

## Reexposure and advection of $^{14}\text{C}$ -depleted organic carbon from old deposits at the upper continental slope

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[1] Outcrops of old strata at the shelf edge resulting from erosive gravity-driven flows have been globally described on continental margins. The reexposure of old strata allows for the reintroduction of aged organic carbon (OC), sequestered in marine sediments for thousands of years, into the modern carbon cycle. This pool of reworked material represents an additional source of  $^{14}\text{C}$ -depleted organic carbon supplied to the ocean, in parallel with the weathering of fossil organic carbon delivered by rivers from land. To understand the dynamics and implications of this reexposure at the shelf edge, a biogeochemical study was carried out in the Gulf of Lions (Mediterranean Sea) where erosive processes, driven by shelf dense water cascading, are currently shaping the seafloor at the canyon heads. Mooring lines equipped with sediment traps and current meters were deployed during the cascading season in the southwestern canyon heads, whereas sediment cores were collected along the sediment dispersal system from the prodelta regions down to the canyon heads. Evidence from grain-size, X-radiographs and  $^{210}\text{Pb}$  activity indicate the presence in the upper slope of a shelly-coarse surface stratum overlying a consolidated deposit. This erosive discontinuity was interpreted as being a result of dense water cascading that is able to generate sufficient shear stress at the canyon heads to mobilize the coarse surface layer, eroding the basal strata. As a result, a pool of aged organic carbon ( $\Delta^{14}\text{C} = -944.5 \pm 24.7\text{‰}$ ; mean age  $23,650 \pm 3,321$  ybp) outcrops at the modern seafloor and is reexposed to the contemporary carbon cycle. This basal deposit was found to have relatively high terrigenous organic carbon (lignin =  $1.48 \pm 0.14$  mg/100 mg OC), suggesting that this material was deposited during the last low sea-level stand. A few sediment trap samples showed anomalously depleted radiocarbon concentrations ( $\Delta^{14}\text{C} = -704.4 \pm 62.5\text{‰}$ ) relative to inner shelf ( $\Delta^{14}\text{C} = -293.4 \pm 134.0\text{‰}$ ), mid-shelf ( $\Delta^{14}\text{C} = -366.6 \pm 51.1\text{‰}$ ), and outer shelf ( $\Delta^{14}\text{C} = -384 \pm 47.8\text{‰}$ ) surface sediments. Therefore, although the major source of particulate material during the cascading season is resuspended shelf deposits, there is evidence that this aged pool of organic carbon can be eroded and laterally advected downslope.

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## 1. Introduction

[2] During periods of high stand in sea level, similar to today, prodeltas and shelves are the predominant locations of sediment accumulation and organic carbon (OC) burial [Bernier, 1987, 1989, Hedges and Keil, 1995]. Conversely, throughout falling stages of sea level, shelf deposits are exposed to subaerial erosion, whereas sediment and OC deposition occur primarily on the upper slope owing to the seaward migration of river outlets [de Haas et al., 2002]. As a result, most of the continent-ocean exchange of sediment and particulate OC takes place during eustatic low stand of sea level. However, several geophysical studies and models have amassed widespread evidence of active transport on slopes throughout the Holocene as a result of gravity-driven processes, including submarine failures, turbidity currents, earthquake-supported sediment gravity flows, and dense water flowing off the continental margin [Fohrmann et al., 1998; Kineke et al., 2000; Mulder et al., 2001; Paull et al., 2003; Walsh and Nittrouer, 2003; Puig et al., 2004; Canals et al., 2006; Tripsanas et al., 2008]. Although these mechanisms have been globally observed along several slopes, the community still lacks a comprehensive estimate of the particulate material supplied to the ocean interior. One major obstacle to this understanding is the stochastic nature of these gravity-driven flows that are generally triggered by events [Paull et al., 2003]. As a result, these processes are extremely difficult to capture, and most of the evidence that we have is indirect, such as alteration and/or formation of strata [Mullenbach et al., 2004; Smith et al., 2005; Shanmugam, 2008; Tripsanas et al., 2008].

[3] Several geological and geophysical studies carried out along continental margins described the erosive nature of these processes, showing that a significant component of the material transported via slopes derives from erosion of old strata at the shelf edge. As a result, it is likely that a fraction of aged OC, temporarily buried in marine sediments at the upper slope, is reexposed to the active carbon cycle. However, there have been almost no biogeochemical studies on the effect of gravity-driven flows on the global carbon cycle. In this study, we focused on shelf dense water cascading (DWC), which generates erosive flows that promote the outcropping of aged strata to the modern seafloor. Specifically, cooling, salinization, and freezing of coastal water create density-driven near-bottom gravity currents which overflow the shelf edge until they reach the hydrostatic equilibrium level. This process has been observed in ~70 locations around the world [Ivanov et al., 2004; Durrieu de Madron et al., 2005] (Figure 1a), mainly in polar regions and midlatitudes, where it represents the major process controlling the shelf-slope exchange of particulate material [Allen and Durrieu de Madron, 2009]. As opposed to many of the aforementioned erosive processes (e.g., earthquake-related submarine failures, turbidites), dense water formation on the shelf is seasonally recurring and relatively predictable. Therefore, these systems are ideal locations to investigate the signature of aged OC reexposed on the upper slope as a result of erosive gravity-driven mechanisms.

## 2. Background: Dense Water Cascading in the Gulf of Lions

[4] The shelf-slope exchange driven by shelf DWC was investigated in the Gulf of Lions (GoL) within the framework of the EuroSTRATAFORM project to understand the forces driving the export of particulate material into the deep Mediterranean Sea (Figure 1b). On this margin, DWC occurs seasonally (late winter-early spring) and is responsible for significant off-shelf export of sediments and dense water to the slope via submarine canyons [Durrieu de Madron et al., 2005; Canals et al., 2006; Palanques et al., 2006; Puig et al., 2008]. In winter, northerly winds cause rapid cooling and mixing of coastal water, and southeasterly storms promote large resuspension events along the coast. These high-energy storm events induce sufficient shear stress on the seabed to resuspend shelf deposits and promote the export of this resuspended material, together with the cold dense water from the inner shelf, mainly via Cap de Creus Canyon (CCC) and Lacaze-Duthiers Canyon (LDC) located in the southwestern GoL (Figure 1c) [Canals et al., 2006; Palanques et al., 2006; Ogston et al., 2008; Palanques et al., 2008]. The export of shelf deposits via these canyons can be particularly significant during intense DWC events, allowing for a shelf-slope particulate exchange similar to the riverine supply [Ferre et al., 2008; Ulses et al., 2008].

