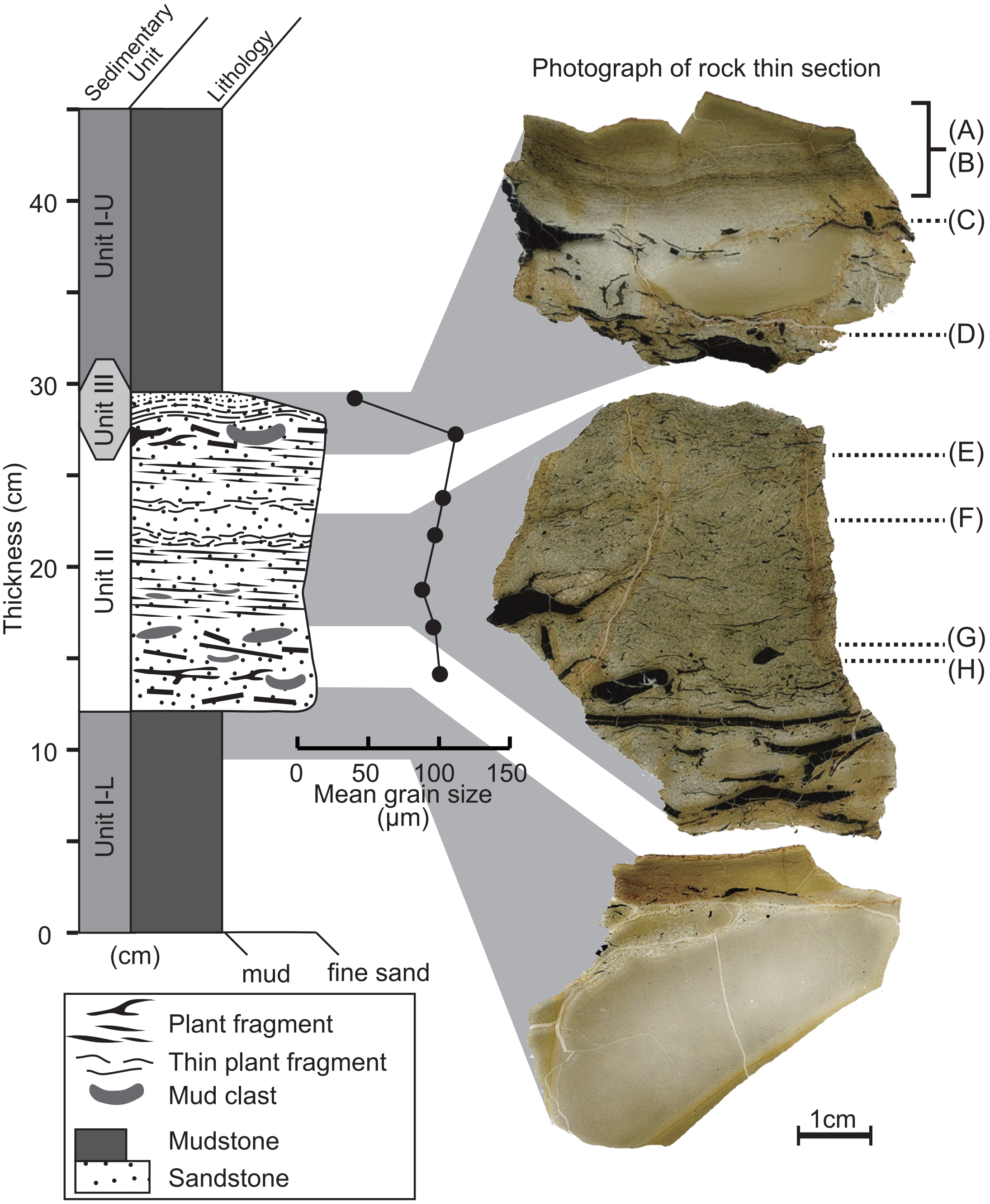

Fig. 3. Geological column and pictures of thin sections of the PFC sandstone layer from the Kawabata Formation in the Higashiyama-gawa River. Horizons of (A) to (H) are point ranges of microphotographs in Fig. 4. Mean grain sizes are also shown.

