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Distribution of the organic matter in the channel-levees systems of the Congo mud-rich deep-sea fan (West Africa). Implication for deep offshore petroleum source rocks and global carbon cycle

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Abstract:

The quantity and the source of organic matter preserved in the Recent turbiditic channel-levees systems around 4000 m-depth off the Congo River were determined using bulk geochemical approaches (Rock-Eval, elemental and isotopic analyses) as well as molecular and optical analyses on selected samples. These mud-rich sediments contain high amount of organic matter (3% Corg on average), the origin of which is a mixture of terrestrial higher-plant debris and deeply oxidized phytoplanktonic material. Although the relative contribution of continental source versus marine source of the organic matter cannot be precisely quantified, the continental fraction appears significant (at least 70–80%) especially for such depths and distances from the coast. The organic matter distribution appears very homogeneous at different scales, from the single turbiditic event to the entire levee, and changes in accumulation rates have a little impact on the quantity and quality of preserved organic matter.

With a petroleum potential around 4.5 kg HC per t rock, the fine-grained turbiditic sediments in the Congo deep-sea system could be regarded as an analog of gas-prone source rocks for the deep offshore of the Atlantic margins. Finally, the Congo deep-sea turbiditic system is a major conveyor of organic carbon to the deep ocean. Further studies are needed to evaluate the efficiency of such systems for the storage of continental organic matter into the deep ocean in relation to sea-level and climatic changes.

Keywords: South-East Atlantic; Turbidites; Carbon isotopes; Nitrogen isotopes; Biomarkers; Source rocks

1. Introduction

With deep-water exploration for petroleum purposes becoming more intensive and successful, it is clearly important to have a better knowledge of the depositional processes of source rocks, reservoirs and seals in the deep sea. Up to now, deep-water reservoirs have received most of the attention from the scientific community whereas the source rocks have been less studied. According to conventional views, deep water settings are not suitable for source rock deposition because organic material is intensely degraded during settling through the water column. However several transport processes exist that may lead to deposition of organic-rich sediments in the deep sea, which can now be regarded as areas favourable for the occurrence of potential hydrocarbon source rocks (Huc et al., 2001; Stow et al., 2001; Saller et al., 2006). Sediment mass transport processes such as turbidity currents provide one efficient way for accumulating both terrestrial and marine organic-rich fine-grained sediments in the deep offshore.

Clay rich fine-grained turbidites are particularly well developed as levees in the deep-sea turbidite systems and are therefore also closely associated to sandy reservoirs that are turbiditic channels. These shaly facies usually act as seals in the petroleum system, but their potential as source rock is poorly known. Moreover, these facies are widely distributed from the upper slope to the distal part of the deep sea turbidite systems, in the abyssal plains, and represent huge volume of sediment in which organic matter can be preserved. The contribution of such facies to the global carbon budget is still poorly constrained.

We attempt here to quantify the organic matter preserved in the channel-levees systems from the Congo mud-rich deep-sea turbidite system as well as to determine its origin (terrestrial versus marine) in order to discuss the importance of such facies in terms of potential petroleum source rocks and their contribution for carbon storage.

2. General setting and studied sites

2.1 General setting

The Zaire/Congo River drains the second largest catchment area of the world ($3.7\ 10^6$ km², Fig. 1) and about 38% (42,800 m^3/s or 1350 km^3/year) of the yearly run-off from Africa

occurs through this river (Kinga-Mouzeo, 1986; N'Kounkou and Probst, 1987). Although the Congo River shows a small variability in its flow (22,000 to 76,500 m^3/s), floods are recorded in May and December.

The Congo River delivers yearly ~55 10^6 t of suspended sediment (Wetzel, 1993), that is 15 to 17 times lower than the Amazon River which has a drainage basin only 2 times higher and a fluid discharge of 130,000 m^3/s. This difference is attributed to the flat morphology of the catchment area of the Congo River and to the presence of several lakes through its course that trap an important part of the suspended material (N'Kounkou and Probst, 1987). Despite its relatively low sedimentary load, the Congo River contributes to 3.9% (13 10^6 t C/year) of the global annual supply of terrigenous organic carbon into the ocean (Martins and Probst, 1991). The dissolved organic carbon and particulate organic carbon near the mouth are 8.5 and 1.0 mg/L, respectively (Meybeck and Ragu, 1996; Coynel et al., 2005). Consequently, the particulate organic carbon/suspended material ratio delivered by the Congo River is high (1/20) compared to other major rivers with higher sedimentary loads, e.g. 1/50 for the Amazon River.

The freshwater outflow of the Congo River into the Atlantic Ocean is detectable by reduced salinity in a 5-10 m thick surface layer as far as 800 km offshore (van Bennekom and Berger, 1984). This freshwater outflow, rich in phosphate and nitrate, induces upwelling and two nearshore coastal cells are seasonally observed just south and north of the Congo mouth at 5 and 7° S (Fig. 1). They are considered to be produced by the piling up of eastward-flowing equatorial undercurrents as they arrive at the continental margin off Congo and Gabon (Voituriez and Herbland, 1981; Servain et al., 1982). As a result of oceanic or river-induced upwellings and the supply of nutrients by the Congo River, the primary productivity is high in the surface waters in that part of the Atlantic Ocean. Berger (1989) gives values of 90-125 g C/m²/year for the area off the Congo mouth and slightly higher values, between 125 and 180 g C/m²/year, for the oceanic upwelling area off Angola.

The strong influence of the river sediment load on the adjacent continental margin is evident from the existence of the Congo mud-rich deep sea turbidite system. This edifice is one of the world's largest active deep sea turbidite systems, with an area estimated to 330,000 km^2 (Savoye et al., 2000). Owing to the narrow (~50 km wide) continental shelf in front of the Congo mouth and the presence of a canyon that begins 30 km within the estuary of the

river (Fig. 1 and Fig. 2), a large part of the sediment load, including organic matter, is transported directly into the deep-sea.

The modern active canyon/channel system extends 760 km westward off the Congo-Angola margin (Fig. 2), but more than 80 inactive paleo-channels have been identified (Savoye et al., 2000; Savoye et al., 2009). The canyon/channel deeply incises the continental shelf and slope, and is very meandering (Droz et al., 1996; Savoye et al., 2000; Fig. 2). The sinuosity of the modern channel decreases downslope from high to moderate (Babonneau et al., 2002). A transition zone starts at about 3300 m-depth and links the canyon area to the channel-levees system (Babonneau et al., 2002). The channel-levees system shows an east-west trend, but abrupt changes of the direction are observed locally (Savoye et al., 2000). The slope of the channel floor decreases from 1.5 to 0.2% down channel. The channel is over-incised, with an incision depth ranging from 200 m at 3000 m-depth to 100 m at 4300 m-depth (Savoye et al., 2000).

Evidence for the occurrence of turbidity currents in the canyon/channel includes submarine cable breaks between 500 and 2300 m-depth, which were attributed to turbidity currents initiated by Congo floods (Heezen et al., 1964). During long-term monitoring along the channel using a series of moorings with currentmeters and sediment traps, several turbiditic events were recorded between 2001 and 2004 (Khripounoff et al., 2003; Vangriesheim et al., 2009). The frequency of turbiditic events is estimated of ca. 60 per century (Heezen et al., 1964), but it is not clear where those turbidity currents start and what causes them.

Turbidity currents are supposed to remain within the canyon/channel all the way down, but in the meander section the upper part of the thick turbidity currents overflows the channel flanks and built levees. Levees are evidenced by seismic surveys all along the present-day active channel. Levees are made up of overflow sedimentation of the turbidity currents on both sides of the channel with a relatively symmetrical morphology; the Coriolis force being negligible in this area given the proximity to the Equator. The lateral extent of levees decreases from 50 to 10 km down slope (Savoye et al., 2000). The presence of sediment waves has also been reported on both right-hand and left-hand levees (Droz et al. 1996; Savoye et al., 2000; Migeon et al., 2004). The frequency of overbank depositional events at the lower channel-levees system is estimated at 2 per century (Savoye et al., 2009).

To the best of our knowledge, information about the nature of organic matter from the channel-levees systems is lacking. The main objective of the present paper was to provide insight into the nature and distribution of the organic matter at different scales in the modern channel-levees system.

2.2 Studied areas

Two areas were selected along the modern active channel in the lower part of the channel-levees system (Fig. 2). Both are composed of three cores that allow study of a transect from the channel to the external part of the levees.

Transect KZAI 04-06 (Figs. 2 and 3)

This transect is located at 712 km from the apex of the canyon, following the main active channel, and is between 4000 and 4150 m-depth. The cores are located in an area where the channel is relatively straight, with a width around 1.6 km and a depth nearly 150 m (Gervais et al., 2001; Fig. 2). Lateral extension of the south levee, studied here, is around 7 km. Levees are symmetrical and show sediment waves with NW–SE orientation, i.e. approximately at 45° of the channel direction (Fig. 2; Gervais et al. 2001). One core (KZAI 06) has been collected in the channel at 4150 m-depth, one core (KZAI-05) has been collected on the proximal part of the levee at 4012 m-depth and one core (KZAI-04) has been collected on the distal part of the levee at 4047 m-depth (Fig. 3). A seismic profile (Fig. 3) shows that core KZAI 05 is close to the crest of the south levee and that core KZAI 04 is 5 km apart where seismic facies are more continuous and bedded. It should be noted that 10 km upstream of the studied area the Congo channel forms a well-developed meander (Fig. 2) that may be a subordinate source of sediments in core KZAI 05, as suggested by the orientation of the field of sediment waves connected to this meander.

Gervais et al. (2001) indicate that sediments from cores KZAI 04 (16.9 m long) and KZAI 05 (13.3 m long) are made of clayey and silty clayey sequences showing millimetric silt beds layered with millimetric to decimetric clay beds (Fig. 3). These small sequences are fining-up and correspond to Td and Te terms of the Bouma sequence or the fine-grained turbidites defined by Piper (1978). Turbiditic clay cannot easily be distinguished from hemipelagic clay. Most of the components of the sediment (quartz, micas, plant fragments, benthic foraminifers) have an allochthonous origin, whereas some diatoms and sponge

spicules constitutes a minor autochthonous component of the sediment. Both cores show the same type of sequences, although core KZAI 04 (more distant from the channel compared to core KZAI 05) shows a lower proportion of fine to medium sand fraction. This maybe reflects the lower sediment accumulation rate, which is averaged to 0.79 m/ka for core KZAI 05 to 0.44 m/ka for KZAI 04 (Gervais et al., 2001).

Sediments from core KZAI 06 (3.3 m long) are made of medium (250-500 μm) to fine (250-125 μm) homogeneous sands, containing some mud clasts and large plant debris. The 20 cm at the top of this core includes silty clays with some sandy lenses (Gervais et al., 2001).

Transect KZAI 13-15

This transect is located at 855 km from the apex of the canyon at about 4350 to 4450 m-depth (Fig. 2). The studied levees are located on the left-hand flank of a meander (1 km of curvature) and show marked sediment waves. The relief is 90 m between the channel and the crest of the levee. Crests of proximal sediment wave mimic the curvature of the meander, and then become straighter down-levee (Fig. 2).

Core KZAI 15 (1.9 m long) was collected in the channel and consists of very fine (100 μm) to very coarse (1–2 mm) sand beds with abundant scattered mud clasts (Fig. 3). Accumulation rates are very low, 0.25 m/ka according to Migeon et al. (2004), confirming that the channel is a zone of sediment bypassing and/or erosion rather than deposition.

Cores KZAI 13 (17.9 m long) and KZAI 14 (17.3 m long) were collected respectively on the downstream and upstream flank of a sediment wave (Fig. 2). Core KZAI 13 is 0.2 km downstream from core KZAI 14, the latter being located at 1 km from the axis of the channel.

Both are made of clayey and silty clayey sequences showing millimetric silt beds layered with millimetric to decimetric clay beds (Fig. 3). Accumulation rate is difficult to estimate because some inversions of the ^{14}C ages are observed in both cores (Migeon et al., 2004). Nevertheless, the average accumulation rate seems fluctuate from 6.5 m/ka in core KZAI 13 and 4.4 m/ka in core KZAI 14. Such values suggest that the mean accumulation rate of levees sharply increases from the area of transect KZAI 04-06 to this area, although the lithology of sediments does not change a lot (Dennielou and Jouanneau, in press; Savoye et al., 2009).

3. Material and methods

3.1 Samples

Three hundred and sixteen (316) samples were collected from these six cores with spacing between samples varying from 2 to 20 cm (Tab. 1). Only the first 10 m of cores KZAI 04, 05, 13 and 14 were sampled (Fig. 3).

