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IDENTIFICATION IN PORE WATERS OF RECYCLED SEDIMENT ORGANIC MATTER USING THE DUAL ISOTOPIC COMPOSITION OF CARBON ($\delta^{13}\text{C}$ AND $\Delta^{14}\text{C}$): NEW DATA FROM THE CONTINENTAL SHELF INFLUENCED BY THE RHÔNE RIVER

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ABSTRACT. Estuaries and deltas are crucial zones to better understand the interactions between continents and oceans, and to characterize the mineralization and burial of different sources of organic matter (OM) and their effect on the carbon cycle. In the present study, we focus on the continental shelf of the northwest Mediterranean Sea near the Rhône river delta. Sediment cores were collected and pore waters were sampled at different depths at one station (Station E) located on this shelf. For each layer, measurements of dissolved inorganic carbon concentration (DIC) and its isotopic composition ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$) were conducted and a mixing model was applied to target the original signature of the mineralized OM. The calculated $\delta^{13}\text{C}$ signature of the mineralized organic matter is in accordance with previous results with a $\delta^{13}\text{C}_{\text{OM}}$ of marine origin that is not significantly impacted by the terrestrial particulate inputs from the river. The evolution with depth of $\Delta^{14}\text{C}$ shows two different trends indicating two different $\Delta^{14}\text{C}$ signatures for the mineralised OM. In the first 15 cm, the mineralized OM is modern with a $\Delta^{14}\text{C}_{\text{OM}} = 100 \pm 17\%$ and corresponds to the OM produced during the nuclear period of the last 50 years. Deeper in the sediment, the result is very different with a depleted value $\Delta^{14}\text{C}_{\text{OM}} = -172 \pm 60\%$ which corresponds to the pre-nuclear period. In these two cases, the marine substrate was under the influence of the local marine reservoir effect with more extreme $\Delta^{14}\text{C}$ results. These differences can be largely explained by the influence of the river plume on the local marine DIC during these two periods.

KEYWORDS: pore waters, radiocarbon AMS dating, rivers, sediments, stable isotopes.

INTRODUCTION

A better understanding of the carbon cycle at the land-ocean interface is crucial to assess the influence of terrestrial inputs and the anthropic impact on the coastal seas (Bauer et al. 2013; Bianchi and Allison 2009). Deltas are particularly active in biogeochemical cycles because, despite their small surface areas compared to the oceans (0.3%), they represent nearly half of all the carbon buried in oceanic sediments (Bernier 1982). These large accumulations of organic matter (OM) are accompanied by high mineralization rates and are a major source of CO_2 production, representing one fourth of the CO_2 absorbed by the whole ocean (Cai 2011). It is thus essential to properly constrain and understand the characteristics of OM deposited in deltaic sediments: its origin (land, river, sea), its nature (soils, vegetation, algae, phytoplankton) and even its age and reactivity (old and refractory or labile and energetic). The study of combined isotopic signatures ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$) of DIC in pore waters is a powerful tool to assess the sources and the mineralization mechanisms of OM deposited in deltas (Bauer et al. 1995; Aller et al. 2008). The $\delta^{13}\text{C}$ signatures of the dissolved organic carbon (DIC) of sediment pore waters provide information about the origin of the OM mineralized in the sediment, with different signatures for terrestrial sources ($\delta^{13}\text{C}$ around -25%) and marine sources ($\delta^{13}\text{C}$ around -20%) (Goñi et al. 1998;

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Burdige 2006). The $\Delta^{14}\text{C}$ signatures provide information about the age of the different OM but can also be used as a tracer for the freshly produced OM of the river (Aller et al. 2008; Aller and Blair 2004). The anthropogenic activities and the presence of nuclear plants on the Rhône river can lead to enriched $\Delta^{14}\text{C}$ -OM signatures (Eyrolle et al. 2015) which can be used to follow the fate of the OM in the different pools of the system originating from the river, delta, or ocean (Pozzato et al. 2018; Dumoulin et al. 2018).