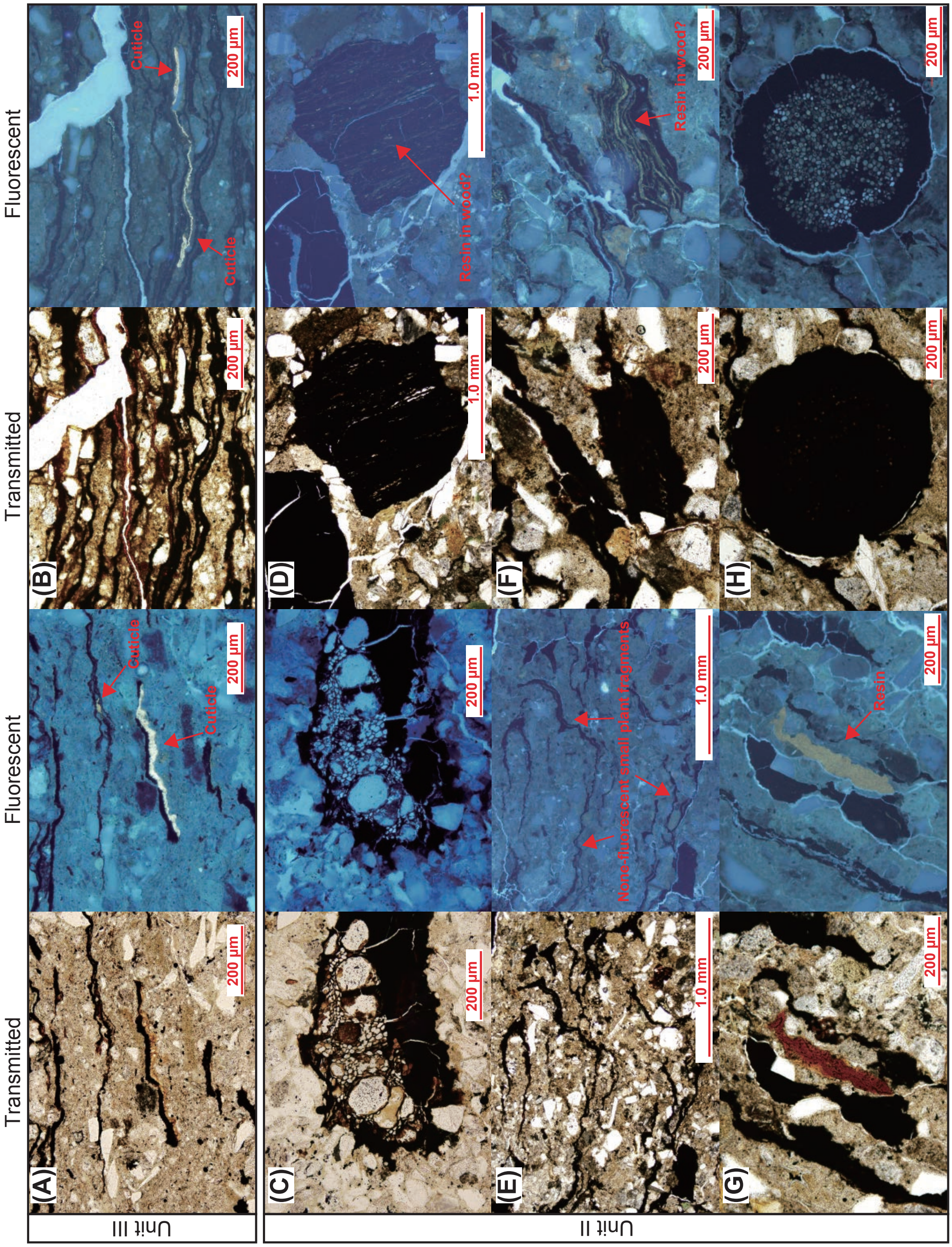

Fig. 4. Microphotographs of thin sections of Unit II (A and B) and Unit III (C to H) under the transmitted and fluorescent light microscopes; (A) - (B) leaf cuticle, (C) woody fragment (remain), (D) woody fragment including resin (weakly fluorescent vein-like structure), (E) minute and thin plant fragments without fluorescence and plant fragment with weak fluorescence (lower right; resin?), (F) woody fragment including resin(?), (G) woody fragment and resin, and (H) woody remain such as root(?).

Table 1. Data of TOC and aliphatic hydrocarbons in Unit I – IV shown in Fig. 6 and 8.

