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# 1 Millennial-aged organic matter preservation in anoxic and sulfidic mangrove 2 soils: insights from isotopic and molecular analyses

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## 11 **Abstract**

12 Mangrove forests are known as coastal carbon sinks, but the long-term (millennium-scale)  
13 preservation processes of organic matter (OM) in their soils and the role of sulphur in these  
14 processes are still not fully understood. These processes are crucial for better estimating the impact  
15 of sea-level variations on the carbon dynamics in mangrove forests, which are particularly sensitive  
16 to sea-level changes due to their direct hydrological interactions with coastal waters. This study  
17 focuses on a soil layer enriched in mangrove-derived OM that accumulated during a stable sea-level  
18 period of the Holocene in New Caledonia (South Pacific). Radiocarbon dating situates this enriched  
19 layer at approximately 4,000 cal BP. The aim of this study is to characterize the enriched OM layer  
20 using bulk (Rock-Eval), isotopic ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ), and molecular (lignin and neutral carbohydrates)  
21 analyses. This OM has undergone diagenetic processes such as dehydrogenation, and the loss of  
22 components such as the main neutral carbohydrates: glucose, xylose, and galactose. However,  
23 some Rock-Eval parameters, the total lignin content, and carbon and nitrogen isotopic ratios are  
24 characteristic of well-preserved OM, suggesting differential decomposition/preservation processes.  
25 In addition, SEM observations highlighted the presence of pyrite associated to preserved root  
26 material. Along with high  $S_{\text{org}}/\text{TOC}$  ratio, these results suggest potential processes of OM  
27 sulfurization preserving it from decomposition. Prolonged sea-level stability in addition to anoxic and  
28 sulfidic soil conditions enhanced OM accumulation and long-term sequestration in mangrove soils.

29 Keywords: mangrove, stable isotopes, Rock-Eval, carbon dating, neutral carbohydrates, lignin

## 30 **1. Introduction**

31 Mangrove forests are efficient carbon sinks due to their productivity, estimated at 11 Mg C  
32 ha<sup>-1</sup> yr<sup>-1</sup>, and their ability to effectively sequester carbon in the soil at an average rate of 180 g organic  
33 carbon (OC) m<sup>-2</sup> yr<sup>-1</sup> (Alongi, 2020). The presence of anoxic and sulfidic soil conditions, especially  
34 at depth, significantly limits OC mineralization, thus facilitating its long-term storage (Kristensen et  
35 al., 2008). The combination of high net primary productivity, rapid sedimentation rates, and soil  
36 anoxia makes mangrove soil an ideal and favourable reservoir for long-term sequestration of OC  
37 (Kristensen et al., 2008). Nevertheless, mangrove forest migration in response to sea-level changes  
38 presents challenges in accurately characterizing the carbon stock of the present mangrove forests  
39 (Marchand, 2017).

40 During the Holocene period, sea-level variations have impacted mangrove distribution  
41 (Woodroffe et al., 2016). For about 3,700 years, sea-level on the West Coast of New Caledonia was  
42 stable 1.1 m higher than today, before falling to the present mean sea-level at 2,800 cal BP (Yamano  
43 et al., 2014). The fall of the sea-level resulted in mangrove seaward migration. However, the  
44 presence of the former mangrove forest was recorded in soils of the present-day upper intertidal  
45 zone as an organic matter (OM)-rich layer characterized by the presence of preserved red tissues  
46 typical of *Rhizophora* trees (Jacotot et al., 2018).

47 The aim of the present study was to gain a deeper understanding of the processes governing  
48 the long-term preservation of millennial-aged OM in anoxic and sulfidic mangrove soils. By  
49 employing isotopic, molecular, and Rock-Eval analyses, we sought to chemically characterize the  
50 OM-rich layer and therefore uncover the mechanisms behind OM decomposition and preservation.