In these previous studies we showed that sedimentation and mineralization of terrestrial OM is very high in the proximal zone near the river mouth, while further offshore on the continental shelf, the organic matter sedimentation is dominated by the mineralization of marine OM. However, the data for the continental shelf were limited in these first studies, and a new sampling cruise, “MissRhoDia II”, was carried out on the RV Tethys II in May 2018. Here we report on these new results from the continental shelf sediments and investigate OM mineralization over a longer period of time (one century) in this zone under the influence of the river plume dominated by autochthonous production.

MATERIALS AND METHODS

Study Site

The Rhône river is one of the largest French rivers and provides the major input of freshwater and OM to the western Mediterranean Sea. The sources of riverine inputs discharged to the delta depend on the hydrological regime which can go from $700 \text{ m}^3 \text{ s}^{-1}$ during low flow periods to over $3000 \text{ m}^3 \text{ s}^{-1}$ during flood periods. Soils of various ages, vegetation debris and river phyto-planktonic production are mixed and carried by the river to the prodelta (Harmelin-Vivien et al. 2010; Cathalot et al. 2013; Copard et al. 2018). Large amounts of sediment accumulate in the river mouth at a very fast sedimentation rate of around 30 to 40 cm y^{-1} (Charmasson et al. 1998) whereas further from the coast, on the continental shelf, the sedimentation rate is less than $<0.3 \text{ cm y}^{-1}$ (Miralles et al. 2005).

The ^{14}C activities in the Rhône river have varied over the last century with two main periods (Dumoulin et al. 2018). During the pre-nuclear period, before 1960, the Rhone river had a freshwater reservoir effect (FRE) for radiocarbon in dissolved inorganic carbon (DIC) because of its multiple tributaries and the dissolution of old carbonates from its drainage basin. The FRE was evaluated at $\Delta^{14}\text{C} = -114\text{‰}$, close to the value found for its main tributary, the Durance river which is known to be depleted in $\Delta^{14}\text{C}$ with a $\Delta^{14}\text{C} = -138\text{‰}$ (Jean-Baptiste et al. 2018). The river OM signature was also impacted by this FRE. On the marine side, the DIC and consequently the marine OM, such as phytoplankton, showed a value of $\Delta^{14}\text{C} = -50\text{‰}$ to $\Delta^{14}\text{C} = -60\text{‰}$ due to the marine reservoir effect in this zone (Siani et al. 2000; Tisnérat-Laborde et al. 2013). Then, during the last 50 years, after the atmospheric nuclear bomb tests and the penetration of the bomb radiocarbon into the river and the ocean, enriched values were measured in the Mediterranean Sea surface waters with $\Delta^{14}\text{C} = +90\text{‰}$ around 1970 and a decrease to $\Delta^{14}\text{C} = +60\text{‰}$ in 2010 (Tisnérat-Laborde et al. 2013; Ayache et al. 2017). After 1980, nuclear energy developed in France. Today, the Rhône River is one of the most nuclearized rivers in Europe. Four nuclear plants are located along the Rhône and legally discharge cooling water in the river (Eyrolle et al. 2015; Jean-Baptiste et al. 2018). It has already been reported that DIC from the river can contain enriched ^{14}C values which can reach a maximum of $\Delta^{14}\text{C} = +393\text{‰}$ with an average value of $\Delta^{14}\text{C} = 60\text{‰}$ (Jean-Baptiste et al. 2018). As a consequence, ^{14}C can be used as a tracer of the fresh water DIC and the freshly produced OM such as