Sample	Thick-ness	TOC	Pr/Ph	Regular sterane	C_{29} Diasterene	Σ *n*-alkane ($>C_{24}$)		Σ Triterpenoid		Σ Des-A triterpenoid		Σ Diterpnenoid	
No.	cm	%		$C_{27}/(C_{27}+C_{29})$	20S/(20S+20R)	μg/g-sed	μg/g-TOC	arb.unit /g-sed	arb.unit /g-TOC	arb.unit /g-sed	arb.unit /g-TOC	arb.unit /g-sed	arb.unit /g-TOC
Unit IV-4	42.5	0.59	1.13	0.38	0.54	2.94	498.2	0.44	74.79	0.15	26.2	0.21	35.3
Unit IV-3	37.5	0.92	1.38	0.39	0.53	3.78	410.4	0.59	63.69	0.16	17.2	0.56	61.0
Unit IV-2	32.5	0.51	1.00	0.41	0.52	1.84	360.8	0.47	92.47	0.12	22.9	0.57	110.8
Unit IV-1	30	0.72	1.34	0.34	0.49	3.92	544.9	0.62	85.85	0.20	28.2	0.81	112.8
Unit III-1	29	3.21	2.43	0.11	0.45	12.60	392.7	2.31	71.97	1.22	38.1	2.51	78.2
Unit II-2	22.5	1.92	3.21	0.16	0.44	1.98	103.3	0.72	37.65	1.25	65.1	0.97	50.6
Unit II-1	19	3.71	2.45	0.06	0.42	1.60	43.2	3.21	86.40	3.86	104.1	3.90	105.1
Unit I-2	11	0.62	1.19	0.42	0.49	2.62	423.1	0.55	89.45	0.42	67.2	1.66	268.2
Unit I-1	7.5	0.56	1.07	0.42	0.48	2.24	400.0	0.36	64.69	0.26	47.0	0.98	175.1

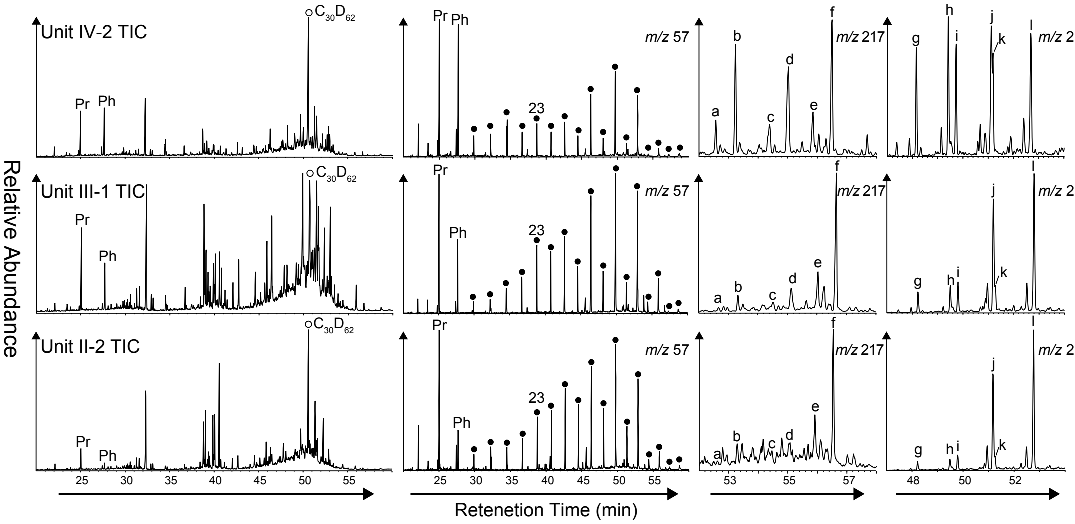

Fig. 5. Total ion chromatograms (TIC) and mass fragmentograms (MF) of *m/z* 57, 217, and 257 of the Unit II, III and IV. Open circle in TIC is internal standards (d_{62}-Triacontane). Solid circles in MF of *m/z* 57 are n-alkanes, Pr and Ph are pristane and phytane, respectively. Alphabet numbers in MF are identified as: a: 5β-cholestane; b: 5α-cholestane; c: 5β-methylcholestane; d: 5α-methylcholestane; e: 5β-ethylcholestane; f: 5α-ethylcholestane; g: C_{27} 20S-diasterene (20S-diacholest-13(17)-ene); h: C_{27} 20R-diacholestene (20S-diacholest-13(17)-ene); i: C_{28} 20S-diasterene (20S-24-methyl-diacholest-13(17)-ene); j: C_{29} 20S-diasterene (20S-24-ethyl-diacholest-13(17)-ene); k: C_{28} 20R-diasterene (20R-24-methyl-cholest-13(17)-ene); l: C_{29} 20R-diasterene (20S-24-ethyl-cholest-13(17)-ene).

sharply decrease at the Unit III, which is corresponding to distinct fining-upward grading. This distinct fining-upward grading observed in the Unit III obviously indicates that the depositional process in this unit was different from the below units, and lofted particles might be deposited from main current of gravity flow. Furthermore, this unit is thought to correspond to Tb in the Bouma sequence (Bouma, 1962).