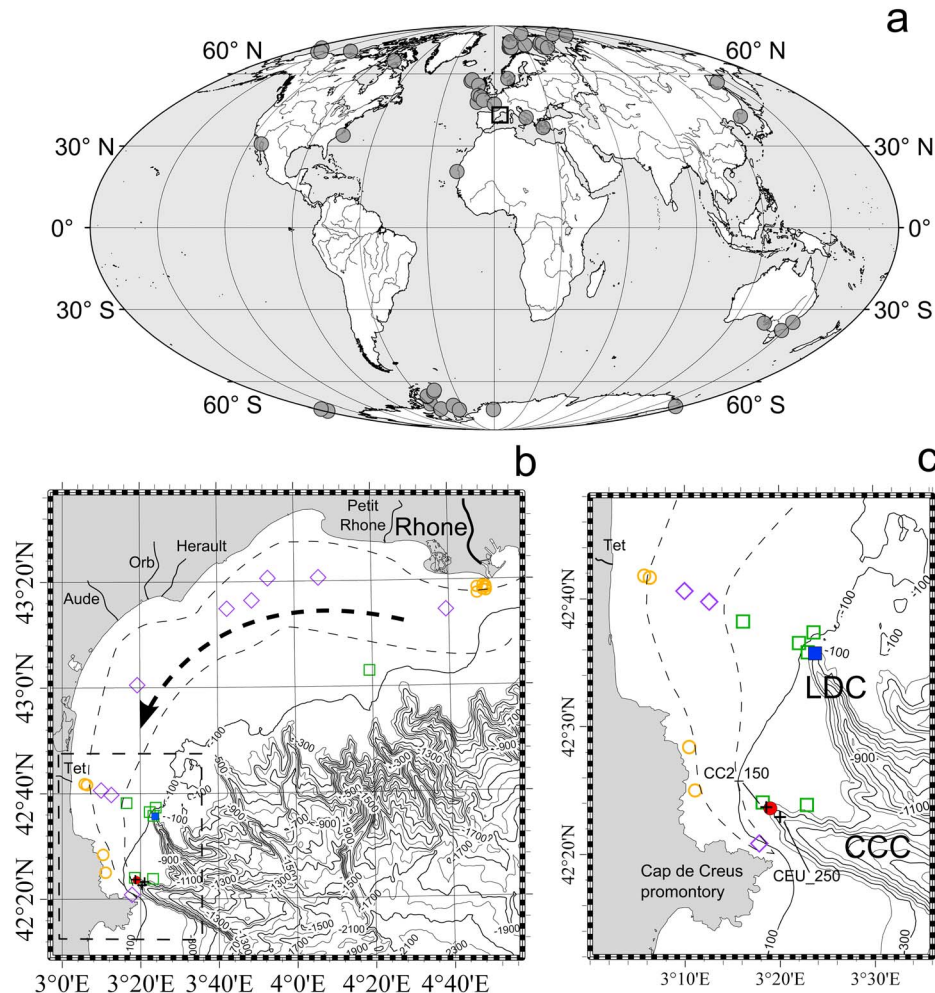
[5] Because of this considerable off-shelf export, DWC has been suggested to have important implications for the OC cycle in the slope environment [Canals et al., 2006; Company et al., 2008]. For example, the mechanism of deepwater cascading allows shelf material, including terrigenous OC adsorbed on shelf sediment, to be flushed via canyon heads and to reach depths that are not generally allowed by wave-supported sediment dispersal systems [Fabres et al., 2008; Sanchez-Vidal et al., 2009; Tesi et al., 2010]. In addition, toward the end of the cascading season, the GoL experiences intense spring phytoplankton blooms [Fabres et al., 2008; Sanchez-Vidal et al., 2009; Tesi et al., 2010]. The phytodetritus settling from the upper ocean to the seafloor are subsequently included in the dense plume flowing off the shelf and laterally advected to the slope, and eventually to the basin, constituting a labile pool of OC available for benthic communities [Company et al., 2008].

[6] Besides off-shelf export, other studies showed that shear stress associated with these down-canyon flows in turn causes significant seafloor erosion of old strata, particularly at the canyon heads [Ogston et al., 2008; Palanques et al., 2008]. In these conditions, cascading currents carrying coarse particles are able to generate erosive sedimentary furrows and truncation of surface reflectors [Canals et al., 2006; Lastras et al., 2007; Puig et al., 2008; García-García et al., 2010] causing the outcropping of old strata to the modern seafloor.

## 3. Methods

### 3.1. Sampling

[7] Sediment cores were collected along the sediment dispersal system, including inner shelf, middle shelf, outer

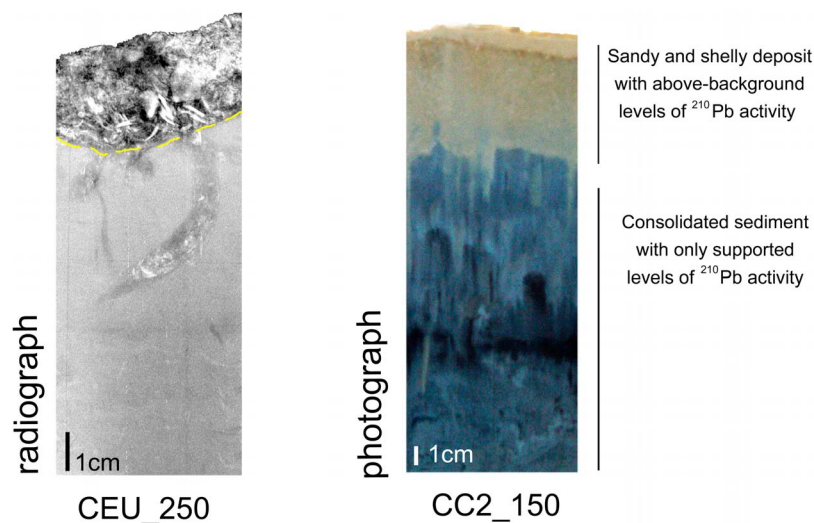


**Figure 1.** (a) Circles show the locations around the world where dense water cascading occurs [Ivanov *et al.*, 2004; Durrieu de Madron *et al.*, 2005]; open square indicates the study area. (b) Map of the study area in the Gulf of Lions (GoL). Open circles, diamonds, and squares indicate the location of surficial sediments in the inner, mid-, and outer shelf, respectively. Crosses show the location of sediment cores collected at Cap de Creus Canyon (CCC) head. The blue dot and the red square indicate the location of the mooring lines deployed in CCC and Lacaze-Duthiers Canyon (LDC), respectively. The arrow shows the direction of the Liguro-Provençal current (LPC). The dashed line shows the extent of midshelf mud deposit. (c) Detail of the southwestern GoL.

shelf, and the heads of CCC and LDC (Figure 1) in October 2004 (Rhône prodelta), February 2005 (canyon heads), and April 2005 (canyon heads and shelf) onboard the *R/V Oceanus* and *R/V Endeavor*. Samples were collected using a  $20 \times 30 \times 60$  cm box corer. Cores were then subsampled using a 15 cm PVC liner extruded and sliced at 1 cm intervals on the ship.

