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Iron promotes the preservation of organic matter in sediments

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33 **The biogeochemical cycles of iron and organic carbon are strongly interlinked. In**
34 **oceanic waters organic ligands have been shown to control the concentration of dissolved**
35 **iron¹. In soils, solid iron phases provide a sheltering and preservative effect for organic**
36 **carbon², but the role of iron in the preservation of organic matter in sediments has not been**
37 **clearly established. Here, we determine the amount of organic carbon, associated with**
38 **reactive iron phases in sediments of various mineralogies collected from a wide range of**
39 **depositional environments, using an iron reduction method previously applied to soils³. Our**
40 **findings suggest that 21.5 ± 8.6 per cent of the organic carbon in sediments is directly bound**
41 **to reactive iron phases, representing a global mass of 19 to 45×10^{15} g of organic carbon in**
42 **surface marine sediments⁴. We propose that these organic carbon-iron associations, formed**
43 **primarily through co-precipitation and/or direct chelation, promote the preservation of**
44 **organic carbon in sediments. Since reactive iron phases are metastable over geological**
45 **timescales, they serve as an efficient “rusty sink” for OC, a key factor in the long-term storage**
46 **of organic carbon and thus contributing to the global cycles of carbon, oxygen and sulphur⁵.**

47

48 Evidence of interactions between Fe and OC in marine sediments was reported nearly
49 40 years ago, where concentrations of Fe and OC were found to co-vary⁶. Since both Fe and OC
50 are commonly associated with clay mineral surfaces, it was simply stated that “where there is
51 more deposited fine-grained material with high surface area for adsorption, we find more
52 organic matter and more Fe”⁶. It is still not clear whether this correlation stems from the strong
53 affinity of both species for solid surfaces or if it reflects enhanced OC preservation by Fe. Iron’s
54 preservative effect on organic matter was previously demonstrated in laboratory studies^{7,8},
55 which report that the presence of iron-rich solid substrates or the formation of organo-ferric
56 complexes hampers microbial degradation of simple organic compounds. Iron also imparts a
57 protective effect to OC in soil systems², but this preservation mechanism has never been
58 explored in sediments.

59

60 In modern sediments, reactive Fe phases (operationally defined here as the solid iron
61 phases that are reductively dissolved by sodium dithionite) are typically found as nano-spheres
62 of goethite of <10 nm in diameter⁹⁻¹⁰. These phases accumulate or are formed within the oxic
63 sediment layer through oxidation and precipitation of dissolved Fe(II) produced during
64 weathering and diagenetic recycling within the sediment¹¹. Over time, reactive Fe phases
65 become more crystalline, resulting in reduced surface reactivity/area and solubility.
66 Crystallization is, however, hindered by the active diagenetic recycling of iron¹², and by organic
67 matter coating of Fe phases¹³. Accordingly, reactive Fe phases have been shown to survive in
68 sediments for hundreds of thousands of years¹⁴.

69

70 We examined sediments collected from a wide range of environments, including
71 freshwaters, estuaries, river deltas, continental margins and the deep-sea, encompassing
72 various depositional environments and mineralogies. These samples include OC-rich sulphidic
73 Black Sea sediments and OC-rich sediments from O₂-deficient zones along the Indian and
74 Mexican (Stn. 306) margins. Also included are sediments from the Arabian Sea, the Saanish
75 Inlet and a boreal lake (Lake Brock) which exhibit a productivity-driven seasonal pattern of O₂-
76 deficient waters. Estuarine, deltaic and margin deposits accumulating below well-oxygenated
77 waters of the Arctic margin, the St. Lawrence Estuary and Gulf, the Mexican margin (Stns. 303-
78 305), the Eel River Basin and the Washington coast and adjacent Columbia River delta are also
79 examined along with pelagic sediments from the Southern Ocean, the Santa Barbara Basin (Stn.
80 M) and Equatorial Pacific Ocean. This sample set comprises freshwater, estuarine and marine
81 clastic sediments, carbonate and siliceous oozes, as well as pelagic red clay sediments. We
82 focused on determining the amount of OC associated with reactive Fe phases by applying the
83 citrate-dithionite iron reduction method of Mehra and Jackson¹⁵, which simultaneously
84 dissolves all solid reactive Fe phases and the OC associated to these phases (OC-Fe) from the
85 sediment matrix. The reduction reaction is conducted at circumneutral pH using sodium
86 bicarbonate as a buffer, thus preventing the hydrolysis of organic matter as well as its
87 protonation and readsorption onto sediment particles which occur under acidic conditions.
88 Whereas the extraction of the same samples with artificial seawater released a negligible
89 fraction of the total OC (less than 3%; results not shown), samples treated under the same
90 experimental conditions after substituting trisodium citrate (complexing agent) and sodium