Observation of the thin section by the transmitted and fluorescent light microscopy shows a variety of plant fragments (Fig. 4). Most of large woody fragments are opaque with sharp shape and have no fluorescence. Cell wall tissues were found to be morphologically preserved in some of these woody remains as Figs. 4C and 4H. These woody remains as Figs. 4C and 4H are thought to be tree branch and root, respectively. Besides, we identified the relatively large woody fragments that have vein-like structures, which might be formed by seeping out of resinous constituent, with weak fluorescence (Figs. 4D and 4F). Resin can be also identified (Fig. 4G). These large woody remains and fragments, and resin were found in the Unit II. On the other hand, small and thin plant fragments with strong fluorescence (Figs. 4A and 4B) are observed in the Unit III. Such plant fragments in the Unit III are presumably leaf cuticles (Sawada et al., 2012). The cuticles cannot be observed in the Unit II, but non-fluorescent small and thin plant fragments as well as minute particles, which are possibly derived from woody tissues, were found in the unit (Fig. 4E).

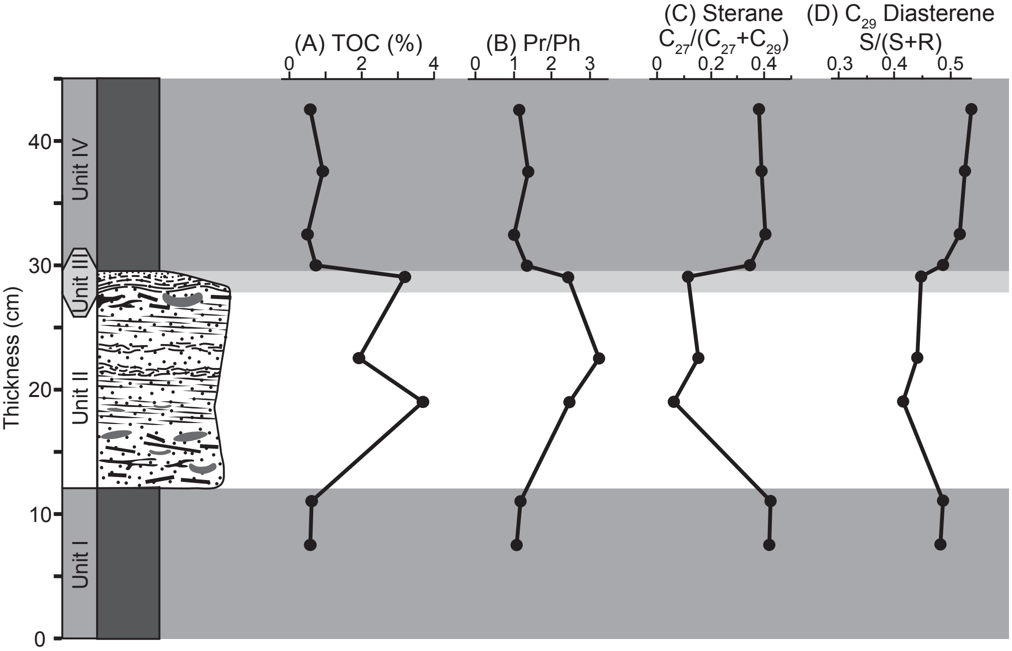

Fig. 6. Profiles of (A) total organic carbon content (TOC; %), (B) pristane/phytane (Pr/Ph) ratio, (C) regular sterane ratio ($C_{27}/[C_{27}+C_{29}]$) and (D) C_{29} diasterene isomer ratio (S/[S+R]).