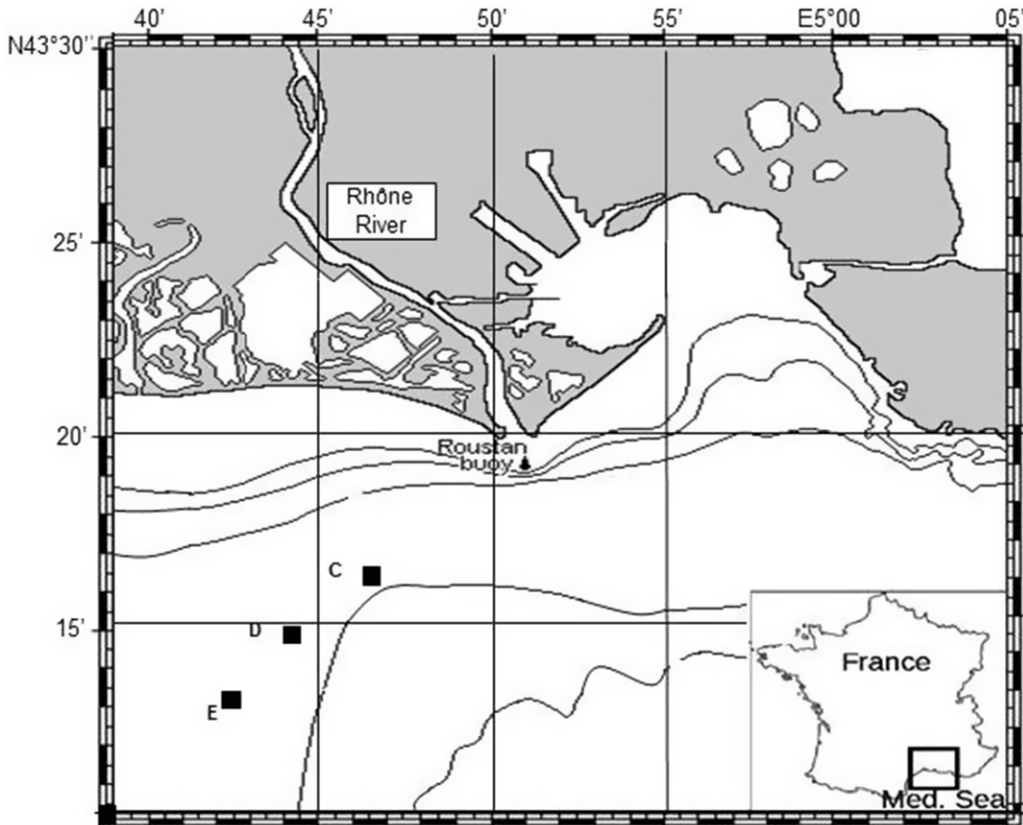


Figure 1 Map of the Rhône prodelta with the sampling station E.

phytoplankton in the ecosystem of the prodelta and the continental shelf (Dumoulin et al. 2018).

In this study, we focused on station E (Figure 1), located in the distal zone of the continental shelf (43°13'12N 4°41'54E, 75 m depth at 17 Km from the River mouth, Cathalot et al. 2013). This station is further from the coast than station C (8.5 km) or D (13 km) studied in our previous work (Pozzato et al. 2018; Dumoulin et al. 2018). Station C provided interesting but scarce data on pore water isotopic signatures. It was important to better constrain the distal zone to refine our conclusions for the continental shelf. At this station, we chose one sediment core and collected pore waters at different depths to analyze the evolution of DIC, $\delta^{13}\text{C-DIC}$ and $\Delta^{14}\text{C-DIC}$.

Sampling

Sampling was carried out in May 2018. Interface sediment cores of nearly 40 cm were collected with a gravity corer (Uwitec) using PVC transparent tubes. At station E, with the sedimentation rate of the distal zone around 0.3 cm y^{-1} a core represents between 100 or 150 years of deposition (Miralles et al. 2005). Pore waters were extracted using $0.2 \mu\text{m}$ rhizons (Rhizosphere Research Products, Seeberg-Elverfeldt et al. 2005) with a 20 mL rubber free syringe. The pore water samples were then sealed in a 15 mL Pyrex glass

ampoules and stored frozen at -20°C until ^{14}C analysis. A small aliquot (2mL) was placed in an individual vial with mercuric chloride (HgCl_2) for ^{13}C analysis. DIC was measured by the calibrated gas pressure gauge at the end of the CO_2 extraction-purification line. A second core was sampled to collect pore waters for more precise DIC measurements. These were also poisoned using mercuric chloride.