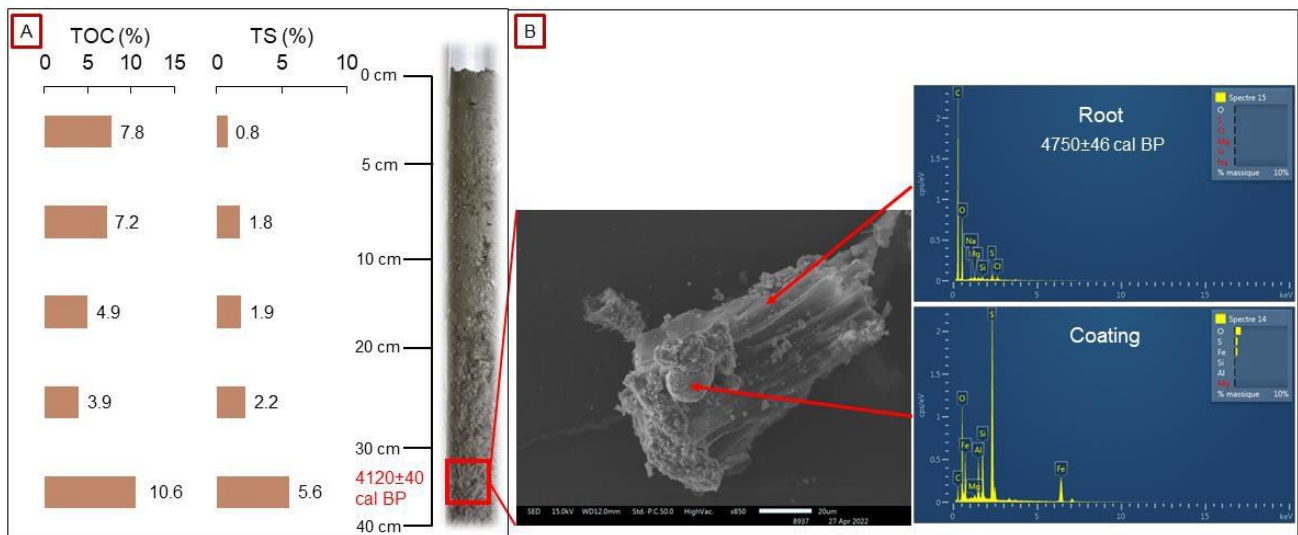
## 51 **2. Methods**

52 The study site is a semi-arid mangrove forest typical of the West Coast of New Caledonia  
53 with *Rhizophora stylosa* present on the seaside of the forest and *Avicennia marina* on the land side.  
54 The fall of the sea-level from the late Holocene period infers the presence of the OM-rich layer in  
55 depth beneath the *A. marina* stand, where an old *R. stylosa* forest stood prior to migration. This layer  
56 is identified at the current study site by the observation of red wood tissues belonging to the  
57 *Rhizophora* genus at depth beneath the *A. marina* stand. Previous studies on mangrove forests from

58 the same coast identified this layer in areas without vegetation, such as salt-flats, down to depths of  
59 260 cm, further supporting its ancient origin. Furthermore, at the current study site, red wood debris  
60 were observed down to 80 cm beneath *A. marina* and over a depth of more than a meter in forests  
61 along the same coast, confirming the stable burial of OM (Jacotot et al., 2018). Triplicate fresh *R.*  
62 *stylosa* coarse roots were cut with a saw, and green leaves were collected from the trees to help  
63 determine the sources of the OM-rich layer. Soil samples in this specific layer, situated between 30  
64 and 40 cm depth beneath the *A. marina* stand, were collected with an Eijkelkamp gouge auger in  
65 May 2021. *A. marina* trees have shallow and widespread root systems (Pi et al., 2009), which limits  
66 their influence on the OM pool in this 30-40 cm depth layer. All samples were freeze-dried and  
67 ground. Rock-Eval pyrolysis was conducted on a Rock-Eval 7S (Vinci Technologies) and gave  
68 multiple parameters on the soil samples including total organic carbon (TOC), total and organic  
69 sulphur ( $S_{\text{tot}}$  and  $S_{\text{org}}$ ), hydrogen index (HI), oxygen index (OI), and the temperature of the oven at  
70 the maximum yield of S2 peak ( $T_{\text{pS2}}$ ), corresponding to the products from OM thermal cracking  
71 (Baudin et al., 2015). From these parameters, the  $S_{\text{org}}/\text{TOC}$  ratio can be calculated, which help  
72 classifies the soil in terms of sulphur content (Orr, 1986). Stable isotopic compositions ( $\delta^{13}\text{C}$  and  
73  $\delta^{15}\text{N}$ ) and C/N ratios were obtained on an isotope ratio mass spectrometer Sercon Integra 2. For  
74 quality control, duplicate samples were passed through the spectrometer and differences between  
75 duplicates were all below 5%. The molecular analysis focused on neutral carbohydrates and lignin-  
76 derived phenols. Neutral carbohydrates were extracted through hydrolysis and analysed via GC-MS  
77 after derivatization with BSTFA in pyridine (Lallier-Vergès et al., 2008). The GC is a Trace1300  
78 (Thermo Scientific) coupled to a MS ISQ7000 (Thermo Scientific). The GC is equipped with a Restek  
79 Rxi-5Sil MS column (60 m x 0.25 mm, 0.25  $\mu\text{m}$  film thickness) (Robin et al., 2024). Quality control  
80 consisted of duplicate technical samples ( $\leq 11\%$  standard deviation) and measurements of the  
81 internal standard (Supplementary Table 1). 11 lignin-derived phenols were quantified after hydrolysis  
82 and extraction (Marchand et al., 2005). Chromatographic separation was achieved using a Vanquish  
83 Flex system (Thermo Scientific). Samples were separated on a Hypersil GOLD column (1.9  $\mu\text{m}$   
84 particle size), 50 x 2.1 mm (Thermo Scientific). The mobile phase was a mixture of ultrapure water  
85 and methanol. MS detection was performed using an Orbitrap Exploris120 (Thermo Scientific)  
86 (Robin et al., 2024). A quality control solution was passed every 10 samples and values obtained