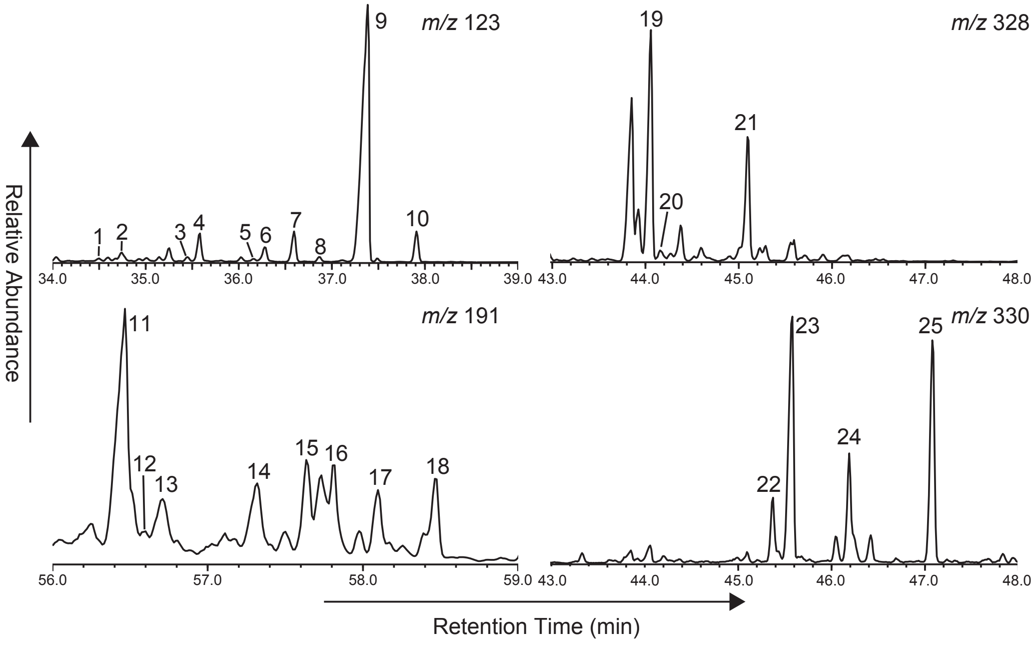

Fig. 7. Mass fragmentograms (MF) of *m/z* 123, 191, 328 and 330. Numbers shown in MF are corresponding to compounds shown in Table 2.

Table 2. Peak assignments for compounds labelled in Fig. 7.

No.	Tentative Identification	Molecular mass	Formula	Reference
	Diterpenoids			
1	8*β*-Labdane	264	$C_{20}H_{38}$	A, B
2	4*β*-19-*nor*-Isopimarane	262	$C_{19}H_{34}$	A, B
3	*nor* -Abietane	262	$C_{19}H_{34}$	A, B
4	4*α*-18-*nor*-Isopimarane	262	$C_{19}H_{34}$	A, B
5	Beyerane	274	$C_{20}H_{34}$	A, B
6	*nor*-Abietane	262	$C_{19}H_{34}$	A, B
7	Isopimarane	274	$C_{20}H_{34}$	A, B
8	16*β*-Phyllocladane	274	$C_{20}H_{34}$	A, B
9	16*α*-Phyllocladane	274	$C_{20}H_{34}$	A, B
10	16*α*-Kaurane	274	$C_{20}H_{34}$	A, B
	Triterpenoids			
11	Olean-13(18)-ene	410	$C_{30}H_{50}$	C, D
12	Olean-12-ene	410	$C_{30}H_{50}$	C, D
13	Olean-18-ene	410	$C_{30}H_{50}$	C, D
14	Urs-12-ene	410	$C_{30}H_{50}$	C
15	Lupane	412	$C_{30}H_{52}$	
	Hopanoids			
16	C_{30} 17*α*-21*β*-hopane	412	$C_{30}H_{52}$	
17	C_{30} hop-17(21)-ene	410	$C_{30}H_{50}$	
18	C_{30} 17*β*-21*β*-hopane	412	$C_{30}H_{52}$	
	Des-A-triterpenoids			
19	Des-A-olean-13(18)-ene	328	$C_{24}H_{40}$	E, F
20	Des-A-olean-12-ene	328	$C_{24}H_{40}$	E, F
21	Des-A-urs-12-ene	328	$C_{24}H_{40}$	E, F
22	Des-A-oleanane/usrane	330	$C_{24}H_{42}$	E, F
23	Des-A-lupane	330	$C_{24}H_{42}$	E, G
24	Des-A-triterpane?	330	$C_{24}H_{42}$	
25	Des-A-oleanane/ursane	330	$C_{24}H_{42}$	E, G

References: A: Nakamura et al. (2010); B: Killops et al. (1995); C: ten Haven et al. (1992); D: Okano and Sawada. (2008); E: Jacob et al. (2007); F: Logan and Eglinton (1994); G: Woolhause et al. (1992)

4.2. TOC, pristane, phytane and steroids

The TOC values range 0.5–1.0% in mudstones from the Units I and IV, while range 1.9–3.7% in sandstones from the Units II and III (Table 1; Fig. 6A). These TOC values are concordant with the distributions of plant fragments in the units.

The ratios of pristane/phytane (Pr/Ph), which is usually used as depositional redox indicator, are lower (1.0–1.4) in Units I and IV, while the ratios are higher (2.4–3.2) in Units II and III as Table 1 and Figs. 5 and 6B. High Pr/Ph ratio (>1.0) indicates oxic condition in depositional environment, while the low value (<1.0) indicates anoxic condition (Didyk et al., 1978). Also, much higher Pr/Ph value (>3.0) is caused by high contribution of terrestrial organic matter (Powell, 1988). Therefore, high Pr/Ph ratios in Units II and III are resulting from high contribution of terrestrial organic matter. On the other hand, low Pr/Ph ratios in Units I and IV suggest smaller input of terrestrial organic matter and more reductive (anoxic) condition in the sedimentary environment. Okano and Sawada (2008) has reported that biomarker data including Pr/Ph of the pelagic mudstones in a turbiditic sequence of the Kawabata Formation distributed along the Somokumaisawa-gawa River, Yubari, showed that the Miocene marine sediments in the Ishikari basin were deposited under anoxic environment. From these insights, Units I and IV were hemipelagic mudstones deposited under anoxic waters that were likely to be widely distributed in the bottom of the Ishikari basin during the deposition of the PFC sandstone (about 9 Ma).