91 dithionite (reducing agent) for sodium chloride (equivalent ionic strength) released on average
92 $7.2 \pm 5.4\%$ of the total OC (Supplementary Table 2). Because the OC released in these control
93 experiments is not associated with Fe, results of individual control experiments were
94 subtracted from the amount of OC released from the dithionite extractions (see Supplementary
95 method for results and discussion on contamination and specificity for the OC-Fe fraction).

96

97 We determined that for all sediments tested, an average of $20.5 \pm 7.8\%$ of the total OC
98 is directly associated to Fe, with the highest OC-Fe concentrations in the uppermost sediment
99 layers where most of the reactive Fe phases accumulate (Fig. 1). Considering OC burial within
100 different depositional settings - deltaic and continental margin sediments account, respectively,
101 for 44% and 45% of global OC burial, while pelagic sediments and high productivity zones,
102 including anoxic basins, account for 5% and 6%, respectively¹⁷ - we estimate that the global
103 pool of OC specifically associated to Fe corresponds to $21.5 \pm 8.6\%$ of the total sedimentary OC
104 or 19 to 45×10^{15} g of OC. Even in mature sediments (1000 to 1500 yrs old), 23-27% of the total
105 OC remains bound to reactive Fe oxide phases, suggesting that the strong association between
106 Fe and OC may inhibit microbial OC degradation and enhance OC preservation.

107

108 In agreement with Wagai and Mayer's calculations³, our measurements reveal that
109 reactive Fe phases do not provide sufficient surface area (<5% of the total surface area of
110 sediments; Supplementary Table 3) for adsorption of the entire OC-Fe pool onto Fe oxides.
111 Alternatively, we propose the existence of largely organic OC-Fe macromolecular structures
112 that are dissolved and dislodged from the sediment during iron reduction. Transmission

113 electron microscopy studies describe sedimentary organic matter as “discrete, discontinuous
114 blebs” that adhere to the surface of sediment clay particles¹⁶. These “blebs” are consistent with
115 our proposed structure of OC-Fe, as are the findings of Mayer¹⁷, who reported that sedimentary
116 organic matter is not spread evenly over clay particles but covers only about 15% of particle
117 surfaces. We believe that Fe or Fe oxides are critical in providing cohesion to these
118 macromolecular structures, possibly fixing them to clay particles through strong covalent
119 bonds.

120

121 Calculations by Wagai and Mayer³ indicate that simple sorption of OM on reactive Fe
122 oxide surfaces results in a maximum molar OC:Fe ratio of 1.0 for the co-extracted organic
123 carbon and iron, based on the maximal sorption capacity of reactive iron oxides for natural
124 organic matter. On the other hand, co-precipitation and/or chelation of organic compounds
125 with Fe generates low density, organic-rich structures with OC:Fe ratios between 6 and 10³.
126 According to the results of our dithionite extractions, typical continental margin sediments
127 overlain by oxic bottom waters yield an average OC:Fe ratio of 4.0 ± 2.8 (Supplementary Table
128 3), greatly exceeding the maximum sorption capacity of Fe oxides but consistent with the
129 formation of OC-Fe chelates. These chelates are predominantly organic structures which likely
130 resemble those depicted by the ‘onion model’ of Mackay and Zirino¹⁸, where organic molecules
131 are ‘glued’ together by Fe ions or nanophases of Fe oxides. The formation of such chelates from
132 solution is possible when the molar porewater OC to Fe ratio is approximately 10¹⁹⁻²⁰. This
133 molar ratio is typically observed in anoxic sediment porewaters such as in the St. Lawrence
134 Estuary (Lalonde unpubl. data) and in the nearby Saguenay Fjord²¹. The diffusion of dissolved

135 Fe(II) from anoxic to surficial oxic sediments would trigger the oxidation of Fe(II) to Fe(III) and
136 the formation of very stable organic complexes ($K \approx 10^{14} \text{ M}^{-1}$ for natural dissolved OC to 10^{52} M^{-1}
137 ¹ for siderophores)²²⁻²³.