87 were all below 15% difference with expected values. Soil samples were also observed on a scanning  
88 electron microscope (SEM) using a JEOL JSM-IT300 LV apparatus coupled with an energy  
89 dispersive spectrometer (EDX) Oxford xmax80T device. Radiocarbon dating of the soil samples was  
90 performed after hot HCl washing at the radiocarbon dating laboratory of the University of Waikato.

### 91 3. Results and discussion

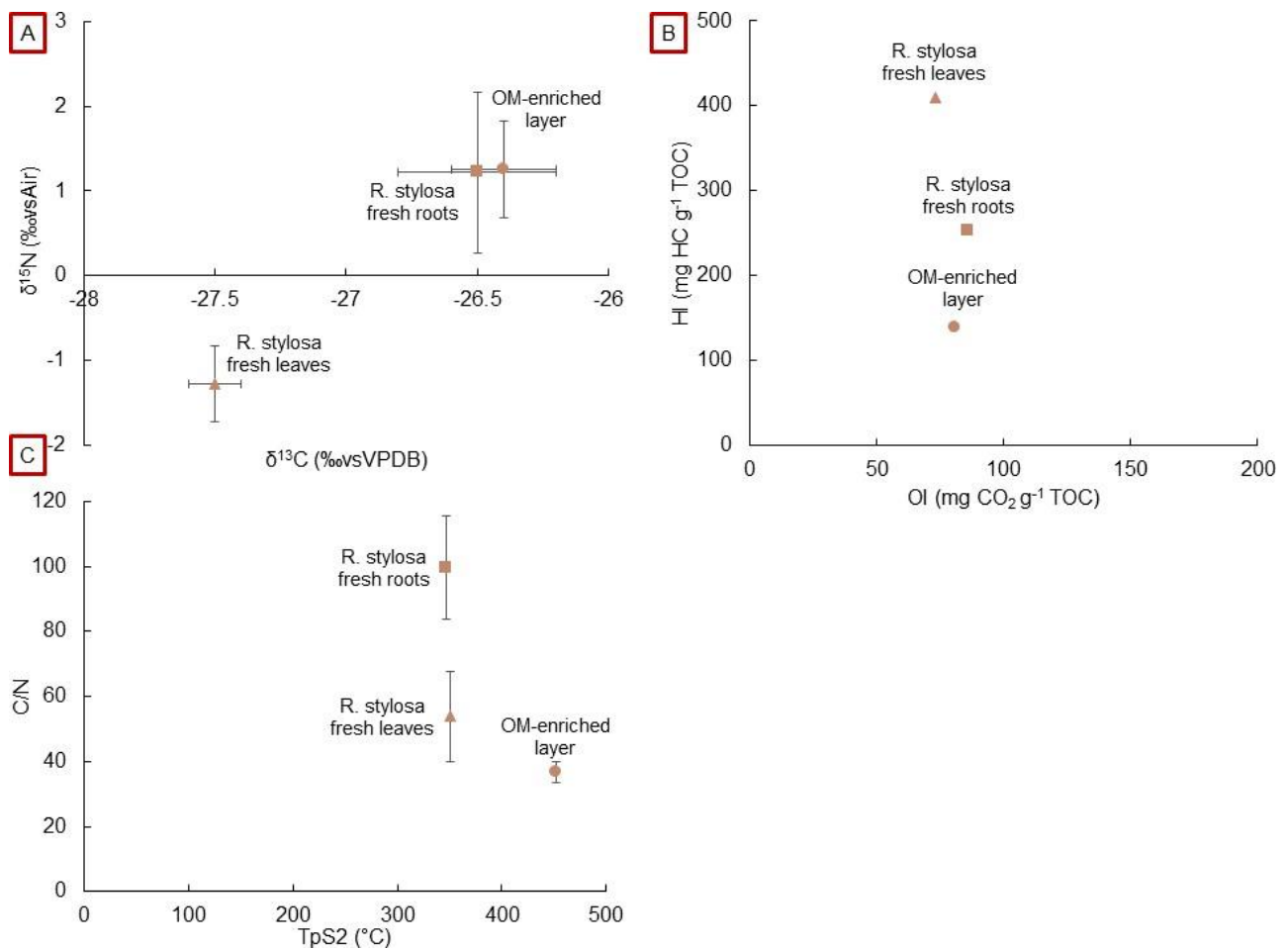


92  
93 **Figure 1.** (A) Vertical soil core with distribution of percentage total organic carbon content (TOC) and  
94 total sulphur content (TS) with depth and (B) SEM photo of preserved root from the organic matter-  
95 enriched layer (30-40 cm) with associated EDX spectra of the root and of the coating. The  $^{14}\text{C}$  dating  
96 for the soil and the preserved roots are given in cal BP.

97 The enriched soil layer was identified where preserved roots, potentially belonging to the *R. stylosa*  
98 former forest, were observed. The radiocarbon dating ( $^{14}\text{C}$ -datation) indicated that the soil layer  
99 dated back to approximately 4,000 cal BP (Fig. 1), aligning well with the stable high sea-level period  
100 (Yamano et al., 2014). In this layer, TOC reached more than 10% (Fig. 1A) while median TOC  
101 content in mangrove soils is 2.2% (Kristensen et al., 2008). Furthermore, the high  $S_{\text{tot}}$  content (5.6%)  
102 (Fig. 1A) and  $S_{\text{org}}/\text{TOC}$  ratio (0.08) values of the soil layer were indicative of a very high sulphur type  
103 of soil (Orr, 1986). The accumulation of roots and other OM debris during this timeframe can be  
104 attributed to the prolonged period of sea-level stability and the limited capacity of microbial  
105 communities to decompose mangrove tissues in waterlogged, anoxic conditions (McKee et al.,  
106 2007). Similar occurrences of mangrove peats with identifiable preserved roots from the Holocene  
107 have been reported in the Caribbeans (McKee et al., 2007). In Belize, a comparable scenario to the  
108 one described in this study was identified, where an enriched OM layer was found beneath a current

109 *Avicennia germinans* forest, originating from an ancient *Rhizophora mangle* forest (McKee and  
110 Faulkner, 2000). However, the authors attributed the formation of peat as an adaptation mechanism  
111 to rising sea-levels, rather than indicating a period of sea-level stability (McKee et al., 2007).