The 20R C_{27}–C_{29} regular steranes are detected from all sediment samples, although 20S regular steranes are hardly detected (Fig. 5). Concentrations of C_{27} and C_{28} steranes are lower in the Units II and III. The C_{27} steroids are generally derived from marine phytoplankton and zooplankton, and C_{28} steroids are derived from more specific phytoplankton such as diatom (Volkman, 1986). The C_{29} steroid is commonly originated from terrestrial higher plants (Huang and Meinschein, 1979). In the present study, the ratios of regular steranes ($C_{27}/[C_{27}+C_{29}]$), which are used for estimating the contribution of terrestrial and marine organic matter, are higher and consistently constant (ca. 0.4) in Units I and IV, while the ratios are lower (ca. 0.1) in the Units II and III (Table 1 and Fig. 6C). These results indicate that the contribution of terrestrial higher plant-derived organic matter was much higher throughout the Units II and III.

We evaluated maturity of organic matter in the turbiditic sequence by C_{29} diasterene isomer ratio (S/[S+R]) (Table 1 and Fig. 6D). The diasterenes are detected from all samples, although the C_{27} and C_{28} diasterene concentrations are much lower than C_{29} diasterene concentrations in the Units II and III (Fig. 5). Therefore, we used only C_{29} diasterene isomers for calculating the isomer ratio. The diasterene isomer ratios of all sediment samples are about 0.4–0.5, which indicate that the organic matter is immature (Brassell et al., 1984). It is found that the isomer ratios in Units II and III (0.41–0.45) are significantly lower than those (0.5) in the Units I and IV (Table 1 and Fig. 6D). Thus, the terrestrial organic matters in the Units II and III may be more ‘fresh’ plant debris that was hardly affected by early diagenesis on land area. Remains of the large amount of less mature plant fragments in the Units II and III suggest efficient transport system such as hyperpycnal flow generated by large flood which transported living plants from fluvial area to abyssal plain (Mulder et al., 2001; Nakajima, 2006; Zavala et al., 2012).