138
139 Sediments bathed by oxygen-depleted bottom waters, such as in the Black Sea, the
140 Mexican margin (Stn. 306) and the Indian margin, host high OC:Fe ratio structures (7 to 32).
141 These organo-metallic structures appear to be particularly stable under anaerobic conditions
142 and survive degradation. In contrast, in oxic environments, the organic lining of these structures
143 is progressively degraded, reducing the OC:Fe ratio to levels observed in typical continental
144 margin sediments (Fig. 1). Long periods of exposure to oxic conditions increase the fraction of
145 the total sedimentary OC pool that is tightly adsorbed to particle surfaces²⁴, owing to the
146 preferential degradation of organic structures that are more loosely attached to the clay
147 mineral matrix, such as the OC-Fe chelates. Very long exposure to oxic conditions results in the
148 very low OC:Fe observed at the deep-sea Equatorial Pacific site (0.36; Fig.1).

149
150 We also analyzed the isotopic ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) and elemental composition (C:N molar
151 ratio) of the bulk OM and the Fe-associated OC fractions of all sediment samples. In most cases,
152 we find that the OC-Fe is enriched in ¹³C ($\delta^{13}\text{C}$ increases by $1.7 \pm 2.8\text{‰}$) (Fig. 2) and nitrogen
153 (C/N decreases by 1.7 ± 2.8) relative to the rest of the sedimentary OC pool whereas $\delta^{15}\text{N}$
154 displayed little or no fractionation (Supplementary Figs. 1 and 2). ¹³C-rich natural organic
155 compounds include proteins and carbohydrates²⁵, which are rich in nitrogen and/or oxygen
156 functionalities that favour the formation of inner-sphere complexes with Fe. The preferential

157 binding of such highly labile organic compounds to Fe may explain why reactive organic
158 compounds can be preserved in sediments while other, more recalcitrant molecules, are
159 degraded⁴.

160

161 Our findings have far-reaching implications on our understanding of organic matter
162 cycling in sediments. First, the protection mechanism described above, which preferentially
163 shields ¹³C- and nitrogen-rich organic compounds from microbial degradation, could help
164 explain a phenomenon that has puzzled organic geochemists for decades: the replacement,
165 seaward of river mouths, of terrigenous organic matter from sediments by compounds bearing
166 a more marine isotopic and elemental signature²⁶. Our data also show that the traditional
167 sorptive stabilization mechanism, which hypothesizes that clay particles have a preservative
168 effect on organic matter through direct adsorption on their surfaces^{4,27-28}, does not describe
169 accurately the mode of stabilization for all organic compounds in sediments. Although more
170 work is needed to elucidate the exact nature of OC-Fe interactions, our data suggest that direct
171 chelation or co-precipitation of macromolecular OC-Fe structures also plays a significant role.
172 Finally and most importantly, our results reveal that $21.5 \pm 8.6\%$ of the OC buried in surface
173 marine sediments (150×10^{15} g of OC⁴), or a global mass of 19 to 45×10^{15} g of OC, is preserved
174 as a result of its intimate association with reactive Fe phases. Assuming that our estimate also
175 applies to OC locked in the sedimentary rock reservoir ($150,000 \times 10^{18}$ g of OC⁴), Fe-associated
176 OC would account for 1900 to 4500×10^{18} g of OC, or roughly 2900 to 6800 times the size of the
177 atmospheric carbon pool. Hence, reactive Fe phases serve as an extremely efficient “rusty sink”

178 for OC, a key factor in the long-term storage of organic carbon and the global cycles of carbon,
179 oxygen and sulphur.
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244 Supplementary Information is linked to the online version of the paper at
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257 and A.M. conceived the project, interpreted the empirical the findings and wrote the

258 manuscript. K.L. gathered all the data. Groundwork for this study was carried out by A.O. and L.