Bottom water samples were collected at around one meter from the bottom using a Niskin bottle, poisoned with mercuric chloride (HgCl_2) and stored in a fridge.

Measurements

DIC Analysis

Inorganic carbon measured in pore waters and bottom waters refers to dissolved inorganic carbon (DIC) because during extraction from the sediment, the water passed through the $0.2\ \mu\text{m}$ ceramic filter of the rhizon and the solid particles were removed. The DIC analysis was carried out with an Apollo Scitech Dissolved Inorganic Carbon Analyzer with a LICOR CO_2 detector (Rassmann et al. 2016). The uncertainty of this analysis is $\pm 10\ \mu\text{mol/L}$ which is around 0.5%.

^{13}C Analysis

The ^{13}C aliquot was measured at GEOTOP-UQAM using an Isoprime 100-DI with a microgas system in continuous flow for both pore waters and bottom waters. Samples were acidified and heated at 60°C for 1 hour to ensure complete separation of CO_2 , which was then introduced in the IRMS for isotope ratio measurements. The precision of the isotopic measurements is $\pm 0.1\text{‰}$.

^{14}C Analysis

The CO_2 extraction from the pore water and bottom water DIC was performed with the CO_2 extraction line installed at the LMC14 as described in Dumoulin et al. (2013). The water samples are introduced through an air-tight septum in the line and 2 mL of 85% phosphoric acid (H_3PO_4) is added to react with the water DIC and produce CO_2 . A helium flow is used to push the CO_2 through the line and two water traps at -78°C remove the water from the gas. A liquid nitrogen trap at -190°C is used to collect the sample in a sealed tube before the graphitization step.

The ^{14}C activities were calculated with the standard of “oxalic acid II”. Radiocarbon calculations were performed using the Mook and van der Plicht method (1999). The background correction was made with C1 AIEA samples and the $\Delta^{14}\text{C}$ uncertainty values are $\pm 3\text{‰}$ at a confidence interval of 1sigma. The ^{14}C results are given in $\Delta^{14}\text{C}$ and recalculated to 1950 with the correction of the delay between sampling year and measurement year (Mook and van der Plicht 1999).

Graphitization and AMS Measurements

The CO_2 was reduced to graphite at the LMC14 laboratory using hydrogen and iron powder at 600°C (Vogel et al. 1984; Dumoulin et al. 2017), then pressed into an aluminum cathode and finally loaded into the ion source of the ARTEMIS facility for the AMS measurement (Moreau et al. 2013, 2020).

Table 1 DIC, $\delta^{13}\text{C}$ -DIC and $\Delta^{14}\text{C}$ -DIC of pore waters at different depths. BW represents the bottom water sample. NA indicates samples which were not measurable. Uncertainties are 0.1‰ for $\delta^{13}\text{C}$ and $\pm 3\%$ for $\Delta^{14}\text{C}$.

SacA	Sample	Depth (cm)	DIC (mM)	$\delta^{13}\text{C}$ (‰)	pMC	$\Delta^{14}\text{C}$ (‰)
56788	BW	—	2.38	-0.30	103.10 \pm 0.36	31.04
56789	2 cm	2	2.90	-1.30	103.33 \pm 0.34	33.26
56790	4 cm	4	2.63	-0.72	103.99 \pm 0.34	39.88
56791	8 cm	8	3.05	-2.01	104.62 \pm 0.36	46.21
56792	10 cm	10	3.32	-6.00	105.50 \pm 0.34	54.98
56793	14 cm	14	3.60	-1.48	105.19 \pm 0.36	51.94
56794	18 cm	18	3.88	-5.73	102.32 \pm 0.34	23.23
56795	22 cm	22	4.67	NA	101.42 \pm 0.38	14.18
56796	26 cm	26	4.96	NA	99.63 \pm 0.34	-3.72
56797	34 cm	34	4.96	-8.52	96.94 \pm 0.33	-30.59