In the laboratory, the samples were washed with deionizated water to eliminate salt that could affect pyrolysis analyses. Indeed, salt generates an artefact at the end of the S_2 peak of the Rock-Eval pyrolysis (see below), which is erroneously interpretated as a fraction of refractory organic matter coming from soils (Holtvoeth et al., 2005). Then, samples were dried in an oven at 50 °C for 24 hours before being pulverized in an agate mortar.

3.2 Methods

Grain-size of the bulk sediment was measured using a Coulter LS200 (93 channels from 0.4 μm to 2 mm).

Carbonate content was measured using a Bernard calcimeter, with an analytical precision of ± 0.2% $CaCO_3$.

Pyrolytic analyses were carried out using both an Oil Show Analyser and a Rock-Eval 6 Turbo device (Vinci Technologies), operating in free cycle mode which is devoted to Recent sediments (Espitalié et al., 1985; Lafargue et al., 1998; Béhar et al., 2001). This technique provides five fundamental parameters: S_1 (representing free and adsorbed hydrocarbons released during 3 min at 180 °C, in mg/g); S_2 (pyrolytic hydrocarbons generated from 180 to 650 °C, in mg/g); S_3 (CO_2 released during the pyrolysis phase of the analysis, in mg CO_2/g); S_4 (CO_2 released during the oxidation phase of the analysis, in mg CO_2/g); and Tmax (the temperature of maximum pyrolytic hydrocarbon yield, in °C). Hydrocarbons are detected by a flame ionization detector, and CO_2 by a thermal conductivity detector or infra-red detector.

These fundamental parameters are used to obtain derived parameters that are: TOC (Total Organic Carbon, in wt %); Hydrogen Index (HI = S_2/TOC × 100, in mg HC/g TOC); Oxygen Index (OI = S_3/TOC × 100, in mg CO_2/g TOC); and Petroleum Potential (PP = S_1+S_2, in mg HC/g or kg HC/ton of rock). The precision for the parameters is ± 0.1% for TOC, ± 1 °C for Tmax, ± 10 mg HC/g TOC for HI, ± 5 mg CO_2/g TOC for OI, and ± 1 kg/t for PP.

C/N and isotopic ratios were determined on 50 selected samples from cores KZAI 04, 05 and 13. Samples were acidified with 1N HCl to remove inorganic carbon prior to carbon isotopic measurements. Total Organic Carbon (TOC) and Total Nitrogen (TN) were measured by high temperature combustion on a Carlo Erba NC 2500. The average standard deviation of each measurement, determined by replicate of the same sample is ± 5%

Stable carbon and nitrogen isotope composition of the sedimentary organic matter was determined by on-line combustion in a Carlo Erba NC 2500 interfaced with a Isoprime isotope ratio mass-spectrometer. $^{13}C/^{12}C$ and $^{15}N/^{14}N$ are expressed by the conventional δ notation in ‰ relative to PDB and air, respectively. Analytical precision is ± 0.15 ‰ for δ^{13}Corg and ± 0.2 ‰ for $\delta^{15}N$.

Thermochemolysis was carried out on 9 samples from cores KZAI 04, 05, 13 and 15 following the procedure described by Disnar et al. (2008). Briefly, about 25 mg of dried and crushed kerogens were introduced in SVL® screw-cap glass tubes with 50 µL of standard solution (heptylbenzoic acid 21 µg/100 µL MeOH) and 100 µL tetramethyl ammonium hydroxide solution (TMAH; 25 % in MeOH). The tubes were placed open in an oven at 75 °C for 3 to 5 hours to evaporate the excess methanol, then cooled and closed under vacuum. Then they were placed vertically in a sand-bath and heated at 220 °C during 20 min. After cooling in ambient air, 1.5 mL diethylether was introduced to extract the pyrolysis products. After evaporation of the ether, the extracts were diluted in 50 or 100 µL CH_2Cl_2 and analysed by GC-MS with a Thermo-Finnigan TRACE-Polaris GCQ gas chromatograph–mass spectrometer. The gas chromatograph was fitted with an Rtx™-5Sil MS capillary column (30 m x 0.32 mm i.d., 0.25 µm film thickness) with 5 m of guard column. The GC operating conditions were as follows: temperature hold at 40 °C for 1 min, then increase from 40 to 120 °C at 30 °C/min, 120 to 300 °C at 3 °C/min with final isothermal hold at 300 °C for 30 min. The samples were injected splitless, with the injector temperature set at 280 °C. Helium was the carrier gas. The mass spectrometer was operated in the electron ionization (EI) mode at 70 eV ionization energy and scanned from 50 to 650 Daltons. Compounds were tentatively identified by comparison with library (NIST) mass spectra and relative retention times.

Forty-five samples were selected and prepared for palynofacies analysis, which is the microscopical study of all the particulate organic matter present in sediment. Neither oxidation nor ultrasonic probe was carried out during processing as all the particles were of

interest in this study and may selectively be destroyed by such procedures. The residue was directly mounted on glass microscope slides.

The classification of palynofacies has always been rather subjective (Tyson, 1995), and for this study, the following particles were identified:

- Phytoclasts: comprise all opaque and translucent land-plant debris. Different subgroups can be observed within this fraction and they were distinguished during the counting.
- Sporomorphs: comprise the land-derived pollen grains and spores.
- Fungal debris: comprise all the filamentous segmented particles and sclerotes.
- Marine algae: comprise the dinoflagellate cysts and other organic walled algae.
- Amorphous organic matter (AOM): comprise all particulate organic components that appear structureless at the scale of light microscopy.

4. Results

4.1 Organic matter distribution and characteristics in the clayey-silty facies of the levees

Grain-size determinations indicate that most of the sediment is made by clayey and silty fractions (up to 80 to 90%) with a median grain-size around 10 µm for cores KZAI 04 and 05 and 15 µm for cores KZAI 13 and 14 which are located at 1 km from the axis of the channel (Fig. 4). The sandy fraction usually represents less than 15% in cores KZAI 04 and 05 and less than 20 % in cores KZAI 13 and 14, except for various short-term spikes (30% in cores KZAI 04 and 05, 40 % in core KZAI 14 and up to 50% in core KZAI 13) which correspond to coarser turbiditic events.

Calcium carbonate contents remain generally low (<6 %, Tab. 2) with an average around 2.5 %. Thus, these sediments can be regarded as virtually devoid of carbonate.

Total Organic Carbon (TOC) contents are extremely homogeneous in the four studied cores with a value around 3% (Tab. 2). Some samples, however, are richer in organic carbon with a TOC content reaching 5.6% in core KZAI 04, whereas others show values as low as 0.1 % in core KZAI 13 (Fig. 4). These organic-lean samples correspond to the sandy turbiditic facies. Except for these rare sandy facies, no relationship appears between TOC and the granulometric characteristics of the sediment.

Hydrogen Index (HI) values fluctuate between 82 and 236 mg HC/g TOC (Tab. 2) with a mean value around 145 mg HC/g TOC in the four studied cores (Fig. 4). The HI-values are extremely constant in cores KZAI 04 and 05 and show a wider range and more abrupt fluctuations in cores KZAI 13 and 14 (Fig. 4). Nevertheless, these variations are not very important if we consider that HI-values may fluctuate from 0 to 1000 (Espitalié et al., 1985).

C/N ratios are also very homogeneous with a mean C/N ratio around 13 (range between 10.7 and 15.7). Similarly, isotopic ratios do not vary greatly with a mean δ^{13}Corg around -26 ‰ (range between -23.8 and -27.1 ‰) and a mean δ^{15}N around 5.5 ‰ (range between 5 and 6.3 ‰; Tab. 2 and Fig. 4).

Palynofacies analyses indicate that amorphous organic matter (AOM) represents almost the half of total particles (between 33 and 62% with an average around 46.5%). The AOM particles can be classified into two main subgroups. The first subgroup is composed of fluffy AOM (Fig. 5A) which is probably derived from phytoplankton. The second subgroup is represented by AOM particles with remains of phytoclasts inside (Fig. 5B). Variations in AOM aspect probably highlight the origin of the organic matter (marine versus terrestrial) but also the role of the depositional setting, i.e. the intensity of oxidation.

The structured particles consist exclusively of higher plant debris at different states of preservation. Different types can be recognized from yellow coloured cuticles or woody fibres with well preserved cellular structures (Fig. 5C) to dark-brown and gelified ligno-cellulosic debris (Fig. 5D). Ligno-cellulosic particles represent between 20 and 53% (34% on average) of total particles. Black particles with different shapes, rounded or bladed, are a subordinate group of phytoclasts and represent char or highly oxidized particles from soil (Fig. 5E). Cuticles are present at a low level (0.5 to 6%), whereas sporomorphs are rare (< 2% on average; Fig. 5F). Fungal remains are frequent and may represent few percents in some samples. Marine palynomorphs are scarce in the palynofacies.To summarize, the palynofacies analysis indicates that half of the organic matter is clearly terrestrial in origin, and part of the amorphous organic matter is also derived from higher plants.

At the scale of the bulk sediment of the levees the organic matter content appears very homogeneous, both in terms of quantity (TOC) and quality (HI, C/N and isotopic ratios, palynofacies).

4.2 Organic matter distribution and characteristics in the turbiditic beds

Using detailed lithological descriptions, X-radiographs, and grain size analyses, six types of turbiditic beds have been distinguished within the levees (Gervais et al., 2001; Migeon et al., 2004). We sampled several of these beds with a 2 cm-spacing in cores KZAI 04, 13 and 14 in order to investigate the variations of organic matter content and its quality within different types of small fining-up sequences.

Type 1-beds consist of highly bioturbated dark silty clays grading upward into grey clays, with thickness ranging from several centimeters to several decimeters (Fig. 6A and B). Dark silty clays are probably true turbidite deposits whereas grey clays are probably hemipelagic deposits, but discriminating between them is difficult (Migeon et al., 2004). In most cases, the grain size is near constant whatever the facies. The organic matter content of both the dark and grey clays is very homogeneous (3% in average), but dark clays may contain a little bit more organic matter than grey hemipelagic clays (Fig. 6B). Such beds resulted from fallout of suspended flocks and characterize dilute and low-velocity spillovers from the uppermost part of channelized turbidity currents (Migeon et al., 2004).

Type 2-beds show a basal unit with the alternation of infra-millimetric to millimetric silty laminae and millimetric to centimetric clayey laminae, and an upper unit with dark silty clays grading upward into grey clays (Fig. 6C and D). The basal contact is always sharp and beds present thickness ranging from 5 to 30 cm. The contact between the two units is gradational, the whole sequence is normally graded, and grain-size analyses display several normally graded sub-intervals. Bioturbation is always absent from the basal unit but commonly observed in the upper unit. The absence of bioturbation in the basal unit suggests rapid deposition by a single channelized turbidity current. Such type 2-beds result from the spillover of the upper muddy part and deeper parts of channelized flows, where silts are carried in suspension, and correspond to divisions Td and Te of the Bouma sequence (Gervais et al. 2001; Migeon et al., 2004). The organic matter content of such type 2-beds are usually high (3% TOC) except in the first coarser centimeters of the basal unit where lower TOC content are noted (1.5 to 2%; Fig. 6D).

Type 3-beds consist of three units: from base to top, dark silty clays 1–3 cm thick (unit 1), alternating silty and clayey laminae (unit 2), and grey clays (unit 3; Fig. 6E). All contacts between the three units are gradational. In unit 2, silty laminae first coarsen and thicken upward, then fine and thin upward. The whole bed exhibits a basal inverse grading and an upper normal grading. The basal contact is sharp or gradational. Bed-type 3 is uncommon and

its thickness varies between 10 and 20 cm (Migeon et al., 2004). Organic carbon content of such beds shows a wider range in accordance with the median grain size. As coarser the sediment as lower the organic matter content, with values as low as 0.2% in fine sands (Fig. 6E).

Type 4-beds consist of three units from base to top: a centimeter-scale silty bed passing upward to alternating silty and clayey laminae, and finally grey to beige clays (Fig. 6F). The basal silty bed is structureless, and rarely laminated or cross-laminated. The whole bed is normally graded, and the basal contact is sharp. This type 4-bed has thickness varying between 10 and 30 cm and result from processes similar to those described for deposition of type 2-beds (Migeon et al., 2004). Organic carbon content is almost constant (3 % TOC) within this type 4-beds except at the basal part of the small sequence when grain size increases (Fig. 6F).