112 SEM-EDX analysis revealed the association between the root material and pyrite ( $\text{FeS}_2$ ) (Fig.  
113 1B). We suggest that the intricate interaction between OM and pyrite, probably through adsorption,  
114 contributed to an enhanced preservation of OM within the waterlogged and anoxic soil conditions  
115 (Shawar et al., 2018; Tessin et al., 2016). The association of OM with minerals slows decomposition  
116 processes, and in environments characterized by high sedimentation rates, facilitates the burial of  
117 OM (Wakeham and Canuel, 2006). Also, the mineral-OM interface evolves with changes in the  
118 chemistry of aqueous phases, OM, and mineralogy (Kleber et al., 2021), but the stable anoxic  
119 environment provided by the mangrove soil favours stable OM adsorption onto minerals. We  
120 hypothesize that the OM-rich soil layer has remained anoxic due to the inherent anoxic nature of the  
121 substrate under *R. stylosa* (Alongi et al., 2000; Lacerda et al., 1995; Leopold et al., 2013).  
122 Additionally, during the sea level drop, the migration of the mangrove led to soil coverage. A total of  
123 30 cm of mineral particles were deposited over this layer, restricting exchange between the studied  
124 layer and the atmosphere, thus maintaining anoxic conditions. Furthermore, the sulphur parameters  
125 indicated a high sulphur-OM type (Orr, 1986). We suggest that it is not only the organo-mineral  
126 associations that promote preservation, but also the natural sulfurization of OM (process of  
127 incorporating sulphur in OM) in sulfidic soils (Raven et al., 2019). In fact, in anoxic environments as  
128 in this study, sulphur can form covalent bonds with a carbon atom from the aromatic rings of lignin,  
129 enhancing lignin preservation, therefore providing OM resistance to decay (Crémière et al., 2017;  
130 Karunarathna et al., 2020). However, sulphur does not tend to form covalent bonds with molecules  
131 such as neutral carbohydrates in anoxic environments. This type of bonding is favoured in the  
132 presence of oxygen (Lin et al., 2013; Paulsen, 1966). The preservation of root materials can also be  
133 attributed to the long period of sea-level stability, which associated with the high primary production  
134 of *R. stylosa* trees, enhanced OM accumulation by limiting sediment transport through erosion or  
135 disturbances.



136

137 **Figure 2.** (A) Stable isotope ratios, (B) hydrogen and oxygen indexes, and (C) C/N ratios and TpS2  
 138 values of the soil organic matter-enriched layer and the fresh leaf and roots of *R. stylosa*.

139 The carbon and nitrogen isotopic compositions of the layer (-26.4‰ and 1.26‰, respectively)  
 140 were close to those of the fresh *R. stylosa* roots (-26.5‰ and 1.22‰, respectively) (Fig. 2A). This  
 141 result indicates that the preserved roots present in this layer may contribute significantly to the OM  
 142 composition as their isotopic values must be similar to that of the modern fresh *R. stylosa* tissues.  
 143 However, the oxygen and hydrogen indexes (OI and HI) obtained after Rock-Eval pyrolysis showed  
 144 that the OM from the soil layer, if derived from *R. stylosa* tissues, has undergone diagenetic  
 145 processes, including dehydrogenation, as indicated by the lower HI value (139 mg HC g<sup>-1</sup> TOC)  
 146 compared to the fresh tissues (252 and 410 mg HC g<sup>-1</sup> TOC) (Fig. 2B). The higher TpS2 values of  
 147 the soil layer (452 °C) compared to that of the fresh tissues (347 and 351 °C) (Fig. 2C) also  
 148 demonstrated more thermally stable OM in the enriched layer, indicative of a mature OM. Still, the  
 149 OI value of the soil layer was low (81 mg CO<sub>2</sub> g<sup>-1</sup> TOC) and close to that of the fresh tissues (Fig.  
 150 2B), indicating no oxygenation of the OM. Therefore, soil anoxia may help OM preservation in this  
 151 layer. The OM in the soil layer exhibited lower C/N ratios (37) than fresh tissues (100 and 54) (Fig.

152 2C), highlighting either a preference for the degradation of C-rich compounds over N-rich  
 153 compounds, or the enrichment of N in soil from accumulation of microorganisms biomass, which  
 154 can obtain N from N<sub>2</sub> fixation (Gotto and Taylor, 1976).

155 **Table 1.** Neutral carbohydrates and lignin-derived phenols parameters in the soil organic matter-  
 156 enriched layer and in the fresh roots and leaves of *R. stylosa*.