[8] Instrumented moorings were deployed in the thalwegs of CCC and LDC at 300 m depth and left in place from November 2003 until April 2004 (Figure 1). Each mooring was equipped with a sediment trap (Technicap PPS-3) and a current meter (Aanderaa RCM-11) equipped with temperature, conductivity, pressure, and turbidity sensors. Sediment traps and current meters were deployed at 30 m and 5 m above the seafloor, respectively. Frequency collection for

the sediment traps was 7 days. The sampling interval of the current meter was set to 20 min. Temperature and conductivity data were calibrated using CTD casts. Turbidity values (optical backscattering data) were calibrated in Formazin turbidity units (FTU) and were converted into suspended sediment concentration (SSC) following the calibration curve described in Guillén *et al.* [2000]. Sediment trap cups were filled with a buffered 5% formaldehyde solution in  $0.45\text{-}\mu\text{m}$ -filtered seawater (buffered with sodium borate). After sediment trap recovery, samples were stored at  $4^\circ\text{C}$  until analysis. After decantation of the supernatant, trapped material was wet sieved through a 1 mm nylon mesh to retain the large swimming organisms. The remaining swimmers were picked at the microscope. Using a wet sampler divider, each sample was then precisely divided into



**Figure 2.** X-ray radiograph of core CEU250 and photograph of core CC2\_150 [from DeGeest *et al.*, 2008] collected in the upper reaches of CCC. Their location is shown in Figure 1b as crosses.

subsamples for subsequent analyses. Sediment trap samples from November through December 2004 are not available for CCC because of a mechanical failure.

### 3.2. Analytic Methods

[9] Samples for stable isotopic analyses of OC ( $\delta^{13}\text{C}$ ) were preacidified in glass tubes to remove the inorganic carbon (1.5 M HCl). Acidified samples were then placed in the oven (50°C) and ground once dry. Carbon stable isotope composition was measured using a ThermoQuest-Finnigan Delta Plus XL, which was directly coupled to the Carlo Erba NA1500 Elemental Analyzer by means of a CONFLO II interface. NIST standards were used as reference for the mass spectrometer calibration. Uncertainties were lower than  $\pm 0.2\%$  as determined from replicates of the same samples. Alkaline CuO oxidations were carried out on the basis of the protocol described in Goñi and Montgomery [2000]. The yields of individual lignin and nonlignin oxidation products were quantified by GC-MS. The reaction products were separated chromatographically in a 30 m  $\times$  250  $\mu\text{m}$  DB1 (0.25  $\mu\text{m}$  film thickness) capillary GC column using an initial temperature of 100 °C, a temperature ramp of 4 °C/min, and a final temperature of 300 °C. CuO reaction products were quantified according to the procedure described in Goñi *et al.* [1998].

[10] Radiocarbon analyses were performed at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS, Woods Hole Oceanographic Institution). The  $\text{CO}_2$  samples were obtained by the combustion of bulk OC from preacidified samples to remove the inorganic fraction. The gas was then purified cryogenically and converted to graphite using hydrogen reduction with an iron catalyst. The graphite was pressed into targets, which were analyzed on the accelerator along with standards and process blanks. Oxalic Acid II (NIST-SRM-4990C) was the primary standard used for all  $^{14}\text{C}$  measurements. Radiocarbon measurements results are reported as  $\Delta^{14}\text{C}$  (‰) and age (years

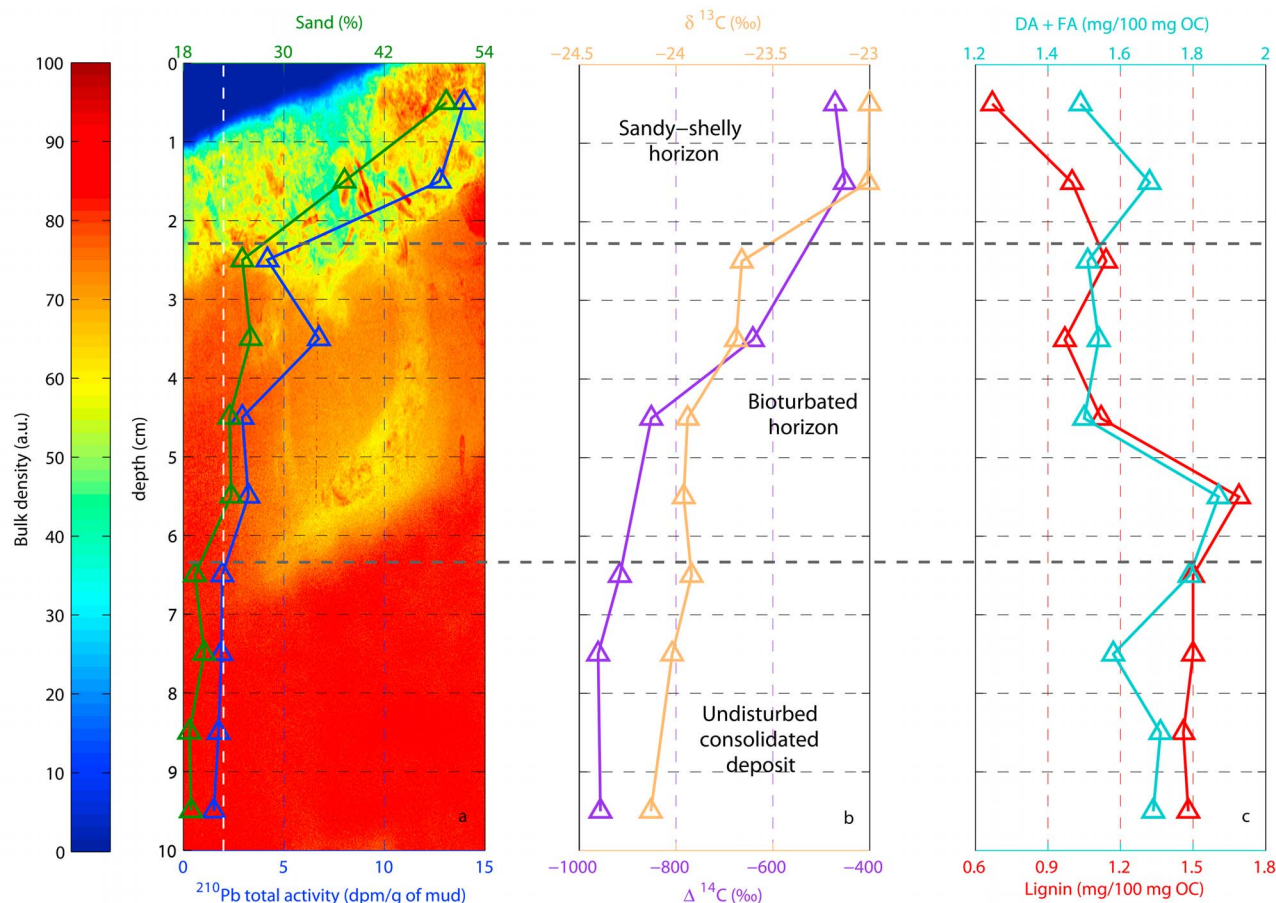
before present, ybp). For further details on the radiocarbon dating, please visit <http://www.nosams.whoi.edu>.

