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Early diagenesis in the Congo deep-sea fan sediments dominated by massive terrigenous deposits: Part I – Oxygen consumption and organic carbon mineralization using a micro-electrode approach

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ABSTRACT

Organic matter (OM) transfer from the continent to the ocean occurs across margins which constitute a major area of OM recycling and burial. The lobe complex of the Congo deep-sea fan is connected to the river mouth by a canyon and alimented by recurrent turbidity currents, containing a large proportion of labile terrigenous OM and producing high sedimentation rates. These inputs support the development of ecosystems harboring rich assemblages of vesicomyid bivalves and bacterial mats, called Habitats. Here, we present O_2 microprofiles and diffusive oxygen uptake rates (DOUs) obtained during the CONGOLOBE project at six sites of this active lobe complex by *in situ* and on-board methods based on micro-electrode profiling. The dataset is used to determine remineralization rates and study the biogeochemical dynamics of different ecosystems of the lobe area, in order to compare levee and background sediments to the Habitats developed on the flanks of the main turbiditic channel. Levee and background sediments are characterized by significantly higher DOUs than abyssal sediments at 5000 m meters depth (2–5 mmol O_2 m^{-2} d^{-1} *versus* 1.5–2.5 mmol O_2 m^{-2} d^{-1}) and the Habitats are hotspots of OM remineralization with DOU values ranging between 8 and 40 mmol O_2 m^{-2} d^{-1}. By comparing sites near the active channel to a site located 50 km away, we show that the lobe connection to the main turbiditic channel is vital to the dense benthic communities.

1. Introduction

Continental margins represent the transition zone between land and the open ocean and are an area of active carbon transfer (Spitzy and Ittekkot, 1991), due to river discharge and subsequent sedimentary deposition and recycling in river deltas. It has long been recognized that margins are an important compartment in the global carbon cycle (Degens et al., 1991) and that they host productive and diverse pelagic and benthic ecosystems. The Congo River system, in particular, is unique: it is the second largest river in the world by water discharge (Milliman, 1991) and it is the only large river on the planet to be still connected to its submarine canyon (Babonneau et al., 2002). These two characteristics allow a massive transfer of particles and particulate organic matter (POM) from land to the river mouth and to the deep ocean, through strong turbidity currents that flow up to 60 times per century in the canyon (Heezen et al., 1964) and up to 16 times per century in the Congo fan lobe complex (Dennielou et al., In this issue) and transport sediments down the canyon and channel/levee systems (Babonneau et al., 2002; Savoye et al., 2009b). Efforts have been made in the last 15 years to unravel the mechanisms underlying the long-term functioning of the Congo fan region through a series of programmes (ZAIANGO, 1998–2003; Savoye et al., 2000; BIOZAIRE, 2000–2005; Sibuet and Vangriesheim, 2009) and these have provided extensive information on the geology and sedimentology. However, limited information regarding the biogeochemistry and biology of the active lobe area were available. On the most recent lobes of the fan, video surveys using a Remotely Operated Vehicle (ROV) showed biological assemblages similar to those found in cold seep areas (Rabouille et al.,

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In this issue). These communities differ from one another but are composed of microbial mats and *Vesicomyidae* bivalves macrofaunal species that harbour sulphide-oxidizing symbionts (Decker and Olu, 2010; Fiala-Médioni and Felbeck, 1990). Three distinct assemblages were identified and will be referred to here after as "Habitats" (Rabouille et al., In this issue). The relation between the existence of these Habitats and the mineralisation of organic matter (OM) which takes place in the lobes of the Congo fan, was questioned: indeed, intense mineralization may promote sulfate reduction, producing hydrosulfide (HS^-) which could then be used by sulfur-oxidizing bacteria, living in mats or in symbiotic association with the bivalves (see Pastor et al., In this issue; Taillefert et al., In this issue).

The recent CONGOLOBE project (2012–2016) focused on the channel-mouth lobe complex of the Congo River deep-sea fan and produced an important multidisciplinary dataset. Different sites located inside the channel and on the levees were investigated and Habitats compared to background sediment areas. The aim of the present study is to quantify the rates of oxygen consumption and OM remineralization in the lobe region in order to unravel the benthic functioning of the active part of the fan system. We present a large set of oxygen microprofiles that were collected both *in situ* and *ex situ* on background and Habitat sediments. Diffusive fluxes, calculated using these microprofiles, are used as a proxy for OM remineralization rates (Wenzhofer and Glud, 2002 and references therein). We compare these remineralization rates with biogeochemical descriptors of the OM (Stetten et al., 2015) to discuss the hypothesis that the "Habitats" are important hotspots of terrigenous and riverine OM processing and that they depend upon the OM delivered by the turbidity currents to develop and thrive.