Types 5 and 6-beds are rare, different from the classical fine-grained deposits commonly described on levees as they correspond to structureless Ta and/or laminated Tb of the Bouma sequence with maximum grain-size up to 400 μm (Migeon et al, 2004). They were not studied so far for their organic matter content.

Whatever the small changes in organic matter content within the small-scale fining-up sequences described above, they are not associated with lower HI-values. On the contrary, both HI and OI-values are rather constant (Fig. 6), which indicates a similar type of organic matter and probably a comparable preservational state of the organic particles in these different facies.

4.3 Organic matter in the sandy facies of the channel

The sandy facies from the channel have been analyzed in core KZAI 15 and only 4 samples were investigated. Even if we cannot generalize these observations, it appears that the sands contain two times less organic carbon than the clayey facies (Tab. 2). The HI-values of the sandy facies from the channel are quite comparable with that of levee facies (Tab. 2) and geochemical data indicate the same molecular proportion of terrestrial organic material and the same state of degradation compounds from lignin (see TMAH results in section 5.1 and Tab. 4). It suggests that size sorting, which explain the difference in TOC between channel and levee, did not influence the quality of particulate organic sediment. Any generalization of

these observations for the entire Congo deep-sea turbiditic system is limited because of the small number of the samples in our study.

5. Discussion

5.1 Sources of organic matter and estimation of the terrestrial organic carbon contribution

The identification and quantification of sources, whether terrestrial or marine, of organic carbon in the sediment are always difficult because several parameters influence the bulk and molecular characteristics of the preserved organic matter. In order to estimate the amount of terrestrial organic matter relative to total organic matter in the Congo deep sea fan sediments we used binary mixing models with different sets of proxies (HI, C/N ratio, δ^{13}Corg and δ^{15}N), defined as follow:

$$Fter = [(Xsample-Xmar)/(Xter-Xmar)] \times 100$$

Where Fter is the terrestrial organic carbon fraction and Xsample is depending on the proxy analysed. Xmar and Xter are the marine and terrestrial end-member values, respectively, of these proxies.

Information on the origin of organic matter can be achieved by pyrolytic measurements if the thermal evolution of organic matter is low (Espitalié et al., 1985; Peters et al., 1986). Measured Tmax values are always low (< 420°C), indicating that organic matter did not experience strong thermal maturation and therefore contains very little charcoals or recycled material from older mature rocks.

Although the type of organic matter is usually defined by the mean of elemental analysis, the Hydrogen Index (HI) parameter approximates the H/C atomic ratio, which determines the organic matter type (Tissot and Welte, 1984). According to the low range of HI values (82 to 236 mg HC/g TOC, Tab. 2), the organic matter of the studied samples could be attributed mainly to Types III to IV (Fig. 7). Type IV, however, appears as a subordinate type for some samples (Fig. 7). Type III is usually related to terrestrial higher plants debris, whereas Type IV corresponds to residual deeply altered organic matter; the origin of which is difficult to determine.

If we assume that HI value for fresh marine organic matter is around 400 mg HC/g TOC (Espitalié et al., 1985) and around 100 for the terrigeneous end-member (mixture of Types III-IV; Espitalié et al., 1985), the mean Fter value calculated in the studied cores would indicate that 85% of the organic matter is derived from the detrital source (Tab. 3). Taking into consideration the highest HI values measured on every core (Tab. 2), the terrestrial contribution drops to 67% on average (Tab. 3), which still indicates a major contribution of terrestrial organic matter to the Congo deep sea fan sediments.

The carbon isotopic composition remains also remarkably constant with a range of δ^{13}Corg between –23.8 and –27.1 ‰ (Fig. 4) and an mean-value around –26 ‰ (Tab. 2). Such values illustrate the dominant influence of organic matter inherited from plants with C3 photosynthetic pathway and are in the same range of the particulate organic matter measured in the Congo River (δ^{13}Corg = –26.7 ± 0.4 ‰, Mariotti et al., 1991; Holmes et al., 1996). If we assume that δ^{13}Corg of marine organic matter is –21 ‰ for that part of the equatorial Ocean (Tyson, 1995), and if the detritial end-member presents a mean δ^{13}Corg = –26.7 ‰ as reported by Mariotti et al. (1991), the Fter values calculated in the studied cores would indicate that 93% of the organic matter derives from the detrital source (Tab. 3). This assumption is probably not fully valid, because terrigeneous organic matter fraction is more resistant than the marine fraction. Consequently this terrigeneous input, although important, is probably overestimated.

The relationship between total N (TN) and TOC reveals an intercept that is close to the origin of the cross-plot (Fig. 8), consistent with the idea that most of the nitrogen is associated with organic matter. If we assume an organic origin for nitrogen, the C/N ratios for the studied area range between 10.7 and 15.5 (Tab. 2; Fig. 4). Such values are also indicative of a mixture of marine phytoplankton (C/N~6.7 for Redfield ratio) and terrigeneous sources, which contain lower nitrogen than marine organic matter. The almost constant average C/N ratio (~13) in the different studied cores would require that the relative proportion of these two sources remain constant.

Molar C/N ratios of samples and end members are often used in linear mixing equations to estimate the fraction of terrestrially derived organic carbon in sedimentary environments. Several authors have shown that this calculation actually yields the fraction of terrestrially derived organic nitrogen (Perdue and Koprivnjak, 2007 and references therein). Because terrestrial organic matter is relatively depleted in nitrogen, the fraction of terrestrially

derived organic carbon has been seriously and systematically underestimated by this misinterpretation of C/N mixing lines. Only the mixing equation based on N/C yields the true fraction of terrestrially derived organic carbon.

We choose N/C ratios of 0.0653 and 0.142 as end-members for terrestrial and marine sources, Xter and Xmar respectively. The Xter value chosen here is derived from the C/N ratio (15.3) reported by Mariotti et al. (1991) for suspended particulate organic matter in the load of the Congo River near its estuary, whereas the marine end-member is close to the reverse of the C/N for Redfield ratio. Taking these values, the organic matter preserved in sediments from the levees is clearly dominated by terrestrial organic matter which represents almost 85 % of the preserved organic carbon (Tab. 3).

As δ^{13}Corg and N/C ratio, the nitrogen isotopic composition of sedimentary organic matter (δ^{15}N) has the potential to provide information on the source of organic matter to the ocean (Calvert et al., 2001). δ^{15}N records the isotopic composition of the substrate (nitrate, ammonium or dinitrogen) and the fractionation between the two isotopes ^{14}N and ^{15}N that occurs during photosynthetic pathways so that δ^{15}N will depend on the relative utilisation of the nitrogen source (Altabet and François, 1994). Since nitrate and atmospheric dinitrogen have different isotopic signature (respectively ~5‰ and 0‰) and are the main sources of nitrogen respectively for marine and terrestrial plants, the nitrogen isotopic signature of marine plants and algae is heavier (>4-5‰) than for terrestrial plants (<1‰). Source identification can be complicated in oceanic sedimentary systems when bacterial denitrification occurs in oxygen-depleted waters or when dinitrogen fixation occurs in oceanic waters. However, these processes are negligible in our area off Congo (see Holmes et al., 1996). Finally, the same conclusion may be inferred from the nitrogen isotopic ratios (δ^{15}N around 5.5‰) which indicate a mixture of marine plants and C3 plants (Fig. 9). The terrestrial fraction deduced from δ^{15}N data represents around 44% of the total organic matter (Tab. 3).

This inference for a dominance of land-derived organic matter in levee facies from the Congo fan, based on low δ^{13}Corg and HI-values, is in conflict with the nitrogen isotope values which are too heavy (<15) for such a dominance. The nitrogen isotopic composition of sedimentary organic matter in the deep-sea fan of Congo must be considered with caution. In a previous study in the same area, Müller et al. (1994) and Holmes et al. (1996) reported already δ^{13}Corg typical of a mixing between terrestrial and marine plants whereas δ^{15}N values

were close to a marine end-member. In addition, higher than expected $\delta^{15}N$ values were reported in the Congo estuary (Holmes et al., 1996).

This apparent contradiction in source characterization between carbon isotopic composition, N/C ratio and Rock-Eval, in one hand, and nitrogen isotopic ratios, in other hand, is evidence that the marine organic matter contributes significantly to the organic content of these sediments. As algal marine hydrogen-rich organic matter (Type II) is oxidized, its hydrogen content decreases while its oxygen content increases, and it may take on Rock-Eval characteristics of Type III organic matter. The fact that samples having high TOC content show HI-value reaching 256 mg HC/g TOC supports this hypothesis and suggests that the algal organic matter was deeply oxidized by microbial reworking. Finally, optical investigations of palynofacies reveal high proportion of fluffy amorphous organic matter (Fig. 5A) which is usually derived from phytoplanktonic sources (Tyson, 1995). The quantification using HI-values underestimates the real contribution of the marine source to the enrichment in organic matter.

The thermochemolysis of 9 samples provides another way to estimate the terrestrial versus marine contribution to the organic matter. All chromatograms are similar to that shown on Fig. 10; the main quantitative data are given in Table 4. Compound distributions are dominated by fatty acid methyl esters (FAMEs) and lignin degradation products: vanillic and syringic acids and aldehydes, coumaric and ferulic acids, plus non lignitic pHO-benzoic acid and aldehyde. FAME distributions are dominated by even carbon numbered FA from C_{22} to C_{34}, with a mode at *n*-C_{24} (Fig. 10). These compounds are also accompanied by lower but still notable proportions of odd-numbered *n*-alkanes from C_{27} to C_{31}, with a predominance of *n*-C_{29} (Fig. 10). All these compounds are classically assumed to be typical components of higher plants, the $C20_{+}$ FAMEs and the high molecular weight *n*-alkanes being common constituents of aerial plants cuticular waxes. Relatively high proportions of syringic moieties (i.e. acid plus aldehyde) over their vanillic counterparts (S/V = 0.3-0.61; Tab. 4) reveal that lignin originates from Angiosperms, with a contribution from Gymnosperms being not to be excluded (Hedges and Mann, 1979). Rather extensive lignin alteration is revealed by the predominance of vanillic and syringic acids over the corresponding aldehydes [(Vac+Sac)/(Vald+Sald) = 1.74 to 2.56; Tab. 4), by the high contribution of acid moieties to the total lignin (Vac+Sac)/Ltot =

0.55 to 0.65; table 4) and also by very low proportions of coumaric and ferulic acids (data not shown), these two compounds originally linked to the lignin backbone by labile ester bonds being rather easily degraded during early diagenesis (Bourdon et al., 2000). The importance of the terrestrial organic matter contribution to the sediments is also assessed by rather high lignin and $C20_+$ even-carbon numbered FAMEs concentrations, amounting to 32-48 $mg.g^{-1}$ TOC and 5.7 -26.4 mg g^{-1} TOC, respectively (table 4). For comparison, recent analysis of Holocene peat by the same methods (Disnar et al., 2008) yielded lignin and $C20_+$ FAME concentrations of 4-20 $mg.g^{-1}$ TOC and 2-7 mg g^{-1} TOC, respectively. The higher yields obtained with Congo sediments is very probably due the loss of the more labile constituents (e.g. polysaccharides), during diagenesis.

The presence of FAMEs from C_{16} and C_{18} is noted in all chromatograms. Such compounds are usually produced by both algae and higher plants but they are rapidly destroyed in aerial condition and soils (Marseille et al., 1999). Then, in sediments they can be assumed to derive from autochthonous (marine) production. Hopanoids components are ubiquitous in all analyzed samples, although in very low proportion. This suggests a contribution of bacterial biomass, which may have developed in soil as well as within marine sediments.

To summarize, the recent mud-rich sediments from the Congo deep-sea turbidite system contain high amounts of organic matter, the origin of which is a mixture of terrestrial higher-plant debris and deeply oxidized phytoplanktonic material. Although we have evidence that both sources contribute to the organic matter sedimentation in the Congo deep-sea fan, their relative importance cannot be precisely quantified. In any case, the terrestrial fraction of the organic matter appears very important (at least 70-80%) especially for such depths and distance from the coast. Similar proportion (60 %) of terrestrial organic matter was recently reported in the sediments from the GeoB6518-1 core recovered by 962 m of water-depth close to the canyon/upper channel-levees transition (Weijers et al., 2009). This similarity in the proportion of terrestrial organic matter in both localities is surprising in that the sampling sites are at very different depths and processes that allow the accumulation of sediments on the edge of the canyon and along the middle part of channel-levees system are quite different (Savoye et al., 2000). This suggests a homogeneous distribution of the particulate organic matter delivered by the Congo River in the different parts of the deep-sea fan.