[11] Sediment samples from the cores were sieved with a 63  $\mu\text{m}$  mesh. The fraction  $<63 \mu\text{m}$  was used for  $^{210}\text{Pb}$  analyses [Nittrouer *et al.*, 1979]. An aliquot of dry and homogenized sediment was spiked with a known amount of  $^{209}\text{Po}$ . Digestion was carried out with 15.8 N  $\text{HNO}_3$  and 6 N HCl. Then  $^{209}\text{Po}$  and  $^{210}\text{Po}$  (the granddaughter of  $^{210}\text{Pb}$ ) were plated onto silver planchets and counted by  $\alpha$ -spectroscopy to determine the total  $^{210}\text{Pb}$  activity. The activity of  $^{210}\text{Pb}$  is determined by counting the  $\alpha$  activity of the  $^{210}\text{Po}$  daughter. The  $^{210}\text{Pb}$  activity is reported as *disintegrations per minute per gram of mud* (dpm  $\text{g}^{-1}$ ).

## 4. Results and Discussion

### 4.1. Erosion at the Shelf Break as Potential Source of Aged OC

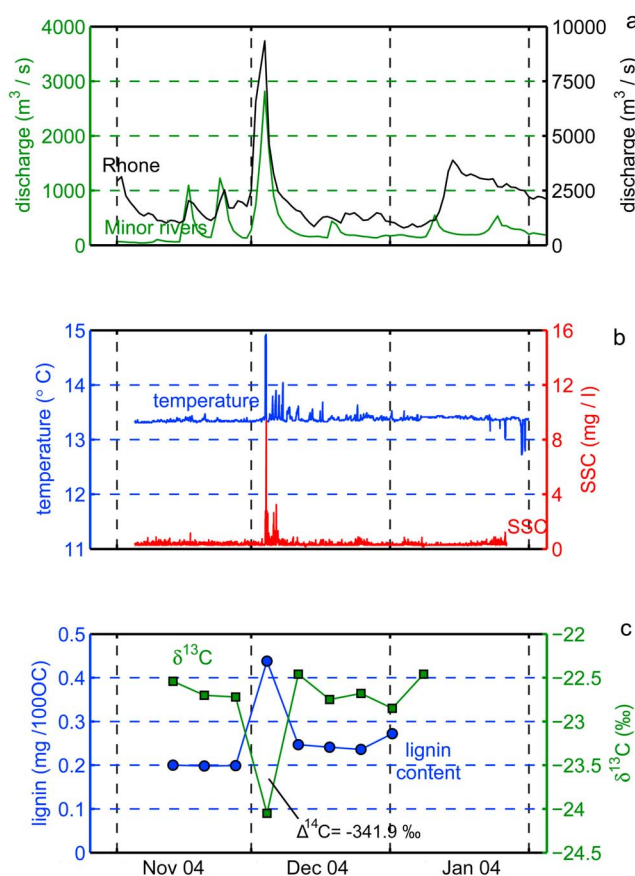
[12] Submarine canyon heads in the southwestern GoL are characterized by modern erosive truncations of seismic reflectors at the seafloor. In CCC head, these erosive features have been attributed to DWC and sediment failures by several geophysical studies that observed chaotic facies and megascale sediment furrows [Canals *et al.*, 2006; Lastras *et al.*, 2007; García-García *et al.*, 2010]. In a recent study, DeGeest *et al.* [2008] described the whole upper CCC head (from  $\sim 150$  to  $\sim 400$  m water depth,  $\sim 7.5 \times 10^6 \text{ m}^2$ ) as an active erosive system on the basis of X-radiographs and  $^{210}\text{Pb}$  profiles of sediment cores. A common feature of these sediment cores was a shelly-coarse surface layer (brown color in the photograph in Figure 2) overlying a basal consolidated mud deposit (dark gray color in Figure 2). This coarse surface layer was found to have relatively constant and above-background levels of  $^{210}\text{Pb}$  activity (half-life 22.3 years), indicating relatively recent deposition within the last 100 years. Conversely, the underlying consolidated deposit only displayed  $^{210}\text{Pb}$  activity in secular equilibrium



**Figure 3.** Compositional analyses of sediment core CEU\_250. (a) Color bar (arbitrary unit, a.u.) shows the relative sediment bulk density mainly driven by the water content in the X-ray radiograph (see Figure 2) and the sand grain-size content shows a coarse-grained layer relatively hydrated (~2 cm thick) overlying consolidated deposit. The  $^{210}\text{Pb}$  activity displays a distinct shift at the coarse-fine sediment interface, indicating not steady accumulation, but rather erosion of the underlying aged deposit. The dashed white line shows the supported  $^{210}\text{Pb}$ . (b)  $\Delta^{14}\text{C}$ ,  $\delta^{13}\text{C}$ . (c) Alkaline CuO reaction products (dicarboxylic acids, fatty acids, and lignin phenols).