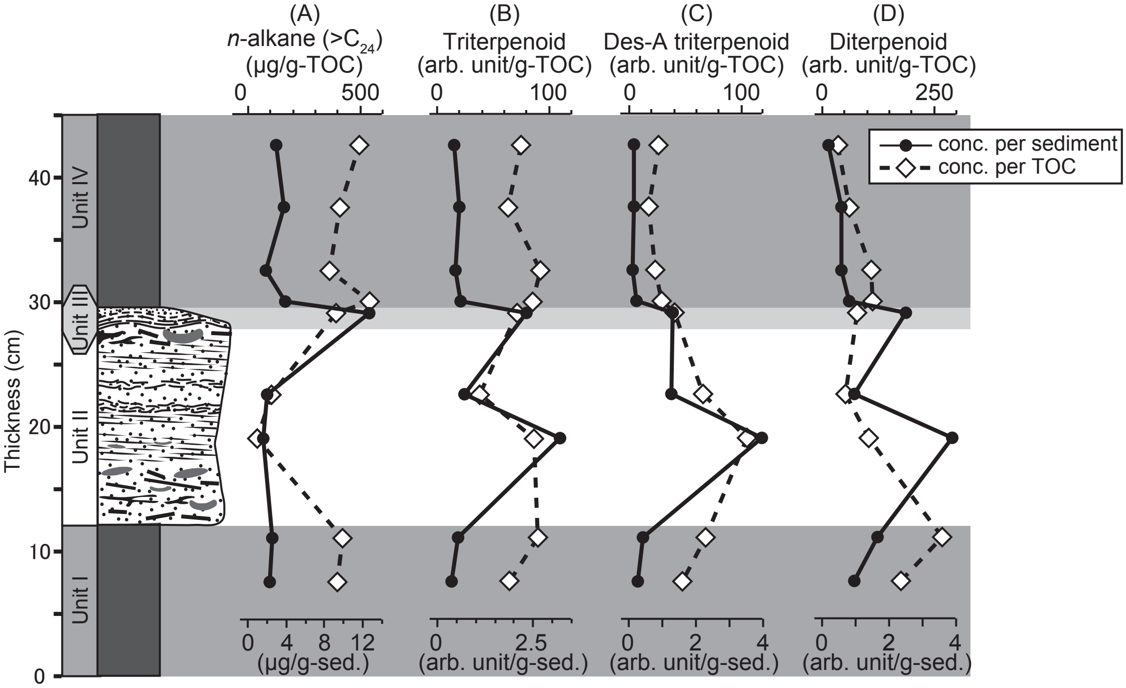

Fig. 8. Relative depth profile of concentration of (A) long-chain *n*-alkanes, (B) pentacyclic triterpenoids, (C) tetracyclic des-A-triterpenoids and (D) diterpenoids to sediment weight (solid circle) and to TOC (open diamond).

4.3. Terrestrial higher plant biomarkers

We analyzed higher plant biomarkers such as long-chain *n*-alkanes, diterpenoids, pentacyclic (normal) triterpenoids and tetracyclic des-A-triterpenoids (ring-A degraded triterpenoid). Individual terrestrial higher plant terpenoid (HPT) compounds are identified on the basis of mass spectra and relative retention times in comparison with previous literatures (Logan and Eglinton, 1994; Jacob et al., 2007; Okano and Sawada, 2008; Nakamura et al., 2010; Sawada et al., 2013), and our identification is shown in Fig. 7 and Table 2. Ten diterpenoids can be identified, and relative abundances of diterpenoids to sediment weight or to TOC are estimated based on the mass fragmentogram of *m/z* 123 (Killops et al., 1995; Nakamura et al., 2010). Diterpenoids are known as gymnosperm biomarkers, which are mainly derived from resin (e.g. Simoneit et al., 1986; Nakamura and Sawada, 2010). A peak of 16α-phyllocladane is found to be remarkably higher than the other peaks in the mass spectra (Peak No.9 in Fig. 7 and Table 2). We distinguished pentacyclic HPTs such as oleanene, ursene and lupane from bacterial hopanoids by retention time and mass fragmentogram (presence of the loss of an isopropyl group $[M-43]^+$ for hopanoids and lupane) and quantified (the relative abundances of compounds to sediment weight or to TOC) by mass fragmentogram of *m/z* 191 (ten Haven et al., 1992; Okano and Sawada, 2008), and six des-A-triterpenoids can be identified and quantified by mass fragmentogram of *m/z* 328 and 330 (Woolhause et al., 1992; Logan and Eglinton, 1994; Jacob et al., 2007). Triterpenoids are generally derived from angiosperm leaf and bark (Barker, 1982; Nakamura and Sawada, 2010), and the des-A-triterpenoids are formed from triterpenoids via biodegradation in aquatic conditions such as pond and rain forest (Trendel et al., 1989; Jaffé et al., 1996), or photochemical reaction (Simoneit et al., 2009). Peaks of des-A-oleanenes and des-A-lupane are the highest in the mass fragmentogram (Fig. 7).

Long-chain (>C_{25}) *n*-alkanes, which derived from higher plant leaves (Eglinton et al., 1962), are commonly detected in all samples (Fig. 5). Concentrations of total $C_{25}-C_{35}$ *n*-alkanes per sediment weight or TOC are about $2-12\mu g/g$ sediment or $50-550\mu g/TOC$, respectively (Table 1; Fig. 8A). The long-chain *n*-alkane concentrations per sediment weight clearly increase in the Unit III, and these values are consistently constant in other units. Also, the long-chain *n*-alkane concentrations per TOC are higher in the Units I, III and IV, while the values decrease in the Unit II. These results suggest that higher plant leaves are highly contributed only to the Unit III, although not to the Unit II despite of high TOC and low regular sterane ratio. Furthermore, it is presumed that high TOC values in the Unit III are attributed to the enormous concentration of plant leaves. On the other hand, high TOC values in Unit II may be