Mixing Model

At each depth in the sediment, pore water DIC (DIC_{pore}) is a mix of bottom water DIC (DIC_{BW} , the original water trapped in the sediment) and DIC originating from the mineralized OM. To calculate the original isotopic signature of the organic matter mineralized in the sediment ($\delta^{13}\text{C}_{\text{OM}}$, $\Delta^{14}\text{C}_{\text{OM}}$) a mixing model similar to that of Bauer et al. (1995) was applied. The calculations were detailed in our previous studies (Pozzato et al. 2018; Dumoulin et al. 2018).

$$\delta^{13}\text{C}_{\text{pore}} = x * \delta^{13}\text{C}_{\text{BW}} + (1 - x) * \delta^{13}\text{C}_{\text{OM}} \quad \text{with} \quad x = \text{DIC}_{\text{BW}} / \text{DIC}_{\text{pore}}$$

& ↓

$$\delta^{13}\text{C}_{\text{pore}} * \text{DIC}_{\text{pore}} = \delta^{13}\text{C}_{\text{OM}} * \text{DIC}_{\text{pore}} + \text{DIC}_{\text{BW}} * \delta^{13}\text{C}_{\text{BW}} - \text{DIC}_{\text{BW}} * \delta^{13}\text{C}_{\text{OM}}$$

And similarly:

$$\Delta^{14}\text{C}_{\text{pore}} * \text{DIC}_{\text{pore}} = \Delta^{14}\text{C}_{\text{OM}} * \text{DIC}_{\text{pore}} + \text{DIC}_{\text{BW}} * \Delta^{14}\text{C}_{\text{BW}} - \text{DIC}_{\text{BW}} * \Delta^{14}\text{C}_{\text{OM}}$$

With this equation, the slope of $\Delta^{14}\text{C}_{\text{pore}} * \text{DIC}_{\text{pore}}$ versus DIC_{pore} provides the isotopic signature of the OM mineralized in the sediment $\Delta^{14}\text{C}_{\text{OM}}$ and similarly for $\delta^{13}\text{C}_{\text{OM}}$ with the $\delta^{13}\text{C} * \text{DIC}$ versus DIC_{pore}). The reported uncertainty on the OM signature was calculated as the uncertainty on the slope due to linear regression.

RESULTS

Sediment Pore Waters

The DIC concentration increases with depth (Table 1) with nearly 100 $\mu\text{mol/L}$ per cm, reaching twice the DIC concentration of the bottom water at 25 cm (from 2.38 mmol/L to 4.96 mmol/L).

The $\delta^{13}\text{C}$ -DIC values follow the opposite trend with a large decrease with depth from -0.3‰ for the bottom water to -8.52‰ at 34 cm. Unfortunately, two results are missing because two vials were broken before the $\delta^{13}\text{C}$ analysis.

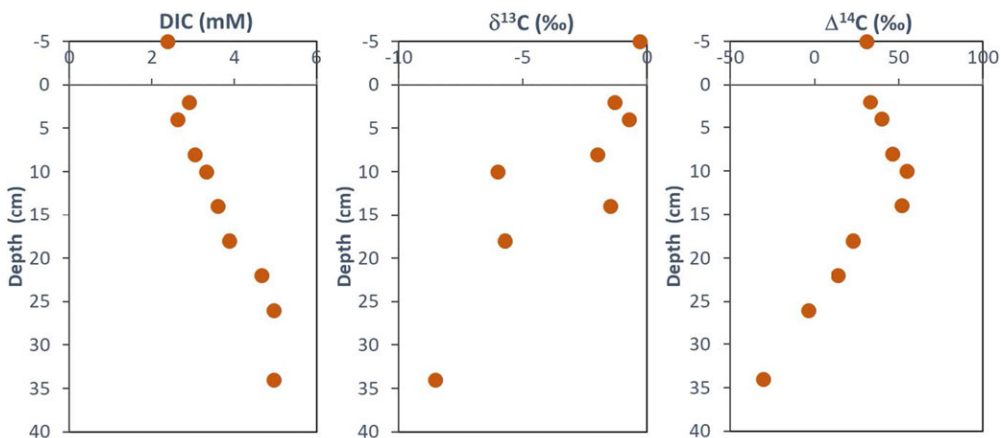


Figure 2 Evolution of the pore water DIC, its $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signature with depth in the sediment at station E. The bottom water value is reported above the sediment-water interface (horizontal line at 0 cm).