with the decay of its parent in the sediment column, indicating that the emplacement of this basal sediment occurred over a century ago. Therefore, the distinct activity change in the down-core profile observed in CCC head was interpreted as an evanescent layer of relatively modern sediment (<120 years) atop an eroded older deposit (>120 years, the age limit of  $^{210}\text{Pb}$  dating) [DeGeest *et al.*, 2008]. To understand the composition of this consolidated basal deposit, down-core biogeochemical analyses were carried out on one of these cores (CEU\_250) collected at the canyon head (Figures 1–3). Vertical profiles of  $^{210}\text{Pb}$  activity and sand grain-size content show the aforementioned erosive discontinuity between the coarse upper sediment and the basal deposit at ~2 cm below the seafloor (Figure 3a). The upper coarse layer shows relatively low  $\Delta^{14}\text{C}$  values (mean  $\Delta^{14}\text{C} = -461 \pm 14.4\text{‰}$ ), whereas the OC included in the consolidated basal deposit displays extremely depleted  $^{14}\text{C}$  values (mean  $\Delta^{14}\text{C} = -944.5 \pm 24.7\text{‰}$ , close to the limit of detection), with a mean age of  $23,650 \pm 3,321$  ybp indicating a significant contribution from aged OC (Figure 3b).

This ancient material displays relatively abundant hydrolysis-derived products, including lignin phenols ( $\Delta$ ), fatty acids (FA), and dicarboxylic acids (DA) (Figure 3c), although the relative proportion of these compounds might have changed through time due to selective degradation processes [Hedges and Prahl, 1993]. Regardless, the relatively high abundance of these hydrolysis-derived products indicates that this aged material is compositionally distinct from bedrock-derived OC (i.e., petrogenic OC) eroded from land and supplied by rivers to the ocean [Berner, 1989; Raymond and Bauer, 2001; Blair *et al.*, 2003; Goñi *et al.*, 2005; Leithold *et al.*, 2006; Copard *et al.*, 2007]. Petrogenic OC included in sedimentary rocks occurs mainly in the form of kerogen, defined as solvent-insoluble, non-hydrolyzable OM that has undergone slow thermal degradation at elevated pressures during sedimentary rock formation for millions of years. In contrast, the presence of lignin phenols and the radiocarbon age of this consolidated basal deposit ( $23,650 \pm 3,321$  ybp) suggest that this material was approximately accumulated throughout the last falling



**Figure 4.** Temporal variability of physical and biogeochemical parameters before the cascading season during an extreme flood event in the GoL (from November through January 2004). (a) Water discharge from Rhône River and from minor rivers (Aude, Tet, Orb, and Hérault). (b) Suspended sediment concentration (SSC) and temperature measured in LDC head at 5 m above the seabed. (c) Lignin content,  $\delta^{13}\text{C}$ , and  $\Delta^{14}\text{C}$  values measured in the suspended material in LDC head at 30 m above the seabed.

stage of sea level, when terrigenous OC deposition occurred mainly on the upper slope during seaward migration of the rivers during the Last Glacial Maximum (~21,000 ybp) [Baztan *et al.*, 2005]. It is worth highlighting that this is a rough estimate because  $^{14}\text{C}$  raw dates cannot be used directly as exact calendar dates. First, the concentration of  $^{14}\text{C}$  in the atmosphere has not been strictly constant since the end of the Pleistocene. Second, these  $^{14}\text{C}$  dates do not take into account the reservoir time before the burial. Finally, these are bulk measurements, and therefore the  $^{14}\text{C}$  age is practically an averaged value of the different OC sources. Despite these uncertainties,  $^{14}\text{C}$  data and lignin phenols clearly indicate the influence of an aged terrigenous source of OC that was likely deposited on the slope more or less during low stand of sea level. After the emplacement, if hemipelagic fallout prevailed over erosion, this carbon should be buried under younger deposits during the Holocene. Conversely, the erosive discontinuity suggests that this

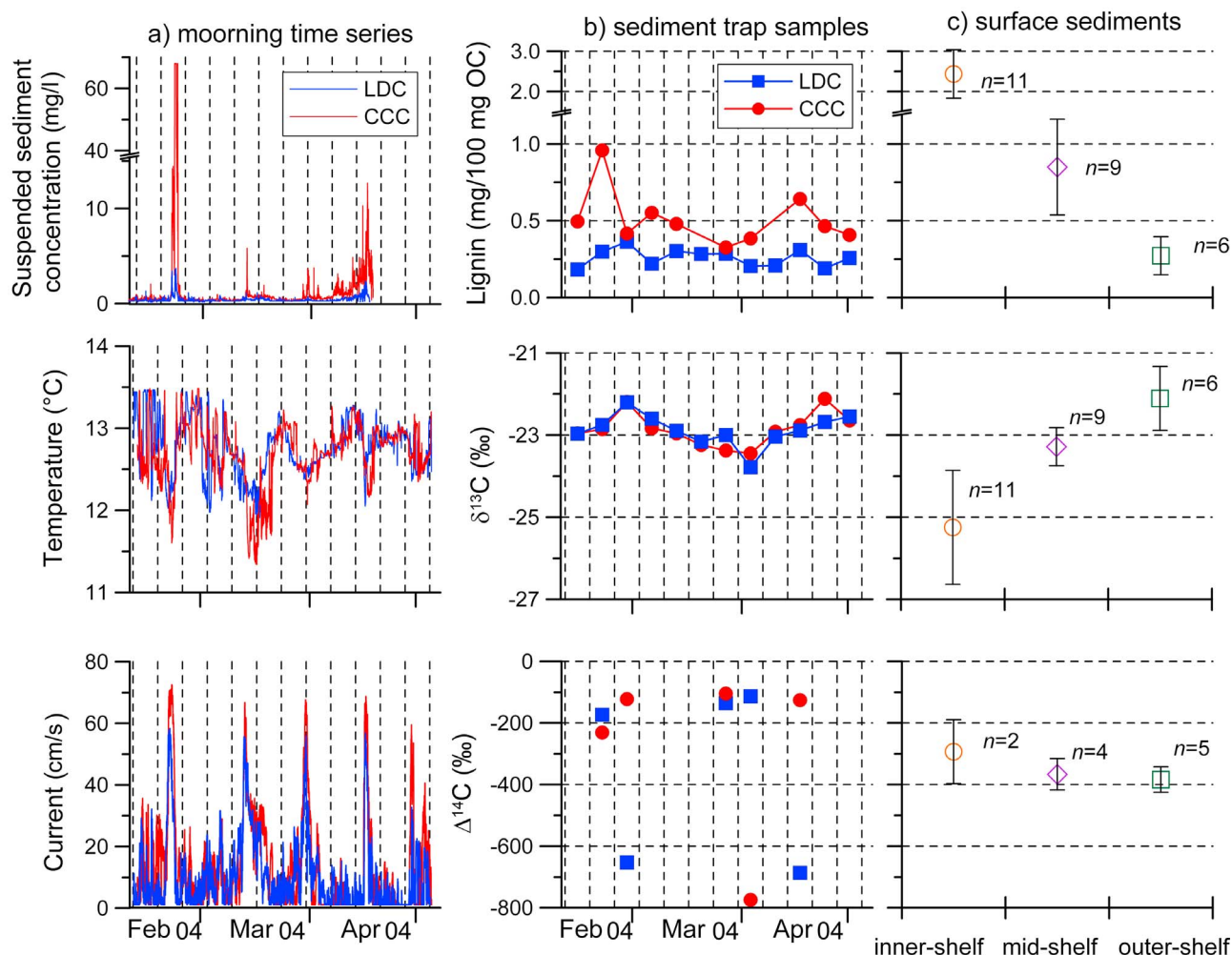
pool of OC has been temporarily buried for several thousand years until erosive processes on the slope remobilize old strata via mechanical erosion. Puig *et al.* [2008] reported a significant sand content (up to ~70%) in suspended sediments collected within sediment traps deployed 30 m above the seafloor within the CCC throughout the cascading season. The authors inferred that mobilization of coarse material from the outer shelf during extreme DWC is sufficient to abrade old strata within the canyon, allowing for the formation of erosive sedimentary furrows [Canals *et al.*, 2006; Puig *et al.*, 2008] and thus allowing for the cropping out of aged OC to the modern seafloor and consequently the reexposure of aged OC to the active carbon cycle.