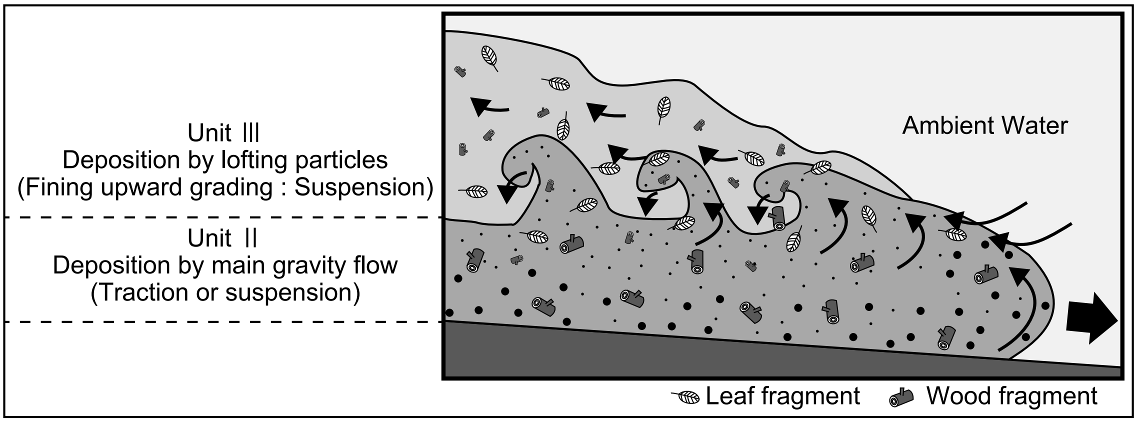

Fig. 9. Scheme for hydrodynamical behavior of terrestrial plant leaf- and woody-derived particles in gravity flow depositional system.

resulted from large contribution of wood fragments.

The relative abundances of diterpenoids to sediments are higher in the Units II and III (Fig. 8D), which is interpreted that resin preserved in gymnosperm wood fragments are more abundant in the plant fragment-concentrated units (Simoneit et al., 1986). Also, both relative abundances of pentacyclic- and des-A-triterpenoids to sediment are higher in the Units II and III, which indicate a large contribution of angiosperm leaves and barks in these units. However, concentrations of long-chain *n*-alkanes per sediment weight are remarkably high only in the Unit III. Thus, the plant leaves are likely to be concentrated only in this unit as mentioned above. This interpretation supports the microscopic results that plant cuticles are appeared mainly in Unit III. Low concentrations of long-chain *n*-alkanes indicate small contribution of leaf fragments to the Unit II. Thus, it is possible that the pentacyclic- and des-A-triterpenoids in this unit are originated from not angiosperm leaves but barks. Moreover, the profile of the relative abundances of diterpenoids is almost similar to those of the triterpenoids. Hence, it is presumed that the angiosperm and gymnosperm barks as well as wood fragments were deposited through the same sedimentary processes. In addition to these results, concentrations of diterpenoids to TOC in the Unit I are higher than those of the Unit IV. This difference may be attributed to the depositional process(es) between these units. Higher diterpenoid concentrations reflect large contribution of gymnosperm wood and bark fragments. Another assumption is that the Unit I was deposited under the influence of large flood that finally generated hyperpycnal flow.

4.4. Sedimentary processes of plant fragment-concentrated sandstone

Data of terrestrial higher plant biomarkers such as long-chain *n*-alkanes and HPTs in our study indicate that types (tissues) of plant fragments in the PFC sand stone layer are distinct between the Units II and III. The distinction is presumably resulted from different hydrodynamical behavior between plant tissues in the gravity flow depositional processes. Specific gravity of plant leaves is lighter than that of woody fragments, and moreover, the plant leaf fragments are more breakable in physical property than wood fragment. Therefore, the leaves tend to be more easily broken to small particles by physical damage during transport processes. Furthermore, leaf fragments are thin and wide, and their shapes are readily influenced by water flow turbulence. Such features lead to giving easy buoyancy of the leaves from main current of gravity flow, and it results in a redeposition from lofting plumes after the deposition by main current of gravity flow (Fig. 9). Conversely, wood fragments are relatively solid and refractory, and specific gravity of them is heavier. Such feature results in preservation of the woody fragments as large particles. Furthermore, hydrodynamical behavior of large wood fragments may be resemble to fine sand particles, so that they tend to be deposited by main current of gravity flow (Fig. 9). On the other hand, the hydrodynamic behaviors of small woody and bark fragments are thought to be similar to other small particles such as leaf fragments. High relative abundances of the HPTs such as pentacyclic- and des-A-triterpenoids as well as diterpenoids in the Unit III can be interpreted significant input of these small woody and bark fragments.

Conclusions

The TOC and biomarker analyses as well as microscopic observation are conducted on the plant fragment-concentrated (PFC) sandstones in a turbiditic sequence of the Kawabata Formation. The TOC contents and biomarker compositions such as Pr/Ph, regular sterane and HPT ratios clearly indicate a large contribution of terrigenous organic matter, especially woody fragments, in all parts of the PFC sandstone layer. However, long-chain *n*-alkane concentrations suggest significant contribution of plant leaves only at the uppermost part of the layer. This interpretation supports microscopic evidence that cuticle fragments are mainly appeared in the uppermost part. These results suggest that plant fragment types (tissues) are differentiated by distinct hydrodynamical behavior in gravity flow, and distributions of terrigenous organic matter in turbidite sediments are controlled by its sedimentological characters.

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