5.2 Controls on the distribution and accumulation of organic matter in channel-levees

Turbidite emplacement is discontinuous and usually produces layers of sediment in which organic matter quantity, type and preservational state are heterogeneous (Cowie et al., 1995; Meyers et al., 1996; Watanabe and Akiyama, 1998; Lindblom and Järnberg, 2004; Saller et al., 2006; Caja and Permanyer, 2008). By contrast, in the levees from the Congo mud-rich deep-sea fan, the organic matter appears very homogeneous regardless of the scale.

At the scale of a turbiditic small sequence, the organic matter shows more or less a constant quantity (3 %) and quality according to the pyrolysis parameters HI and OI. This is mainly due to the fine-grain composition of the turbidite off Congo which are mainly made by clay and fine silt fractions (10 µm as median grain-size). As organic matter particles are less dense than minerals, they are mainly associated with fine-grain component of the sediment. Organic matter particles have larger size in sandy facies but they are less numerous; then the organic content is usually lower at the base of sandy turbidites. Because the sandy fraction is a minor component of the studied levees, the organic matter content is near constant from the base to the top of a single turbiditic bed. Although, turbiditic clays cannot easily be distinguished from hemipelagic clays in such fine mud-rich system, the latter have been analysed at least in several levels and they show changes neither in quantity nor in type of organic matter. This implies that the hemipelagic sedimentary flux has more or less a similar characteristic for organic matter than the turbiditic input or, at least, that the preserved organic matter from hemipelagic sedimentation finally achieves the same characteristics.

Indeed, Treignier at al. (2006) studied the organic matter content and composition of sediment trapped 30 m above the channel before and just after a turbiditic event, as well as the surficial sediment sampled nine months after the event at the same water depth (~ 4000 m) than our studied area.

This sediment contained 4.2 % TOC and showed a predominance of long-chain *n*-alcohols typical for higher plant waxes, in the free lipid extracts. Despite the predominance of these compounds in cuticular waxes, and especially over long chain fatty acids and *n*-alkanes, they were absent among the thermochemolysis products of the nine samples we analyzed (Fig. 10). This absence is undoubtedly due to the microbial degradation of these labile compounds during early diagenesis. Treignier et al. (2006) estimated a degradation constant value

comprised between 0.6 and 1.2 y^{-1} for the $C22_+$ *n*-alcohols that is rather considerable. The fate of these compounds fully illustrates the considerable changes that can affect molecular signatures during sedimentation and diagenesis and the importance of the choice of markers used for assessing the origin and relative importance of original organic matter inputs to sediments.

The quantity of organic matter is near constant in the transect located at 700 km from the apex of the canyon (KZAI 04-05) compared to the transect located 150 km downstream (KZAI 13-14), although the sediment accumulation rate increases by one order of magnitude between these two areas (0.4 to 0.8 m/ka against 4.4 to 6.5 m/ka; Savoye et al., 2009). However, these sedimentation rates are both important for deep-sea environments. Such values indicate that, despite long distance transportation and/or deposition at rather great water depth, sediment emplacement occurred rapidly which is a suitable condition for organic matter preservation. Although the difference in the channel depth (140 m at KZAI 04-05 site and 90 m at KZAI 14-15 site) generates ten times more spillovers downstream (Savoye et al., 2009), the near constant quantity of organic matter suggests that the composition of the spillovers of the channelized flows, where organic matter, clay minerals and silts are carried in suspension, have a more or less similar composition in these different type of particles and that in the channelized flow, between 90 m and 140 m height (50 m thickness), the turbulence does not generate a significant segregation of organic particles. As the lithology of sediments does not change a lot between the two areas, this assumption seems valid.

More surprising is the fact that changes in sediment accumulation rates do not imply changes in the quality of the preserved organic matter. Usually, low sedimentation rates determine a longer residence time of the organic particles in the oxygenated zone near the water-sediment interface and consequently the organic matter is more easily remineralised. On the contrary, high sedimentation rate led to a better preservation of organic particles. Here the organic matter quality parameters (HI, OI, C/N, δ^{13}Corg and δ^{15}N) appear very constant along both the upstream and downstream transect.

This may be due to the fact that terrestrial organic particles, which are the main component of the organic matter in Congo deep sea fan sediments, are more resistant than marine organic matter. Marine organic matter may represent 40% of the preserved organic matter but is also deeply and rapidly altered after deposition as shown by Treignier et al.

(2006) on the *n*-alcohol fraction. Thus, changes in marine contribution during settling have little impact on the final composition of the organic matter of the sediment. It seems that after its deposition, the organic mixture of terrestrial and marine particles is homogenised by oxidative alteration and exhibits constant quality parameters.

A minor change is noted, however, in the HI and OI values with the distance from the channel. Samples from cores KZAI 05 and 14 which are located closer to the channel display higher HI- and lower OI-values compared to samples from cores KZAI 04 and 13 which are 500 to 5000 m separated from the counterpart. The changes are minor (Δ = –40 mg HC/g TOC for HI and +40 mg CO_2/g TOC for OI) but significant if we consider the distribution of analysed samples on a HI-OI diagram (Fig. 11). Moreover, the dispersion of samples is more important in the IH-IO diagram in cores located far from the channel. This is maybe the indication that changes in accumulation rates have already a little impact on the quality of organic matter.

5.3 Implication for deep-sea petroleum source rocks analogs

TOC is the primary parameter of source rock appraisal, with a threshold of 1 wt% at the immature stage for potential source rocks. With an average TOC value which largely exceeds this threshold, the fine-grained turbiditic sediments in the Congo deep-sea fan could be regarded as good future gas-prone source rocks. Mean petroleum potential range between 4 and 4.7 kg HC per t rock and are mainly gas-prone as the organic matter is primarily of terrestrial origin.

The shaly levees are the main sedimentary facies which built the present-day Congo deep sea fan. The volume of potential source rock is here very important, especially if we consider their proximity to the sandy reservoirs located in the channel filling. Such organic-rich facies may also a source for biogenic gas, which is not yet fully characterized. Methane-rich vents are numerous in the Congo deep sea fan and the degassing of studied cores has been noted on board the research vessel just after their recovery.

Fossil analogs of the present-day deep sea fan are distributed along the Atlantic passive margins throughout the geological times, especially in the Congo-Angola basin. Ancient deep-sea fans are now buried and such facies may be regarded as contributors to the regional petroleum systems. A recent study of the Oligocene succession off Angola

demonstrates the petroleum potential of deep-sea claystones deposited as levee facies (Disnar et al., in press).

5.4 Implication for the global carbon cycle

The transfer of carbon from land to sea has been recognized as an important pathway in the global carbon cycle (Milliman, 1991; Burdige, 2005). Rivers play a major role and transport most of the ~500 Tg per year of organic carbon carried from land to the global ocean (Spitzy and Ittekkot, 1991). One critical aspect in the ocean carbon budget is the particulate export flux from the coastal zone to the open ocean (Biscaye and Andersson, 1994; Goni et al., 1997; Hedges et al., 1997; Andersson and Mackenzie, 2004; Dagg et al., 2004). Several programs have addressed this question on different types of oceanic margin and have shown the diversity of the modes of transfer (i) in nature with terrestrial versus marine carbon, (ii) in space with canyons playing a major role in channelling the particulate flux in some places, (iii) in time with storms, instabilities, current surge playing a significant role in transporting particles and carbon from the shelf to the slope and open ocean.

In the case of the Congo deep-sea fan, the main part of the sedimentary load, including organic matter, is transported directly from the river mouth to the deep-sea because the canyon starts within the estuary. Our results indicate that high concentration of organic matter (3% on average) is preserved in the shaly facies developed all along the lower channel/levee systems. These facies are the main deposits through time, as channel sandy facies represent only 20% on seismic profiles (Droz et al., 1996; Savoye et al., 2000). Thus, huge amount of organic matter is preserved in the deep-sea fan system of the Congo.

Anka and Séranne (2004) estimate the volume of ancient fan related to the Congo River from Oligocene to Present to a minimum of 0.7 10^6 km^3. Taking an average of 3% of Corg and 1500 kg/m^3 for the density of dry sediment, we may calculate that 3 10^{13} tons of carbon are stored in that part of the Atlantic margin.

If we assume that the present-day delivery of particulate organic matter by the Congo River (1 mg C/L and a mean flow around 50 000 m^3/s) was constant through time and that this particulate organic flux was totally preserved in the sediment of the margin, we calculate that 5.4 10^{13}t of carbon should be stored since 34 Ma. Despite our roughly assumptions, both estimations are in the same range and the magnitude is probably correct.

The Congo deep-sea turbiditic system is one of the largest in the world still affected by turbidite sedimentation during the interglacial high sea-level (Savoye et al., 2000). Such a phenomenon is unique along the present-day African margin as most of the canyons are not connected with the river. During the glacial periods, when sea-level was low, other huge rivers, including the Amazon River, were directly connected to their submarine canyons and carbon transfer from land to deep sea was much more higher than today. Indeed, the present-day situation of the Congo River cannot be generalized to low seal-level period and further studies are needed to evaluate the efficiency of such systems for the storage of terrestrial organic matter into the deep ocean at that time.

6. Conclusion

The claystones and siltstones deposited in the lower channel/levees system of the Congo deep sea fan are devoid of carbonate and contain a high proportion of organic matter, with total organic carbon content around 3 wt%. This organic richness appears very homogeneous at different scales, although smaller quantities are noted in more sand-rich facies corresponding to the basal part of turbiditic event.

The identification and quantification organic carbon sources are difficult because several parameters influence the bulk and molecular characteristics of the preserved organic matter. Hydrogen Index values, carbon isotopic ratios and molecular data, all indicate a strong influence from the detrital source, with proportion as high as 90%. C/N ratios and nitrogen isotopic ratios, on the contrary, suggest that marine contribution to the organic matter sedimentation may represent up to 40 %. Although evidence exist that both sources contribute to the organic matter sedimentation in the Congo deep-sea fan, their relative importance cannot be precisely quantified. In any case, the terrestrial fraction of the organic matter appears very important (at least 60%) for such depth and distance from the coast.

The quantity and quality of organic matter is near constant in cores located at 700 km from the apex of the canyon compared to cores located 150 km downstream, although the sediment accumulation rate increases by one order of magnitude between these two areas. This suggests that the spillovers of the channelized flows, where organic matter, clay minerals and silts are carried in suspension, have a more or less similar composition in these different types of particles. Change in accumulation rates has already a little impact on the quality of

organic matter, as higher plant and soil organic matter particles, which seem to be dominant, are more resistant than marine organic matter.

With a TOC content of 3% and petroleum potential around 4.5 kg HC per t rock, the fine-grained turbiditic sediments in the Congo deep-sea fan could be regarded as good future gas-prone source rocks. Analogs of the present-day deep sea fan are distributed along the Atlantic passive margins throughout the geological times, and should be considered as potential source rocks for the deep offshore realm.

Finally, the Congo deep-sea fan is a major conveyor of organic carbon to the deep Atlantic Ocean in the present-day high sea-level situation. This system where the canyon is connected to the estuary can be generalized to other deep sea fans during low seal-level periods. Further studies are needed to evaluate the efficiency of such systems for the storage of terrestrial organic matter into the deep ocean.

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Captions of figures and tables

Fig. 1. General map of central Africa and the Gulf of Guinea in eastern equatorial Atlantic Ocean, showing the course of the Congo River, its main distributaries and its drainage area (watershed), the surface and subsurface currents (open arrows: cold currents; black arrows: warm currents), and highly productive areas (the latters modified from Schneider et al., 1994).

Fig. 2. Top: bathymetric map (contour interval: 100 m) showing the general morphology of the Congo canyon and the modern meandering channel along the Congo fan. Limits of the canyon, upper fan, channel/levee systems and lobes are from Babonneau et al. (2002). Studied areas are located in the lower channel/levee systems. Bottom: Detailed bathymetric map (contour interval: 10 m) and location of studied cores within the two studied areas, modified after Gervais et al. (2001), Migeon et al. (2004).

Fig. 3. Top: line drawings of 3.5 kHz profiles showing the internal structures of the studied levees and location of studied cores along these schematic cross-sections (Migeon et al. 2004 ; Gervais et al. 2001). Bottom: core logs showing the sediment grain-size changes and the sampled interval along each core, redrawn after Migeon et al. (2004), Gervais et al. (2001) and Migeon (2000).

Fig. 4. Vertical distribution of grain-size parameters (granulometric composition, median grain-size), Total Organic Carbon (TOC, in weight %), Hydrogen Index (in mg HC/g TOC), C/N and δ^{13}Corg (in ‰) of the four cores studied in the levee facies with a 20 cm-spacing. Core location is shown on figs. 3 and 4.