[13] Although oxygen and redox profiles are not available for these cores in the upper slope, the geologic setting of these deposits coupled with visual images of the sediment cores (Figure 2) suggest that the consolidated material was temporarily buried under anoxic conditions during sediment accumulation and now is reexposed to an oxic environment at the coarse-fine sediment interface. In addition, the radiograph of core CEU\_250 in Figure 2 displays clear evidence of bioturbation at the core top, implicating biological activity, in parallel with the physical erosion, as a contributor to reworking as well as oxygen penetration [Warme *et al.*, 1971].

#### 4.2. Sediment Traps

[14] Evidence from sediment traps deployed at the canyon head of CCC and LDC heads suggested that this aged OC, besides being reexposed to the active carbon cycle, can be mobilized during the cascading season. These sediment traps were deployed at CCC and LDC heads at ~300 m water depth from November 2003 to April 2004, when the GoL experienced a significant flood and five DWC events [Palanques *et al.*, 2006; Ulses *et al.*, 2008]. The December 2003 flood of the Rhône River was particularly remarkable (Figure 4a), with discharge reaching nearly 10,000 m³ s⁻¹ (75 year flood; Palanques *et al.* [2006]). This event was coupled with an intense southeastern storm that caused re-suspension of shelf sediments and induced downwelling of relatively warm and turbid shelf water into the CCC and LDC (Figure 4b) [Palanques *et al.*, 2006]. During the flood, anomalies in lignin and  $\delta^{13}\text{C}$  were recorded in the LDC head (Figure 4c), and MODIS images of the GoL showed the pathway of the turbid surface plume moving along and across shelf above sediment trap locations [Palanques *et al.*, 2006], suggesting that a certain fraction of land-derived material reached the upper slope.

[15] Concerning the cascading season (February–April 2004), five DWC events were triggered by southeasterly storms that enhanced the downwelling of unstable dense water masses off the shelf (Figure 3a). Moored instruments deployed at the canyon heads recorded these events as rapid drops in water temperature of 1–2 °C and sharp increases in the current speed (~70 cm s⁻¹). Most of the off-shelf export of sediment occurred in February, when a major peak in SSC was recorded [Palanques *et al.*, 2006; Ulses *et al.*, 2008]. The major component in the downslope fluxes is thought to be resuspended shelf sediment [Palanques *et al.*, 2008] advected predominantly from the northwest and in

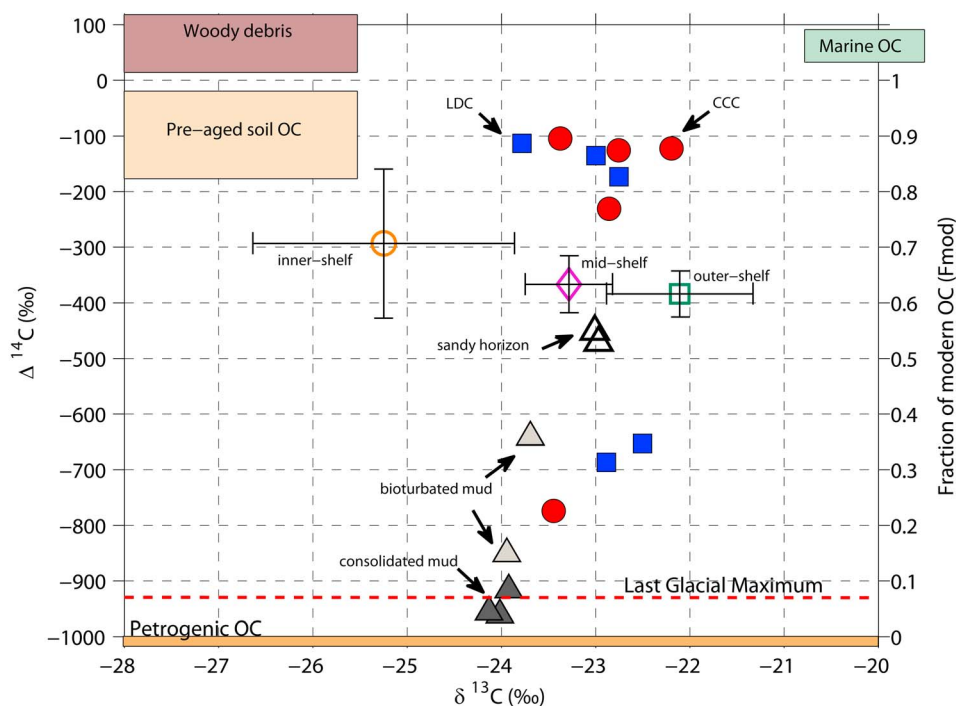


**Figure 5.** Spatial and temporal variability of physical and geochemical parameters in the GoL. (a) Temporal evolution of suspended sediment concentration, temperature, and current speed in CCC (red line) and LDC (blue line) (from February through April 2005). (b) Temporal evolution of lignin content,  $\delta^{13}\text{C}$ , and  $\Delta^{14}\text{C}$  in CCC (red circles) and LDC (blue square) (from February through April 2005). (c) Mean value of lignin content,  $\delta^{13}\text{C}$ , and  $\Delta^{14}\text{C}$  with relative standard deviation in the GoL shelf surficial sediment (0–1 cm). Samples were grouped on the basis of water depth: inner shelf, midshelf, and outer shelf.