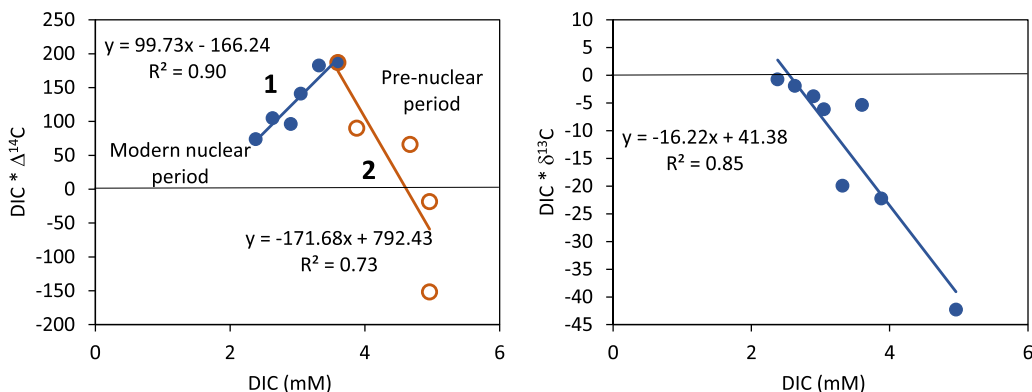


Figure 3 Mixing model for $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$. The slope of the mixing curve provides the isotopic signature of the mineralized OM. For the $\Delta^{14}\text{C}$ mixing model, the blue part (closed symbols) corresponds to the first 15 cm (nuclear period, see text) and the brown part (open symbols) corresponds to depths below 15 cm in the pre-nuclear period. (Please see online version for color figures.)

The $\Delta^{14}\text{C}$ -DIC in the pore waters follows two trends (Figure 2). In the first 15 cm, the activity increases from 30‰ to 55‰ but deeper down, it decreases from 55‰ to -30‰.

Original isotopic signature of the organic matter mineralized in sediment pore waters:

Figure 3 shows the mixing model and the isotopic signature of the OM mineralized in the sediment.

With the growth of DIC concentration in the pore water, the $\delta^{13}\text{C}_{\text{pore}} \cdot \text{DIC}_{\text{pore}}$ decreases. The slope of the mixing line for $\delta^{13}\text{C}$ gives a $\delta^{13}\text{C}_{\text{OM}}$ signature around $-16.2 \pm 3\text{‰}$ for the OM mineralized in the sediment. For the $\Delta^{14}\text{C}$ mixing model, the plot shows two different trends corresponding to different gradients observed on the $\Delta^{14}\text{C}$ -DIC distribution. For the

first part of the graph, the slope of the mixing model indicates $\Delta^{14}\text{C}_{\text{OM}} = +99.7 \pm 17\%$ and for the second part of the graph, the slope of indicates $\Delta^{14}\text{C}_{\text{OM}} = -171.7 \pm 60\%$.

DISCUSSION

Mineralization of the Organic Matter and DIC Increase

The measured DIC concentrations in the pore waters of continental shelf sediments at station E double from the surface sediment to the bottom of the core at 34 cm. This DIC concentration increase with depth is the result of oxic and anoxic OM mineralization in the sediment conducted by microorganisms (Rassmann et al. 2016, 2020). On the continental shelf, the low concentration of nitrate and the low production of reduced metals in the pore waters highlight that oxic mineralization and sulfate reduction are the major organic carbon mineralization pathways (Pastor et al. 2011; Ait Ballagh et al. 2021). It follows the equation (Rassmann et al. 2016, 2020):



For the anoxic part of the sediments (directly after the first centimeters), carbonate dissolution can be excluded as a source of DIC since in this zone, carbonate minerals (calcite and aragonite) are supersaturated and cannot therefore dissolve (Rassmann et al. 2016).