Fig. 5. Microphotographs of palynofacies of the fine grained sediments of the levees from the Congo deep sea fan near 4000 m-depth. a: Amorphous organic matter (AOM) having a fluffy aspect. b: AOM containing small ligno-cellulosic debris. c: Structured phytoclast, apparently derived from root cortex tissues. d: Partly-gelified ligno-cellulosic debris on which vegetal fibre are still discernible. e: Opaque particle with corroded outlines on the right and small piece of structurless phytoclast on the left. f: Spore.

Fig. 6. Vertical distribution of median grain-size (in μm), Total Organic Carbon (TOC, in weight %), Hydrogen and Oxygen Indexes (in mg HC/g TOC and mg CO_2/g TOC, respectively) in several elemental turbiditic beds from cores KZAI 04, 14 and 15 with a 2 cm-spacing. Core location is shown on figs 3 and 4.
A and B: type1-bed, C and D: type 2-bed, E: type 3-bed, F: type 4-bed following the nomenclature defined by Migeon et al. (2004).

Fig. 7. Kerogen type in the silty-clayey sediments of the lower channel/levee systems from the Congo fan as defined by the cross-plot of TOC and pyrolysis S_2 parameters. Nearly all samples are located in the domain of Type III organic matter which usually derives from higher plant debris.

Fig. 8. Relationship between total organic carbon and total nitrogen for three core sediments from the lower channel-levees system of the Congo fan. The linear regression line based on all data points (R^2=0.81) is indicated by the dashed line.

Fig. 9. Kerogen type in the silty-clayey sediments of the lower channel/levee systems from the Congo fan as defined by the cross-plot of δ^{13}Corg (in ‰) and δ^{15}N (in ‰). Here the organic matter derives from a mixture of C3 land plants and marine algae.

Fig. 10. Example of partial reconstituted Total Ion Current (TIC) chromatogram of the products of thermochemolysis with TMAH of sample from the silty-clayey sediments of the lower channel/levee systems from the Congo fan (sample KZAI 05 – 540-541 cm). The dominance of lignin-derived compounds (L), long-chain and odd-numbered *n*-alkanes, and long-chain fatty acid methyl esters (FAMEs) indicate the predominance of terrestrial organic matter. Nevertheless, nC16:0 and nC18:0 FAMEs may be interpreted as derived from algal biomass whereas the presence of hopanoid testifies from a bacterial origin of some part of the organic matter.
L = lignin derivatives and others phenolic compounds, all as Me ester and ethers (in increasing elution order) : pHO-benzaldehyde, pHO-benzoic acid, vanillin, vanillic acid (dominant), syringaldehyde, coumaric acid, syringic acid, ferulic acid.

Hopanoids : the first compound H_{30} is the regular hopane, the three following ones (H_{30}-H_{32}) are hopanoic acids (as Me esters).

Fig. 11. van Krevelen diagram showing the homogeneity of the organic matter in the silty-clayey sediments of the lower channel/levee systems from the Congo fan. The samples which are more distant from the axis of the channel show lower HI-values and higher OI-values indicating a little bit stronger oxidation effect.

Tab. 1. Location of the studied cores (Lat., Long., water-depth), penetration into the sediments, length of studied interval and number of studied samples.

Tab. 2. Bulk inorganic and organic characteristics of the studied samples in each studied core. Minimum, mean and maximum values are given for $CaCO_3$ (in %), TOC (in %), Hydrogen Index (HI, in mg HC/g TOC), C/N, δ^{13}Corg (in ‰) and δ^{15}N (in ‰).

Tab. 3. Estimates of terrestrial organic matter fraction (in %) of the total organic matter in marine sediments from KZAI cores based on the binary mixing models of different proxies.

Tab. 4 . Main data on lignin-derived products and on FAMEs released by thermochemolysis
Sac, Sald & S = syringic acid, aldehyde and total, respectively
Vac, Vald & V = vanillic acid, aldehyde and total, respectively
Ltot = total lignin = S + V + (coumaric and ferulic acids)
*Compound concentrations in $mg.g^{-1}$TOC. Note that sample from core KZAI 15 corresponds to a sandy facies from the channel.

Figure 1

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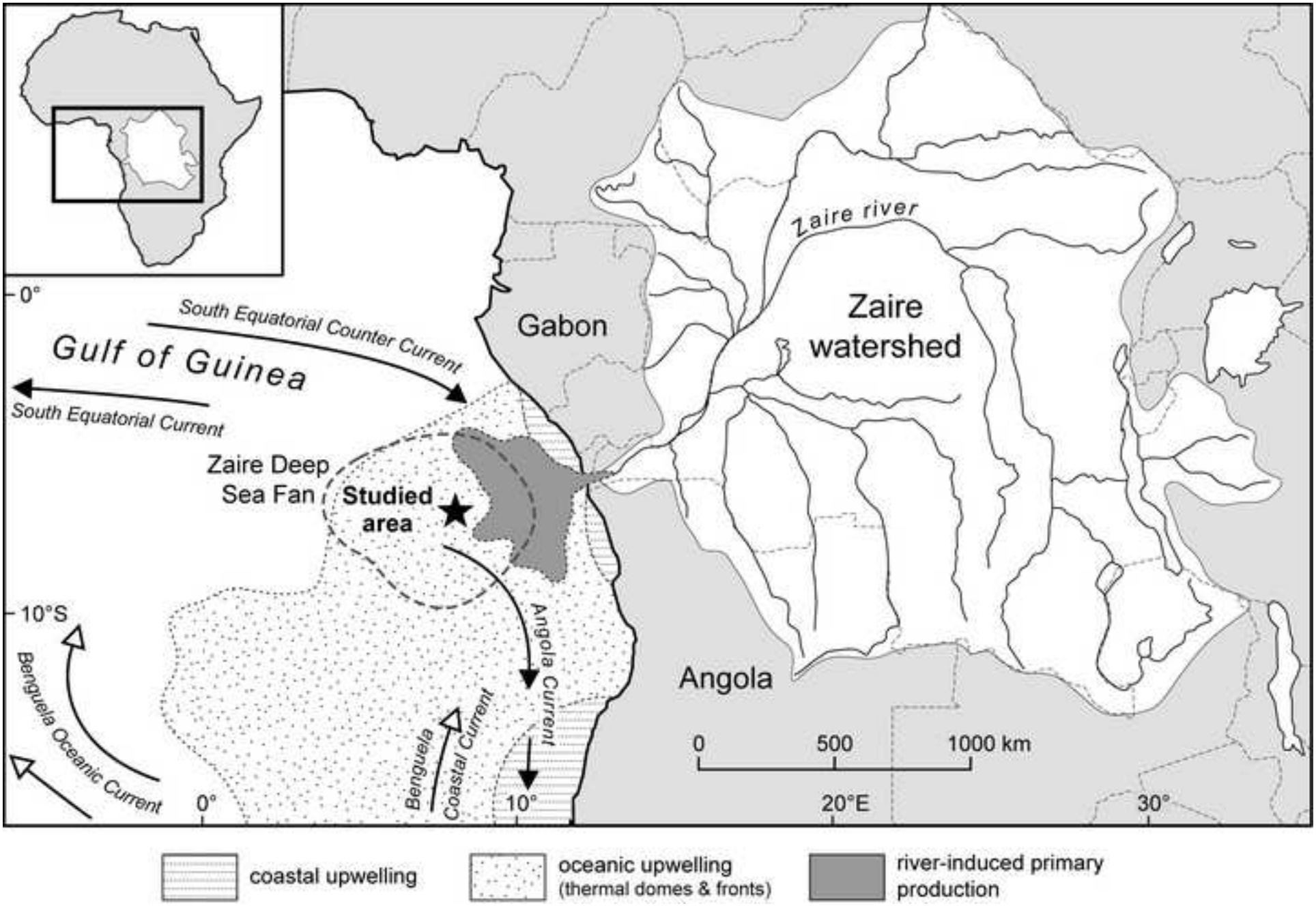

Figure 2

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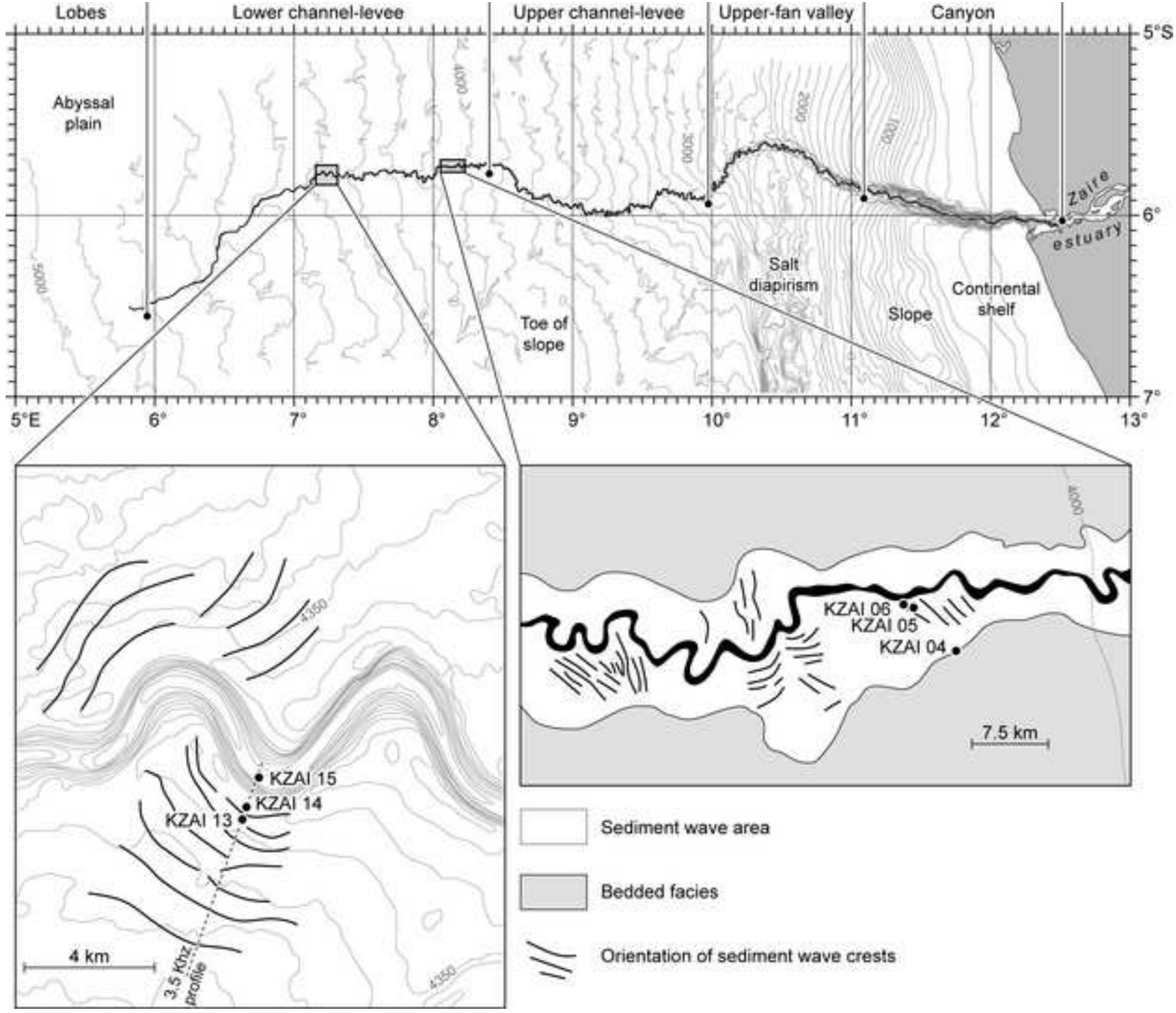