particular from the Rhône River (Figure 1), which supplies ~90% of the sediment to the GoL [Bourrin and Durrieu de Madron, 2006]. Specifically, southeasterly storms caused resuspension of Rhône prodeltaic deposits generating an along-shelf cyclonic mud belt (Figure 1) that bypasses the LDC head and, upon reaching Cap de Creus promontory, deviates its path toward the southern flank of CCC [DeGeest *et al.*, 2008], explaining the differences in SSC and lignin content (i.e., terrigenous biomarker) in the suspended material between LDC and CCC (Figures 5a and 5b).

[16] As the major source of the sediment in the downslope fluxes are shelf deposits [Palanques *et al.*, 2008; Ulses *et al.*, 2008], suspended materials collected during the DWC season might be expected to exhibit radiocarbon ages consistent with values observed for the shelf sediments, and indeed most of them do (Figure 5b). However, some of the

sediment trap samples (i.e., three samples) displayed OC compositions highly depleted in  $^{14}\text{C}$  ( $\Delta^{14}\text{C}$  from  $-652.8$  to  $-773.9$  ‰,  $^{14}\text{C}$  ages from ~8,500 to ~12,000 ybp), indicating a significant contribution from a  $^{14}\text{C}$ -poor source such as aged OC. It could be speculated that this aged OM was supplied by rivers in the form of petrogenic OC during flood events and then advected across-shelf as a result of DWC. However, surface samples (0–1 cm) collected from the Rhône prodelta ( $\Delta^{14}\text{C} = -198.6$  ‰) and along the sediment transport system ( $\Delta^{14}\text{C} = -366.6 \pm 51.1$  ‰) do not exhibit extremely depleted  $^{14}\text{C}$  values, consistent with previous studies that observed modern OC in the Rhône prodelta area and more depleted  $^{14}\text{C}$  ages along the mud belt [Stanley, 2000; Cathalot, C., C. Rabouille, N. Tisnerat-Laborde, R. Buscail, P. Kerherve, and G. Gontier (2010), Sources and fate of particulate organic carbon export from



**Figure 6.** OC origin in sediment trap samples. Five different sources (marine phytoplankton, C3 woody debris, pre-aged C3 soil-derived OC, fossil, and aged OC from old strata) are included in the plot to show their contribution in the sediment trap samples. Radiocarbon measurements are reported as  $\Delta^{14}\text{C}$  (‰) and fraction of modern OC (Fmod). The symbols for sediment trap and surficial sediment samples are the same as in Figure 5. Standard deviations are the same as in Figure 5. The triangles show the composition of the uppermost coarse sediment (open symbols), the bioturbated mud (gray), and the preserved mud (dark gray) layers in the core CEU250 as delineated in Figure 3. The dashed red line corresponds to a  $^{14}\text{C}$  age of 21,000 ybp.

the Rhône River in the Mediterranean Sea: combined use of  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$ , Submitted]. Slightly more  $^{14}\text{C}$ -depleted values were observed in local surface sediments collected in the Tet river prodelta ( $\Delta^{14}\text{C} = -388.1$  ‰) and in the outer shelf next to the canyons ( $\Delta^{14}\text{C} = -383.8 \pm 41.5$  ‰), but these are still incomparable to the anomalously aged suspended sediments. In Figures 5c and 6, all these samples were grouped on the basis of the water depth to show their mean values and standard deviations relative to the suspended material trapped at the canyon heads. Shelf surface sediment samples exhibited significantly younger radiocarbon age relative to those three  $^{14}\text{C}$ -depleted samples, suggesting that the contribution of aged OC in these samples is somehow independent from shelf advection. In addition, suspended material collected at LDC head during the December 2003 flood (Figure 4c) did not display particularly depleted  $\Delta^{14}\text{C}$  values ( $-341.9$ ‰), weakening the hypothesis of significant fossil OC being supplied from land during flood events as observed in other systems [Masiello and Druffel, 2001]. Finally, because the land-derived material is more efficiently exported via CCC during DWC events (Figure 3), we would have expected to see a distinct difference in radiocarbon ages between the two canyons as observed for lignin values and SSC (Figure 5).

#### 4.3. OC Mixing and End-Members

[17] While our results do not support the hypothesis that land-derived petrogenic material was the major source of  $^{14}\text{C}$ -depleted OC in the suspended material at the canyon heads, multiple evidence from the sediment cores coupled with previous geophysical studies point toward the erosion of paleodeposits in the upper slope as the potential source of aged OC. However, some trends in our data set are not completely understood in terms of OC mixing, and more work is needed in this area to better constrain the biogeochemical compositions of the sediments at the canyon heads.

[18] For example, the influence of the aged consolidated deposit in downslope fluxes is somewhat difficult to establish on the basis of  $\delta^{13}\text{C}$  that exhibits a synchronous temporal trend in CCC and LDC with no apparent relationship to the  $\Delta^{14}\text{C}$  data (Figure 5b). It is worth noting that, in addition to OC from resuspended deposits, sediment traps in submarine canyons collected fresh phytodetritus as suggested by the concentration of chloropigments in our sediment trap samples [Fabres et al., 2008]. This material, in addition to having higher  $\Delta^{14}\text{C}$  ratios than sedimentary OC due to its comparatively young age, exhibits relatively enriched  $\delta^{13}\text{C}$  with a broad range of values (from  $-21.1 \pm$