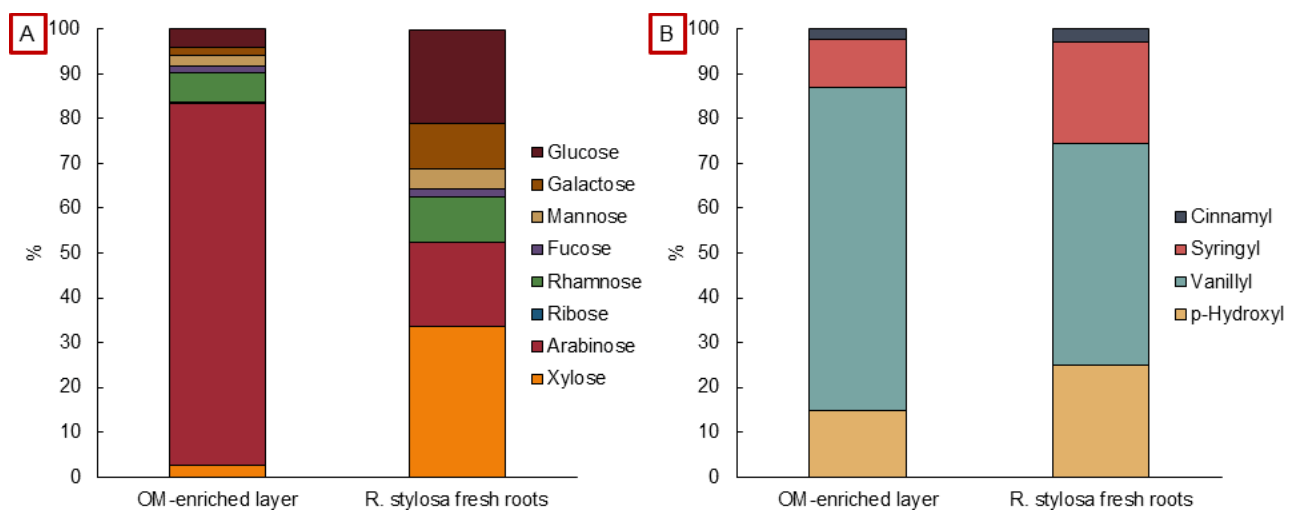
Variables	OM-enriched layer	<i>R. stylosa</i> fresh roots	<i>R. stylosa</i> fresh leaves
Total neutral carbohydrates (mg.g <sup>-1</sup> TOC)	323	1,030	616
Hex/Pen	0.05	0.28	0.34
Total lignin-derived phenols (µg.g <sup>-1</sup> TOC)	4,257	4,054	3,581
C/V	0.03	0.06	0.61
S/V	0.15	0.45	0.39
P/(V+S)	0.18	0.35	0.27
PON/P	0.17	0.03	0.08
(Ad/Al) <sub>p</sub>	0.75	0.34	1.00
(Ad/Al) <sub>v</sub>	0.13	1.10	4.73
(Ad/Al) <sub>s</sub>	2.66	3.20	1.88

157 Hex = Hexoses (mannose + galactose), Pen = Pentoses (xylose + arabinose), P = p-hydroxyl, V = Vanillyl, S  
 158 = Syringyl, C = Cinnamyl, PON = p-hydroxyacetophenone, and (Ad/Al) = acid over aldehyde ratio.

159 At the molecular level, the overall neutral carbohydrate (lacking N atoms) content measured  
 160 in the soil (323 mg g<sup>-1</sup> TOC) was lower compared to the fresh roots (1,030 mg g<sup>-1</sup> TOC), while the  
 161 lignin content was similar (4,257 and 4,054 µg g<sup>-1</sup> TOC, respectively) (Table 1). In fact, in anoxic  
 162 mangrove soils, neutral carbohydrates are usually more labile than bulk OC, while lignin is more  
 163 refractory (Lallier-Vergès et al., 2008; Marchand et al., 2005). The Hex/Pen ratio within the soil's  
 164 enriched layer (0.05) was nearly an order of magnitude lower than that of the fresh roots (0.28) and  
 165 leaves (0.34) (Table 1). Polysaccharides originating from plants are notably rich in pentose content,  
 166 whereas those arising from microbes primarily consist of hexoses (Kögel-Knabner, 2002).  
 167 Consequently, the reduced Hex/Pen ratio underscores the substantial contribution of plant-derived  
 168 OM to this layer, in addition to the selective loss of hexose during OM transformation processes.  
 169 Thus, hexose was removed as CO<sub>2</sub> while pentose stayed in the soil. The smaller ratio was linked to  
 170 a significant relative increase in arabinose from the fresh roots (19%) to the buried layer (81%) (Fig.  
 171 3A), indicating the more refractory behaviour of arabinose compared to bulk OC, alongside the loss  
 172 of galactose (Fig. 3A). Previous research has highlighted arabinose's refractory behaviour  
 173 (Marchand et al., 2005), given its presence in hemicellulose, but also pectin, which exhibits higher



174 resistance to decomposition compared to cellulose and hemicellulose (Benner et al., 1990).  
 175 Additionally, glucose and xylose were measured in relative lower concentrations within the enriched  
 176 layer (Fig. 3A). Among the fresh tissues, xylose, galactose, and glucose were the most abundant  
 177 sugars. We suggest that, as neutral carbohydrates serve as a significant energy source for soil  
 178 microbial communities, the major molecules underwent degradation upon OM burial (Opsahl and  
 179 Benner, 1999). This degradation is particularly pronounced due to the labile nature of glucose and  
 180 xylose, which are the least stable carbohydrates (Marchand et al., 2005). Conversely, mannose,  
 181 ribose, and the deoxy sugars (fucose and rhamnose) remained relatively preserved (Fig. 3A).