Figure 3

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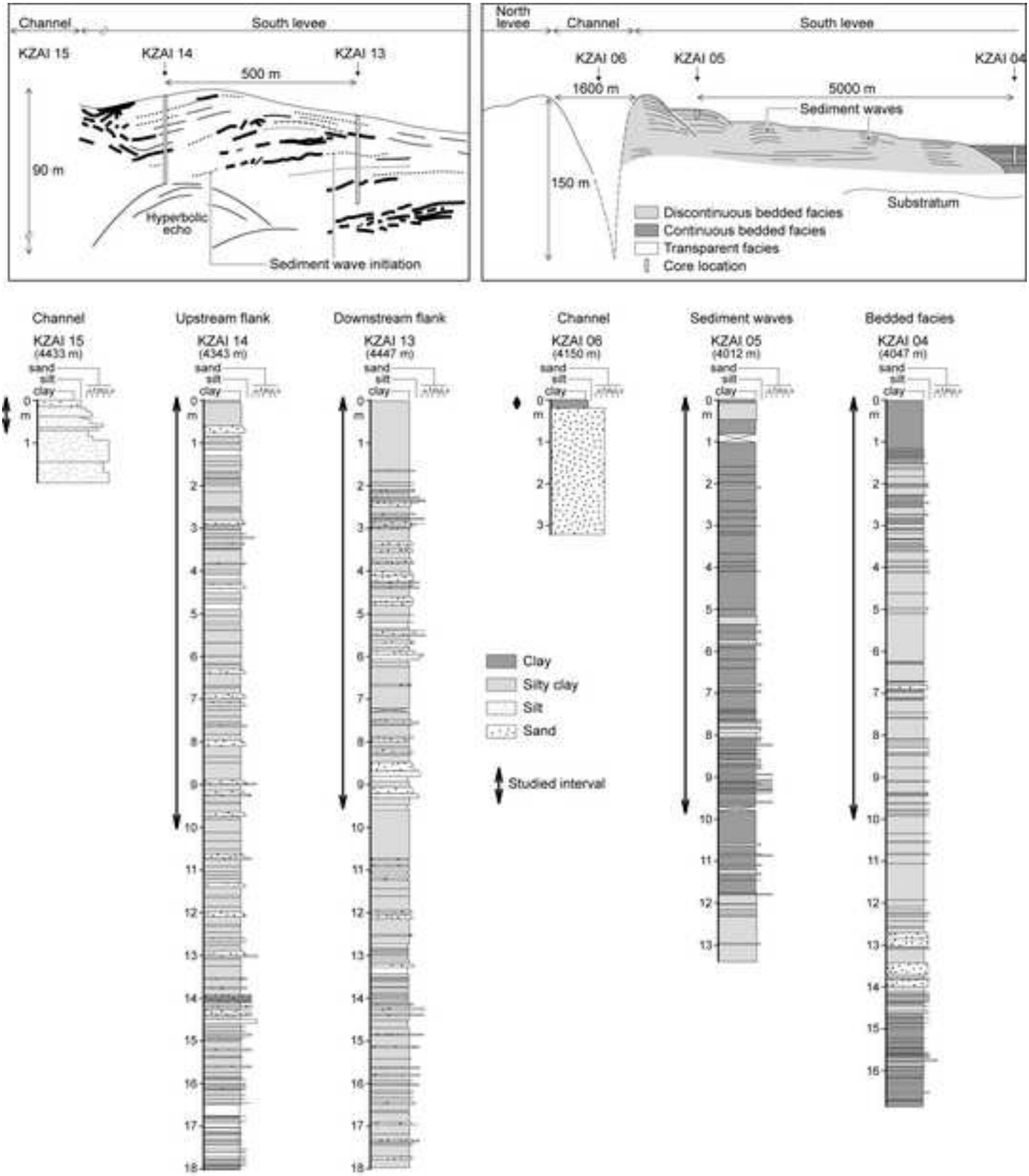

Figure 4

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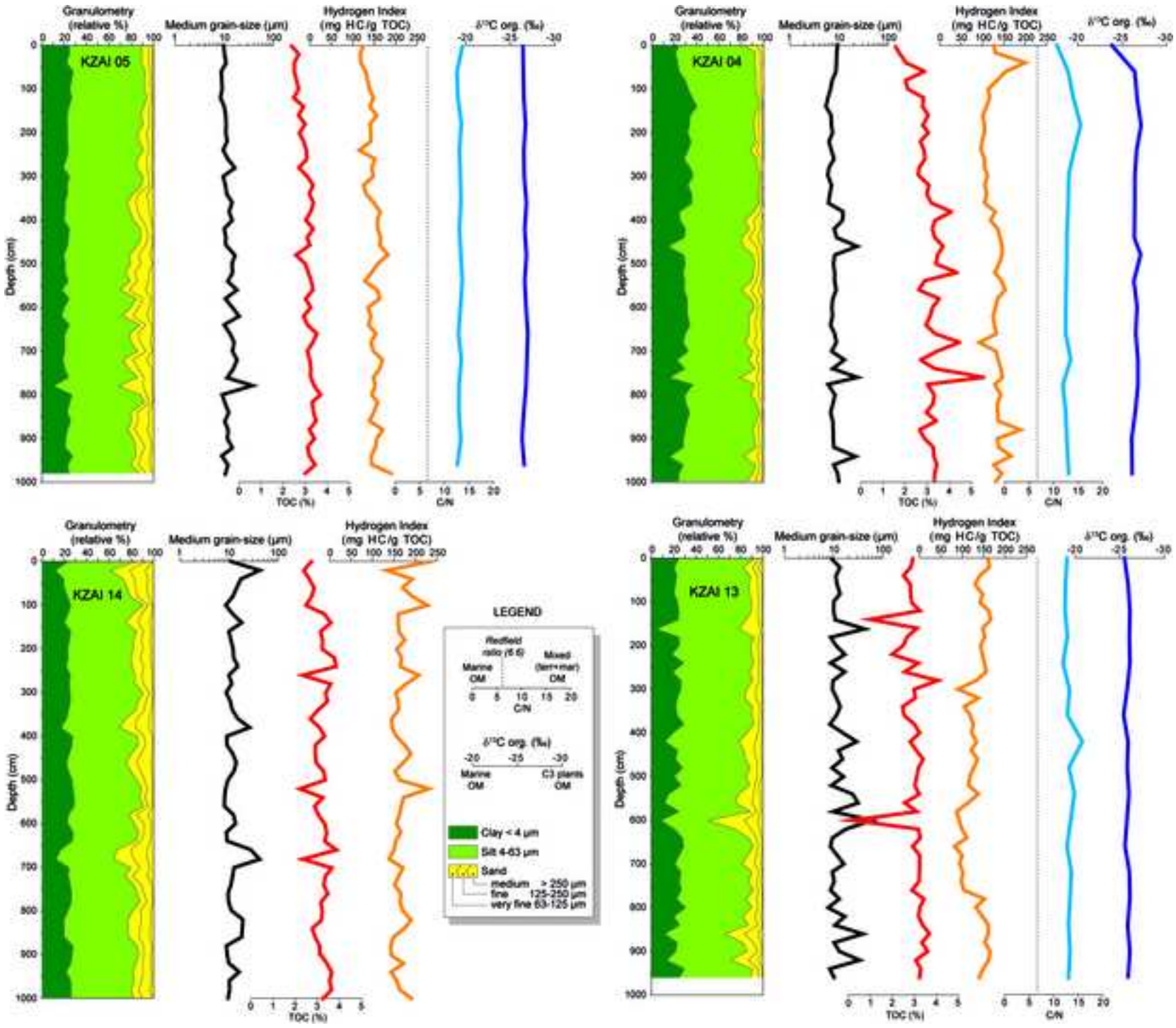

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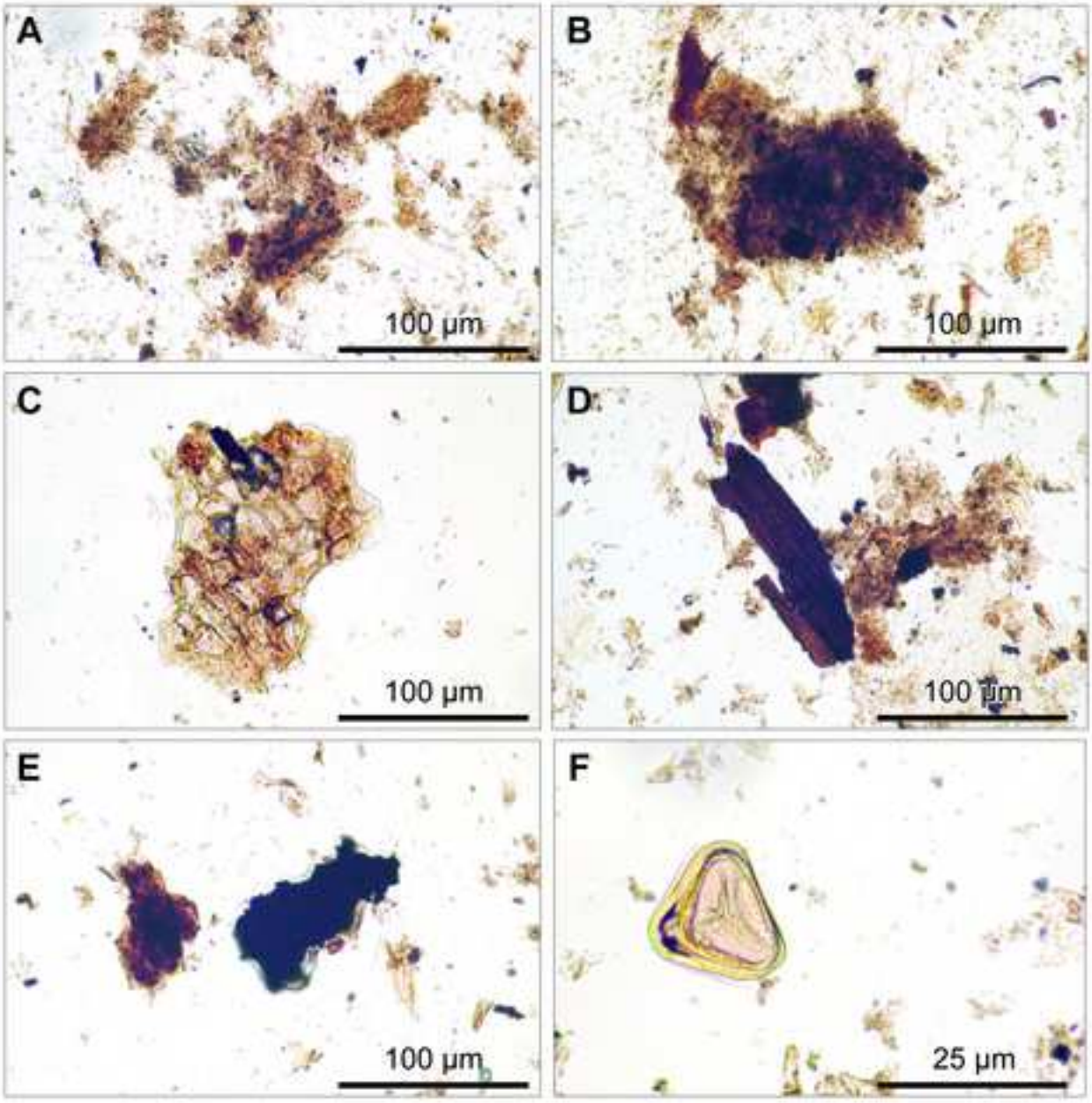