0.7‰ to  $-18.7 \pm 0.5$ ‰) as shown by an in situ study carried out in the GoL the same year as the sediment trap deployments [Harmelin-Vivien *et al.*, 2008]. In terms of OC mixing, the advection of deposits from mid- and outer shelf and slope environments (core CEU\_250) in different proportions would not significantly affect the  $\delta^{13}\text{C}$  as the mean isotopic signature of these sediments is relatively similar ( $-23.3 \pm 0.5$ ‰,  $-22.1 \pm 0.8$ ‰, and  $-23.7 \pm 0.4$ ‰, respectively, see Figures 5 and 6). Therefore, this might indicate that the aforementioned diversity in the marine phytodetrital signature has influenced the temporal variance of the  $\delta^{13}\text{C}$  in the sediment trap samples, explaining the synchronous temporal trend in both canyons. It is certain that the dilution with fresh marine phytoplankton affected the  $\Delta^{14}\text{C}$  values in the sediment trap samples, which exhibit overall younger radiocarbon ages ( $\sim +200$ ‰) than sedimentary OC from shelf deposits (Figure 5). As fresh chloropigments were also measured in those extremely depleted sediment trap samples [Fabres *et al.*, 2008], it is likely that the dilution with modern OC occurred in these samples, too. As a result, the radiocarbon values of the aged material might be even more  $^{14}\text{C}$ -depleted than the measured bulk  $^{14}\text{C}$  values.

[19] In terms of OC mixing, the lignin phenols present a different problem. The lignin content, which we might expect to predictably increase with a decrease in radiocarbon values, consistent with the composition of the basal deposit collected at CCC head (Figure 3c), fails to do so. However, this aged material might be supplied from other old deposits within the canyon head, where the OC composition is likely to be variable as a result of the different emplacement mechanisms related to differing eustatic stages (e.g., transgressive versus regressive). Indeed, sediment samples from the lowermost intervals of box cores collected in CCC head [Garcia-Garcia *et al.*, 2007] display relatively variable  $\delta^{13}\text{C}$  isotopic compositions, suggesting that the aged OC is compositionally heterogeneous even within a single canyon head and certainly between canyons, consequently compromising the use of the consolidated basal deposit as a distinct end member.

#### 4.4. Implications

[20] The conceptual model that we are describing in this study can be essentially divided into two separate sub-processes: outcropping of aged OC as result of gravity-driven flows and potential transport of this reexposed OC to the interior ocean. Both processes have been observed on globally distributed slopes during rises and high stands of sea level, suggesting that this model can be broadly applied to Holocene systems. For instance, erosive truncations of reflectors at the modern seafloor induced by active gravity-driven flows were observed on a variety of disparate slopes, including the Eastern Black Sea [Dondurur and Cifci 2007], Iberian Atlantic Margin [Hernandez-Molina *et al.*, 2008], East Antarctica [de Santis *et al.* 2007], and Mediterranean Sea [Trincardi *et al.*, 2007]. In parallel, evidence of relocation of this eroded, aged OC is provided by irregular sequence of dated sections within Holocene stratigraphy. For example, in the Monterey Canyon (North Pacific), where the modern erosion at the canyon head outpaces deposition due to frequent submarine landslides, Paull *et al.*

[2006] observed extremely  $^{14}\text{C}$ -depleted clay clasts (mean  $\Delta^{14}\text{C} = -977.2 \pm 30.7$ ‰) included within contemporary gravity deposits, providing further evidence of physical erosion of paleodeposits from the upper canyon reaches. Similarly, along the New Jersey slope and rise (North Atlantic), Stanley *et al.* [1984] observed irregular  $^{14}\text{C}$  dates in bulk sediments within late Holocene deposits as result of episodic sediment failures.

[21] Although it is well acknowledged that gravity-driven processes are enhanced during falling or low sea level [Lee, 2009], an obvious question remains: Is this erosion and relocation of aged OC sufficient to affect the age of dissolved and particulate OC of the interior ocean during the Holocene, and, if this is the case, what is the extent of its importance? A key consideration in evaluating this contribution to the carbon cycle is the frequency and spatial distribution of these erosive events. A survey of the current literature reveals relatively broad coverage and a wide spectrum in the frequency of erosional events, from seasonal to millennial scales. For instance, a semiannual pattern of erosion was observed in the upper Monterey canyon in the North Pacific [Smith *et al.*, 2005]. On centennial scales, tsunamogenic landslides from the past 80 years have been reported in the Grand Banks (1929, Canada; [Lee *et al.*, 2006]), Nice (1970, France; [Seed *et al.*, 1988]), Kitimat (1975, British Columbia; [Prior *et al.*, 1982]), and Papua New Guinea (1998; [Tappin *et al.*, 2003]). In some areas, such as in the North Pacific along the Cascadia subduction zone and Northern San Andreas fault, large earthquake-driven sediment failures occurring simultaneously along over a thousand miles of margin have been observed with periodicities of a few thousands years [Goldfinger *et al.*, 2003]. On the basis of empirical data, Shanmugam [2008] estimated that  $\sim 200,000$  tropical cyclones (Indian and Atlantic oceans) and  $\sim 140,000$  tsunamis (Pacific Ocean) occurred during the present high-stand interval, allowing for significant transport of sands and gravels to deep water as a result of turbidites and debris flows. Considering the erosive nature of these processes, it seems likely that the outcropping and erosion of aged OC occurs on margins around the globe as clearly observed in our study area and in Monterey Canyon [Paull *et al.*, 2006].

#### 5. Conclusions

[22] A few years ago, Raymond and Bauer [2001] published a pioneering study to illustrate that rivers are a source of old particulate OC. Following this, several studies have focused their attention on erosion of fossil OC on land and subsequent reburial in marine sediments [Masiello and Druffel, 2001; Blair *et al.*, 2003; Dickens *et al.*, 2004; Goñi *et al.*, 2005; Hwang *et al.*, 2005; Komada *et al.*, 2005; Leithold *et al.*, 2006]. However, although our understanding of fluvial carbon supply is becoming reasonably refined in terms of magnitude [Ludwig and Probst, 1998; Copard *et al.*, 2007], global estimates of aged OC in the ocean do not account for the role of gravity-driven flows occurring in the slope as a potential source of aged OC. Although some trends in our data set are not entirely understood yet, this study suggests the existence of an additional source of aged OC

supplied to the ocean in parallel with the riverine supply. This aged material derives from OC included in consolidated sediments deposited at the upper continental slope during low stands of sea level. Erosion processes at the shelf edge reexpose this pool of aged OC, temporarily buried in marine sediments, to physical disturbance, as well as to chemical and biological degradation. Further studies in this direction are needed to better understand the magnitude of this reexposure as well as other important aspects, such as the reactivity of this aged OC to the oxic environment and its influence on other carbon pools, including the dissolved phase.

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