2. Materials and methods

2.1. Sites description and sampling

A precise and complete description of the Lobe area and the sampling sites can be found in Rabouille et al. (In this issue). Sites A, B, C, D, E and F were visited and sampled during the CONGOLOBE cruise (Dec 2011-Jan 2012) and all corresponding data are presented; A, C and D were visited also during the WACS cruise (Feb 2011) and the related data are reported here; Table A1 in the Supplementary material describes all samplings per each site. As shown in Fig. 1, the Lobe area is located outside the central-western coast of Africa, off the States of the Congo, Democratic Republic of Congo and Angola, 800 km offshore of the Congo River Mouth, between 4700 m and 5000 m depth alongside the main active channel of the river submarine canyon. Site A is located at the entrance of the lobe complex where a channel-levee has developed. Site F is located downstream where the channel becomes larger and shallower. Site C is located further downstream where the channel has nearly vanished and where the most recent lobe of the lobe complex develops. Site D is located further downstream at the fringe of the most recent lobe. Site B is located near an abandoned channel on the levee located on the north side of the active channel. Site E is located ca. 50 km to the north on another, abandoned, lobe complex that is not connected anymore to the active turbiditic channel. Details on sites and lobe complex morphology, structure and sedimentary processes can be found in Dennielou et al. (In this issue) and Croguennec et al. (In this issue). Each site was sampled at two different station types: levees and channel. All of the sites presented two main types of ecosystems: on the levees and in most of the channel we found light-brown deep-sea sediments hosting burrowing deep-sea fauna (Olu et al., In this issue), on the flanks of the channel and the deposition zone, (mainly at Sites C and A but in limited amount also at Sites B and F)we found different types of biological assemblages referred to as "Habitats". These are patchily distributed (Sen et al., In this issue), have different dimensions (from decimeters to meters) and shapes but all present clear-cut edges, sometimes surrounded by an orange-yellow belt. They can be divided in four main types (Rabouille et al., In this issue): "Black sediment" constituted by reduced sediments, (Fig. 2A); Microbial mats with white filamentous microbes (Fig. 2B); Bivalve beds formed by bivalves of the *Vesicomyidae* family, sometimes associated to reduced sediments and microbial mats (Fig. 2C); "Iron crust", sediment characterized by an orange colour and crusty appearence, very rich in Fe.

The sediment cores used for this study were retrieved in two ways: by the ROV Victor 6000 (named "CT cores") inside or just few centimeters outside of the Habitats and by a multicorer (named "MTB cores") on the levees and in the channel. All MTB cores were therefore taken in areas where no Habitat was present and such sediment will be always referred to as "levee" or "background" sediment. The sediment retrieved by CT cores instead will always be referred to "Habitat" for the cores sampled inside each Habitat and "bare sediment" for those retrieved few cm outside the Habitat.

2.2. Oxygen profiling

Oxygen micro-profiles were measured in two different ways: *ex situ* and *in situ. Ex situ* profiling was carried out on the CTs and on the MTBs using a bench motor-driven micromanipulator interfaced to a computer (Revsbech, 1989; Revsbech and Jorgensen, 1986) (See Fig. 3A). The measurement were conducted in a temperature regulated room set at *in situ* temperature (2 °C) with gentle air bubbling to ensure constant oxygen and slow water mixing. *In situ* profiling was achieved *via* two devices. A standalone UNISENSE lander named DMPS "Deep Micro-Profiling System" (see Fig. 3B) was deployed by the ROV to specifically sample the Habitats and provide profiles very close one another to analyse the differences in a fine horizontal spatial scale: for instance, using this device it was possible to perform measurements inside a microbial mat and few centimeters right outside the border of such Habitat. A larger platform hosting different analytical tools including benthic chambers called RAP "Respiromètre Autonome Profond" (Deep Autonomous Respirometer), (see Fig. 2C and Rabouille et al., 2009a, 2009b) was also deployed on the levees and used to obtain microprofiles using a fixed profiling system. When available, *in situ* measurements made with the DMPS and the RAP were associated respectively to *ex situ* measurements done in CT and MTB cores. All oxygen profiles were made using the same UNISENSE® Oxygen microsensors OX-100, (outside tip diameter 100 µm, total length 150–200 mm, detection limit 0.3 µM, stirring sensitivity of < 1%, 90% response time 5 s, response type linear). In the laboratory, such microsensors are fixed on a support which is moved by a motor connected to a computer. The program selected by the user determines the movements of the sensor, pushing them into the core and making them penetrating the sediment at discrete depth steps and measuring at each interval. The vertical resolution of the measurements was 100–200 µm. Up to 6 oxygen profiles were performed for each core and each profile was later analyzed and calibrated separately, using bottom water oxygen values of 224 µmol/l obtained by Vangriesheim et al. (2009b) and *in situ* zero measurements in the anoxic zone. The signal of the oxygen electrodes is a linear function of oxygen concentration (Cai and Sayles, 1996), thus a calibration using bottom water oxygen concentrations and anoxic pore waters is sufficient. The position of the sediment – water interface (SWI) relative to each profile profiles was determined by assigning the interface position to a break in the oxygen concentration gradient, a modified version of the Sweerts et al. (1989) technique, where the position of the maximum gradient as the sediment–water interface is assigned to the SWI. Oxygen penetration depth (OPD) was determined by using the depth where the O_2 microelectrode signal reached a value < 0.8 µmol L^{-1}. Resistivity profiles were also measured using an electrode similar to that described by Andrews and Bennet (1981), which has a rectangular section of 10 × 3 mm and is edged at the lower end.

Diffusive Oxygen Uptake (DOU) was calculated from the calibrated