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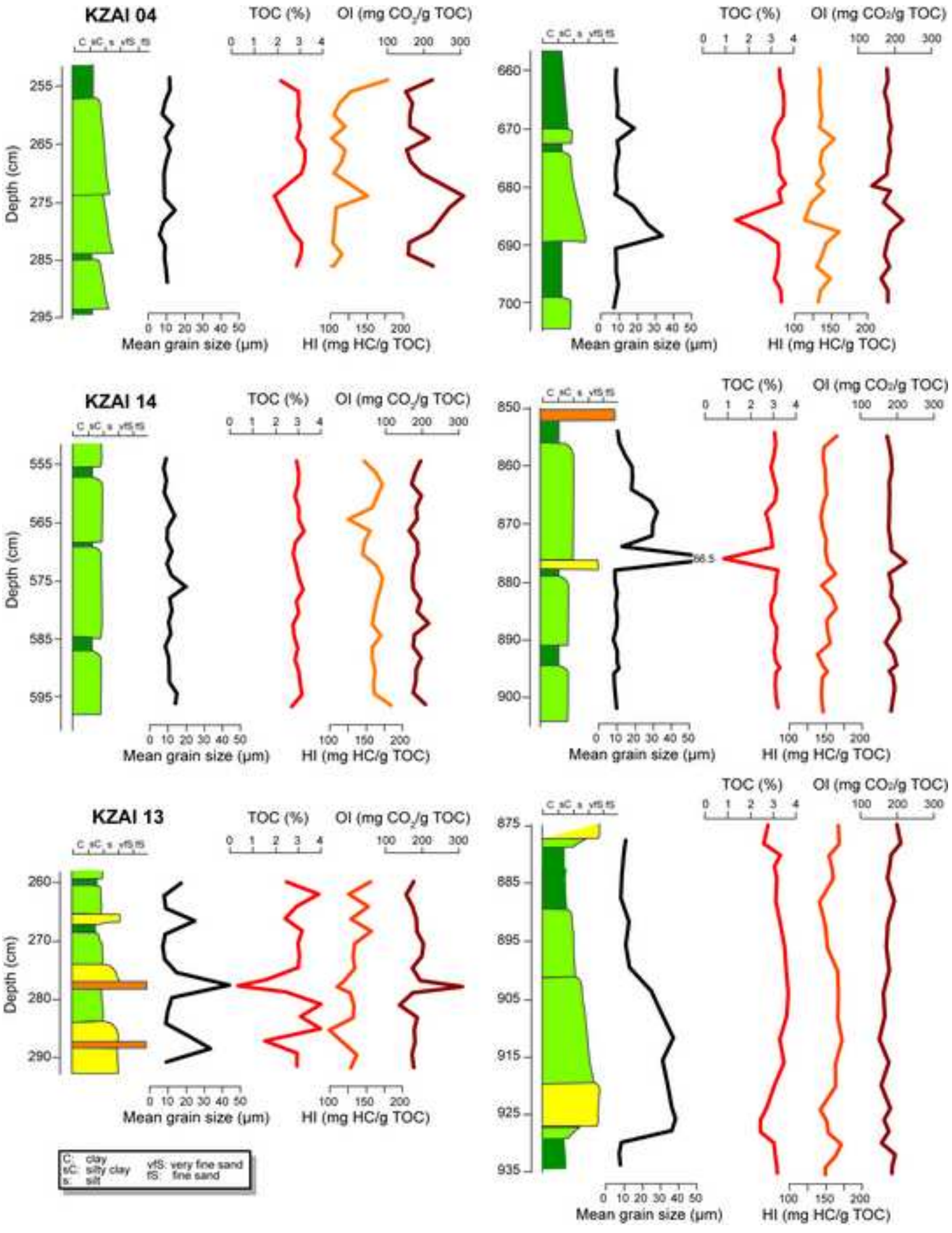

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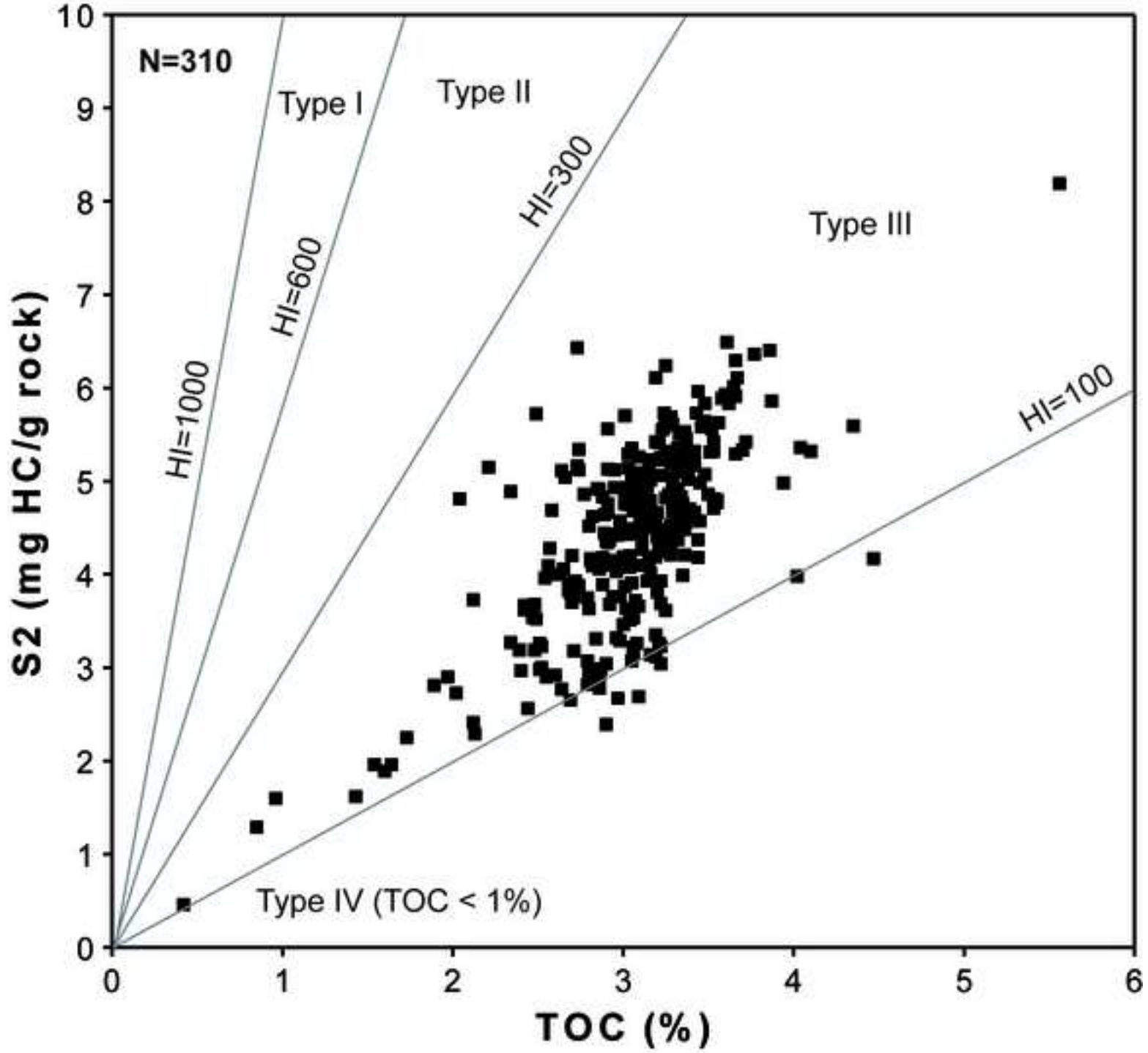

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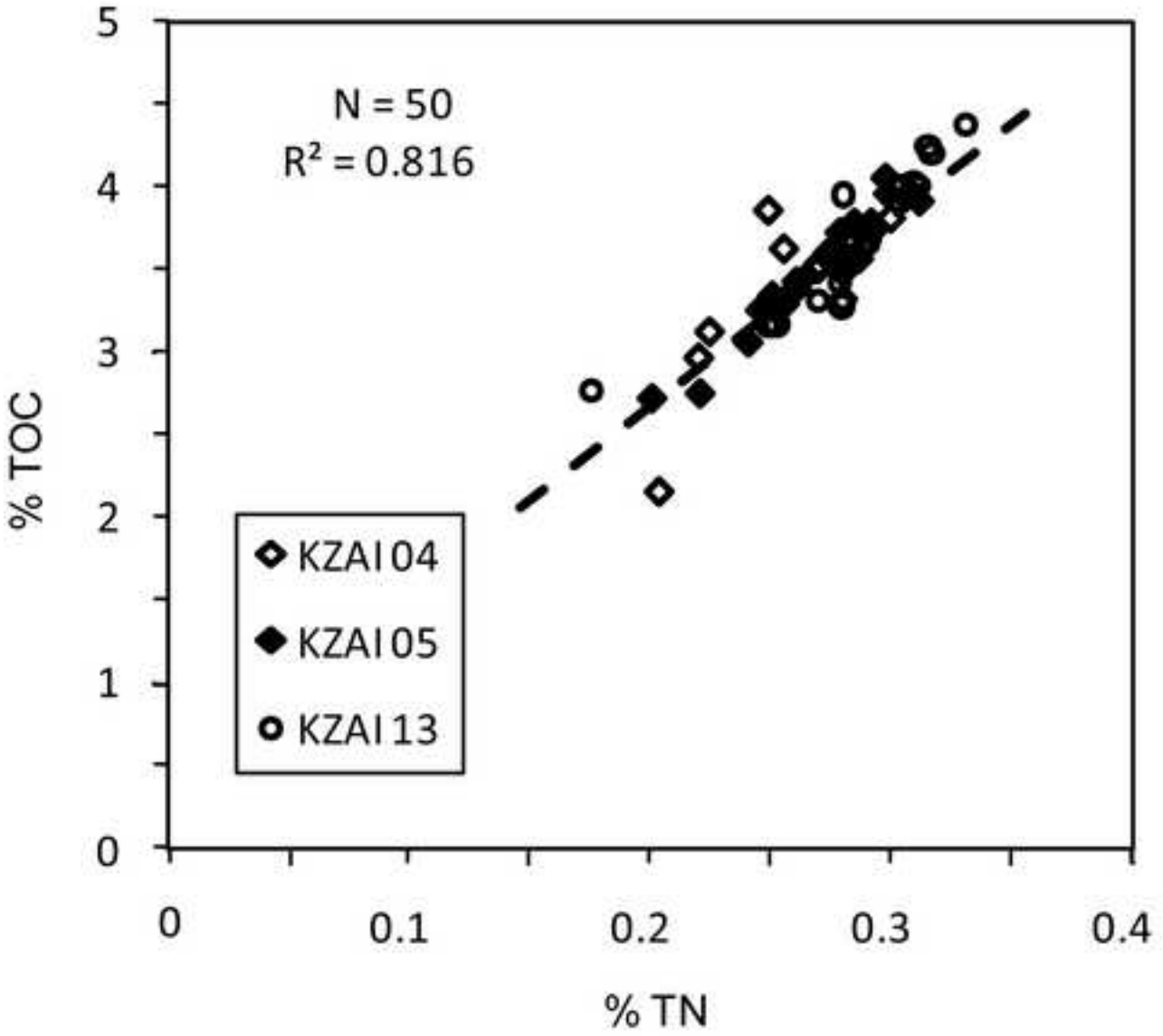

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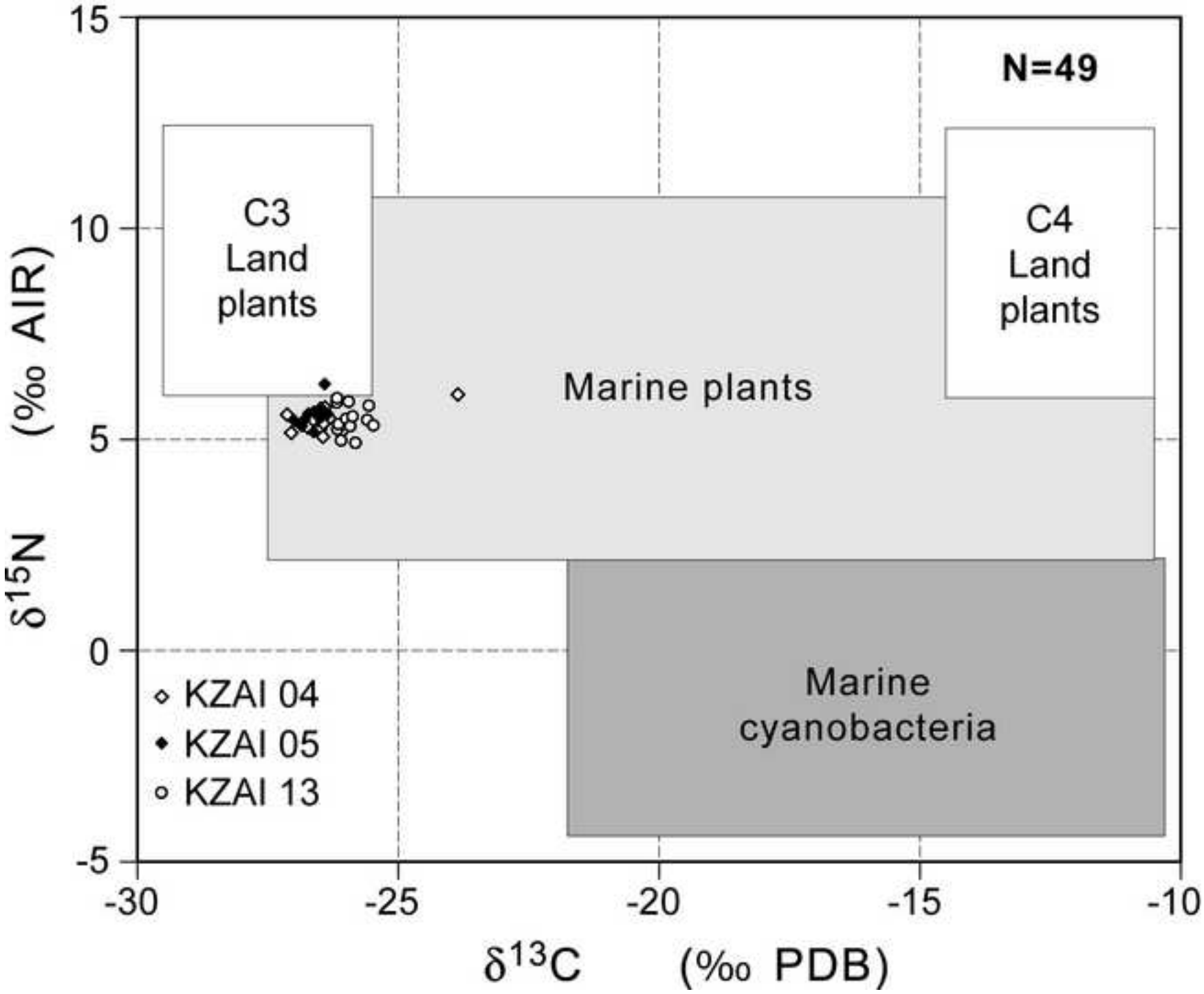