Isotopic signature of the mineralized OM

The slope of Figure 3 provides a $\delta^{13}\text{C}_{\text{OM}} = -16 \pm 3\%$ for the signature of the OM mineralized at station E, providing information about its origin. This result is in the lower range of the $\delta^{13}\text{C}$ signature corresponding to the mineralization of a marine substrate such as marine phytoplankton which commonly have a $\delta^{13}\text{C}$ signature between -19 to -21% (Harmelin-Vivien et al. 2010). This information confirms our previous results (Lansard et al. 2009; Cathalot et al. 2013; Pozzato et al. 2018; Dumoulin et al. 2018) indicating the limited amount of terrestrial organic matter in continental shelf sediments. The majority of OM delivered by the river settles near the river mouth, in the proximal zone. Further out at sea on the continental shelf, local marine OM is predominant. It is noteworthy that the input of C4 plants which have a heavier $\delta^{13}\text{C}$ signature of around -15% can be ruled out based on the $\delta^{13}\text{C}$ data of lignin phenols previously obtained (Cathalot et al. 2013). The absence of a large delivery of river particles to the continental shelf also explains why the sedimentation rates drastically decrease in this zone compared to those in the prodelta which receives large amounts of terrestrial particles and OM from the continent.

The $\Delta^{14}\text{C}$ isotopic signatures of the OM mineralized in the sediment (Figure 3) show two different trends. Line #1, in the first 15 cm, has a slope which gives a $\Delta^{14}\text{C}_{\text{OM}} = 100 \pm 17\%$. This value of $\Delta^{14}\text{C}_{\text{OM}}$ indicates modern organic matter with a slight $\Delta^{14}\text{C}$ enrichment and fits well with the post bomb period expected for the top of the core. A sedimentation rate of less than 0.3 cm/yr (Miralles et al. 2005) represents around 50–60 years for the first 15 cm and encompasses the ^{14}C bomb peak period and the initiation of nuclear activity in the Rhône area which started in the 1980s. This $\Delta^{14}\text{C}_{\text{OM}}$ result is probably linked to the deposition of enriched phytoplankton grown in marine surface waters during the nuclear period which is mineralized in the sediment and which transfers its isotopic signature to the pore water DIC. Evidence for this is the fact that the $\Delta^{14}\text{C}$ values obtained in the NW Mediterranean Sea surface were around $+90\%$ in the 1970s and decreased to 60% in 2010

(Tisnérat-Laborde et al. 2013; Ayache et al. 2017), which is consistent with the signature found in the OM for the nuclear period. As our results are slightly higher than the values of the surface ocean, another possible source of enriched DIC originating from the river plume is the impact of the nuclear power plants along the Rhône during the last 40 years. DIC of the river plume with peaks of $\Delta^{14}\text{C} = +393\text{‰}$ and an average of 60‰ (Jean-Baptiste et al. 2018) can be mixed with DIC of the surface waters and can be used by marine phytoplankton together with plume dissolved nutrients, creating an $\Delta^{14}\text{C}$ enrichment of marine OM.