182  
 183 **Figure 3.** (A) Proportions of the 8 measured neutral carbohydrates and (B) proportions of the 4 lignin-  
 184 derived phenol groups of the soil organic matter-enriched layer and the fresh roots of *R. stylosa*.

185 Lignin-derived phenols are exclusively associated with vascular plants. Total lignin contents  
 186 in the studied layer and in the fresh roots were of the same magnitude (Table 1). Still, across all four  
 187 phenol groups, only the cinnamyl phenols remained constant, while the vanillyl phenols relatively  
 188 increased in proportions and the syringyl and p-hydroxyl relatively decreased (Fig. 3B).  
 189 Consequently, the C/V ratio in the soil was halved, while the S/V ratio was reduced to one-third of  
 190 that found in the fresh roots (Table 1). Among phenol groups, vanillyl predominates in mangrove  
 191 debris (Benner et al., 1990) and is similarly prevalent in mangrove soils (Lallier-Vergès et al., 2008).  
 192 Preservation tendencies favour vanillyl and p-hydroxyl phenols over syringyl and cinnamyl groups  
 193 due to association of some groups to more labile molecules or looser bonds with lignin (Hartley,  
 194 1973; Kirk, 1980; Lallier-Vergès et al., 2008). Depending on the microbial activity associated to soil  
 195 conditions, different lignin degradation mechanisms favour certain phenol groups over others (Chen

196 and Chang, 1985). While the acid/aldehyde ratios were comparable for p-hydroxyl and syringyl  
197 groups, they were substantially lower in the soil than in the tissues for the vanillyl group (Table 1).  
198 This variance was primarily attributed to a significant enrichment in vanillin (Supplementary Table  
199 2). Low Ad/Al ratios are commonly encountered in anoxic environments due to the absence of side-  
200 chain oxidation processes (Lallier-Vergès et al., 2008). In this context, however, vanillin preservation  
201 emerges as a key factor. Additionally, notable stability in p-hydroxyacetophenone was evident  
202 (Supplementary Table 2), leading to a considerably higher PON/P ratio in the soil compared to the  
203 tissues. This may result from the fact that p-hydroxyacetophenone exclusively originates from lignin  
204 oxidation, whereas p-hydroxybenzoic acid and p-hydroxybenzaldehyde may also result from the  
205 oxidation of non-lignin precursors within the fresh tissues (Benner et al., 1990). The elevated PON/P  
206 ratio thus suggests the predominance of lignin within the buried layer.

#### 207 **4. Conclusion**

208 The results of this study provide critical insights into the mechanisms behind the long-term  
209 preservation of OM in mangrove soils. Isotopic, Rock-Eval, and molecular parameters, including  
210 stable isotope ratios and lignin content, indicate that OM preservation is likely enhanced by the soil's  
211 stable anoxic conditions, as evidenced by the oxygen index, over thousands of years. Sulfurization  
212 processes are also thought to play a role in OM preservation, as indicated by the soil sulphur content  
213 and the observed association between pyrite and OM. Nevertheless, the well-preserved OM has  
214 undergone weak diagenetic processes, as suggested by the neutral carbohydrate content, hydrogen  
215 index, and TpS2 values.

216 The study provides valuable context for interpreting preserved mangrove peats globally and  
217 underscores the role of mangroves in mitigating climate change through effective long-term carbon  
218 storage. This study also highlighted the value of using a combination techniques to gain  
219 comprehensive insights into OM preservation.

220 Looking ahead, this research underscores the need for further studies on coastal carbon  
221 dynamics, particularly in the face of ongoing climate change and sea-level variations. Understanding

222 these preservation mechanisms is crucial for predicting the future of OC in mangrove ecosystems  
223 and for developing strategies to protect and enhance these vital carbon sinks.

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