Figure 10

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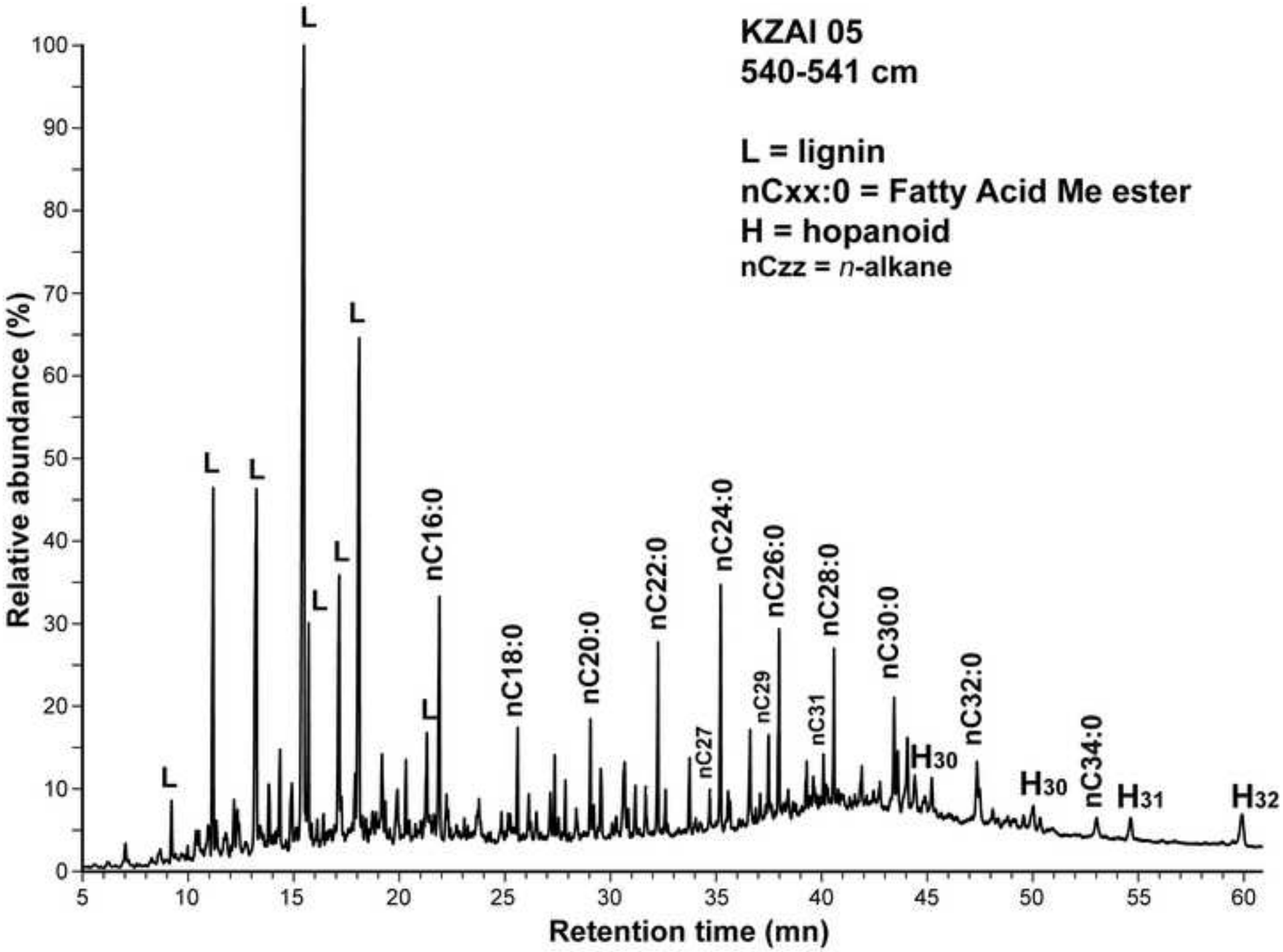

Figure 11

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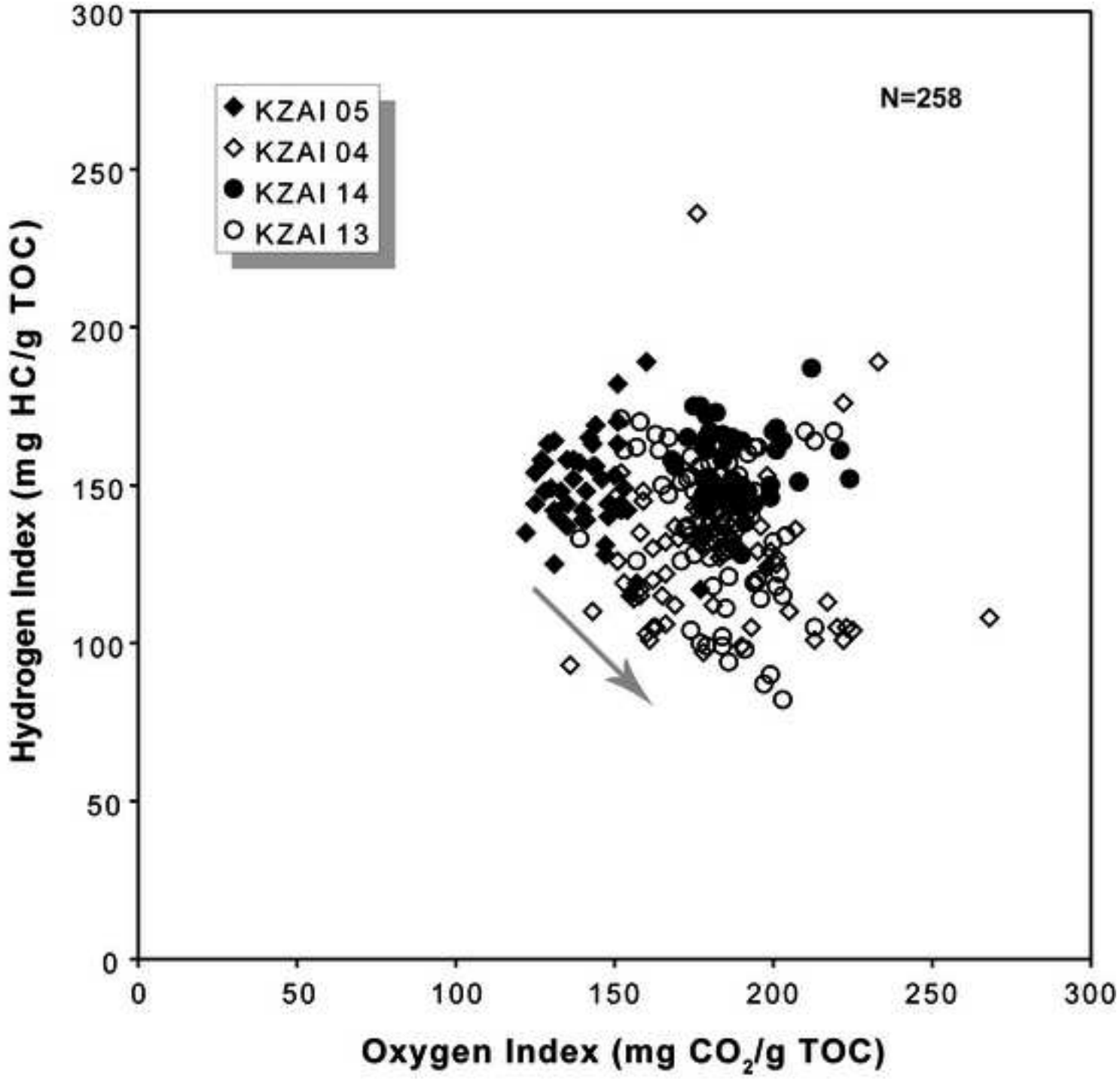

Table 1

	Core	Lat. (°S)	Long. (°E)	Water depth (mbsl)	Situation	Penetration (mbsf)	Studied interval (m)	Number of samples	Mean spacing (m)
Upstream	KZAI 04	5° 48.04	8° 08.96	4047	Levee	16.87	10.0	83	0.12
	KZAI 05	5° 44.50	8° 08.29	4012	Crest of levee	13.34	9.8	49	0.20
	KZAI 06	5° 44.10	8° 08.23	4150	Channel axis	3.24	0.2	1	-
Downstream	KZAI 13	5° 47.30	7° 13.89	4447	Levee	17.92	9.6	79	0.12
	KZAI 14	5° 47.09	7° 13.98	4343	Crest of levee	17.3	10.0	100	0.10
	KZAI 15	5° 46.62	7° 14.19	4433	Channel axis	1.93	0.6	4	0.15

Table 2

	Core	Situation	Number of samples analysed	$CaCO_3$ (%)			TOC (%)			HI (mg HC/g TOC)			Number of samples analysed	C/N			$\delta^{13}C$ (‰)			δ^{15N} (‰)		
				Min	**Mean**	Max	Min	**Mean**	Max	Min	**Mean**	Max		Min	**Mean**	Max	Min	**Mean**	Max	Min	**Mean**	Max
Upstream	KZAI 04	Levee	83	1.5	**2.7**	6.0	1.4	**3.0**	5.6	93	**134**	200	17	10.7	**12.9**	15.5	-27.12	**-26.37**	-23.85	5.12	**5.44**	6.09
	KZAI 05	Crest of levee	49	2.0	**2.6**	3.3	2.4	**3.1**	3.7	115	**148**	189	16	12.6	**13.16**	13.7	-26.96	**-26.61**	-26.3	5.23	**5.61**	6.31
Downstream	KZAI 13	Levee	79	0.8	**2.6**	3.3	0.1	**2.97**	4.04	82	**137**	171	16	11.8	**13.09**	15.7	-26.17	**-25.94**	-25.46	4.98	**5.47**	5.98
	KZAI 14	Crest of levee	100	1.33	**2.5**	3.25	0.85	**3.08**	3.9	128	**163**	236											
	KZAI 15	Channel	4	0.7	**1.88**	3.18	0.0	**1.48**	3.63	118	**145**	182											

Table 3

Core	Proxy				
	Mean HI	Max HI	N/C	$\delta^{13}C$ (‰)	δ^{15N} (‰)
KZAI 04	89	67	84	94	45
KZAI 05	84	70	86	98	42
KZAI 13	88	76	86	87	44
KZAI 14	79	55			
KZAI 15	85	73			
Average	**85**	**67**	**85**	**93**	**44**

Table 4

Core	Depth (cm)	TOC (%)	S/V	(Vac+Sac)/ Ltot	(Vac+Sac)/ (Vald+Sald)	Ltot*	(nC16+nC18)FAMEs*	C20+evenFAMEs*
KZAI 04	1-2	1.54	0.30	0.65	2.56	32.2	8.9	19.5
KZAI 04	297-298	2.60	0.33	0.60	1.74	36.2	5.4	5.7
KZAI 05	2-3	2.40	0.45	0.62	2.02	40.1	8.2	16.5
KZAI 05	540-541	3.28	0.59	0.56	1.83	45.0	7.6	26.4
KZAI 05	960-961	3.45	0.33	0.62	2.05	33.9	7.2	12.5
KZAI 13	540-541	3.20	0.61	0.59	2.37	46.3	7.4	18.7
KZAI 13	926-927	2.42	0.57	0.55	1.75	48.2	3.8	13.7
KZAI 13	928-929	2.42	0.56	0.55	1.81	48.4	5.4	15.8
KZAI 15	4-5	1.59	0.36	0.61	1.98	34.4	7.5	13.0