A different trend is shown by line #2 for the signature of the organic matter mineralized under 15 cm. The slope of the mixing model gives a strongly depleted result with $\Delta^{14}\text{C}_{\text{OM}} = 172 \pm 60\text{‰}$. These sediment layers under 15 cm correspond to a period of time spanning from before 1900 to 1960 as estimated from the sedimentation rate (Miralles et al. 2005), i.e., the pre-nuclear period. Before the anthropogenic nuclear activities of the last 60 years, the $\Delta^{14}\text{C}$ signature of marine OM was directly linked to the local marine reservoir effect of the Mediterranean Sea evaluated around -50 to -60‰ (Siani et al. 2000; Tisnérat-Laborde et al. 2013). The value found for marine plankton degrading in these sediments is lower than these DIC signatures of the Mediterranean Sea, so it certainly indicates a larger influence of ^{14}C depleted waters. As indicated above, the river plume brings a large amount of fresh water and dissolved nutrients to the Mediterranean Sea, modifying the DIC of the surface water. During the pre-nuclear period, the freshwater reservoir effect (FRE) for radiocarbon in DIC was strong in the Rhone River basin. It was generated by the dissolution of old carbonates from the drainage basin which created a freshwater reservoir effect and an apparent ^{14}C aging of DIC (see for the Loire River, Coularis et al. 2016). The FRE measured on the Rhône river DIC was evaluated at $\Delta^{14}\text{C} = -114\text{‰}$, a value indicating the strong influence of one tributary, the Durance river which is known to be depleted in $\Delta^{14}\text{C}$ as indicated by a value obtained in May 2014 ($\Delta^{14}\text{C} = -138\text{‰}$; Jean-Baptiste et al. 2018). As the DIC signature of the river is partly transferred to the river plume, the local marine OM could have been more depleted than the average marine surface waters. Given the large uncertainty of the result found for $\Delta^{14}\text{C}_{\text{OM}}$ ($-171.7 \pm 60\text{‰}$), there is an overall compatibility of the mineralized OM signature with the possible signature of river-influenced marine surface waters.

A final possibility to explain such a depleted result for the OM mineralized in the sediments below 15 cm is a possible “priming effect” (Bianchi 2011 and references therein). This phenomenon occurs when substrates with different labilities co-exist in the sediment. The labile OM is used by the micro-, meio- and macro-organisms to co-metabolize more refractory substrates. At station E in the distal zone, this “priming effect” is possible with the mixture of different sources of substrates. If the sources of energetic OM are limited, the fauna and the different organisms have to mineralize more refractory OM. Cathalot et al. (2013) described a dominant aged OM fraction in shelf sediments including station E, with a high content of black carbon (up to 50%) and a limited contribution of fresh marine OM, providing an old $\Delta^{14}\text{C}$ signature of particulate OM ($\Delta^{14}\text{C} = -312\text{‰}$). Therefore, the mineralization of a small part of this refractory material could explain part of the $\Delta^{14}\text{C}_{\text{OM}}$ depleted results in the deeper layers of pore waters.

CONCLUSION

This new study of the continental shelf of the Rhône River prodelta has shed light on the origin and reactivity of organic matter present in the sediments and the coastal carbon cycle in river-

dominated ocean margins. The large increase in pore water DIC concentration indicates active OM mineralization by micro and macro fauna over a period of 100–150 yr. This process transfers the OM signature to the pore water DIC. The $\delta^{13}\text{C}$ signature of the pore water DIC indicates that mostly marine organic matter is mineralized in these sediments. It also confirms that a limited particulate substrate from the continent is mineralized in continental shelf sediments, confirming its efficient trapping in the proximal zone. The $\Delta^{14}\text{C}$ signature indicates two behaviors that coincide with the post-bomb/pre-bomb periods. Mineralized OM in the first half of the 20th century (below 15 cm) shows a depleted ^{14}C composition in line with low $\Delta^{14}\text{C}$ marine DIC values corresponding to the local marine reservoir effect and additions of river plume waters with lower $\Delta^{14}\text{C}$ -DIC values impacted by a freshwater reservoir effect. Contrarily, mineralized OM of the top of the core is enriched and $\Delta^{14}\text{C}$ results fit well with the expected values for the nuclear period impacted first by the penetration of bomb radiocarbon in the ocean and later by the anthropic nuclear activities present along the Rhône River. The larger contrast between the $\Delta^{14}\text{C}$ signature of mineralized OM between the two periods ($-172 \pm 60\%$ to $+100 \pm 17\%$) and that of the marine surface waters (-60% to 90% ; Tisnérat-Laborde et al. 2013) could be explained by a significant influence of the river plume waters and its DIC on marine phytoplankton production. This could have contributed a more depleted DIC during the pre-nuclear period and a more enriched DIC during the nuclear period.

Overall, the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signature of pore water DIC confirms our previous findings that reactive organic matter mineralized in sediments imprints its signature on the pore waters. We show here that this signature can be maintained on timescales of the order of a century.

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