259 N. Barazzuol. A.O. also contributed to the writing of the manuscript.

260

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262 www.nature.com/reprints. The authors declare no competing financial interests.

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266 *Figure captions:*

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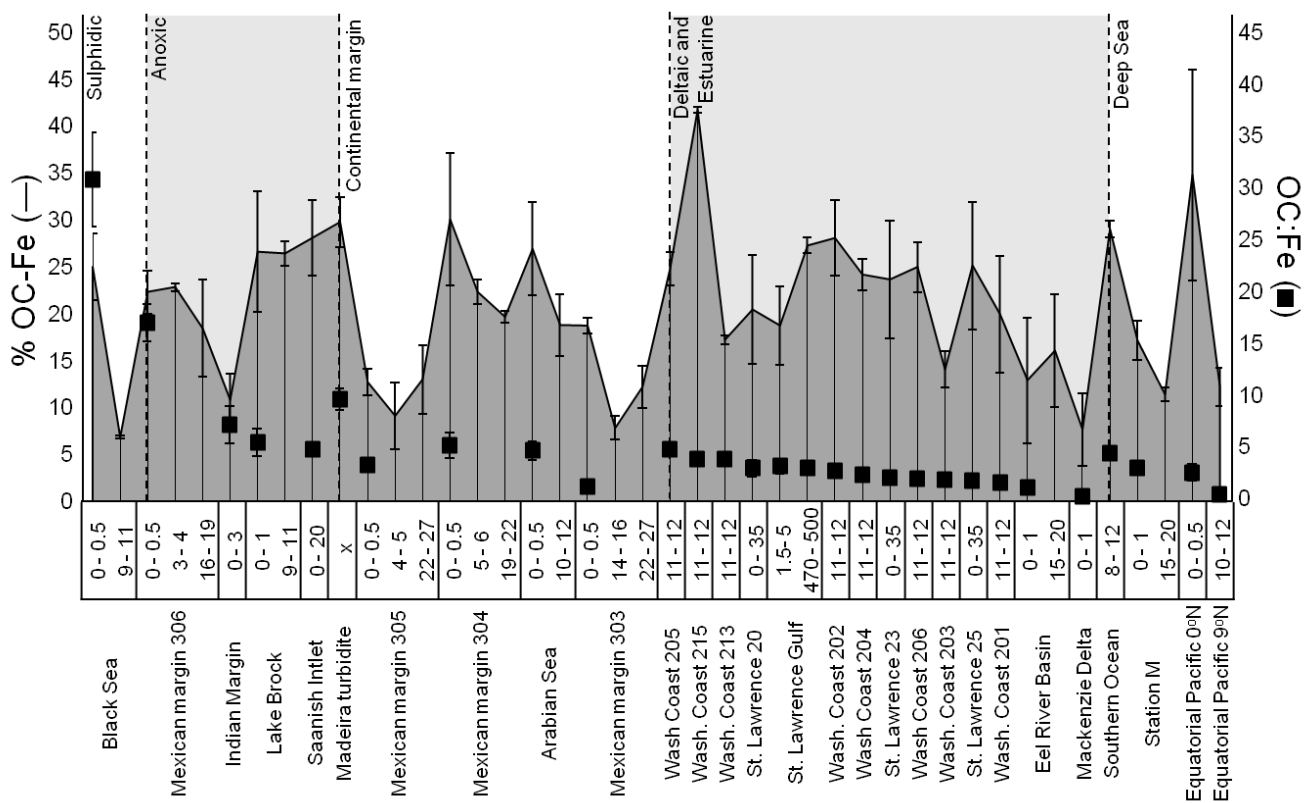
268 Figure 1: Control-corrected percentage of the total sediment organic carbon (OC) bound to
269 reactive iron phases, i.e., dislodged from the sediment during the reductive dissolution of
270 reactive iron oxides. Depth intervals (cm) and sample names are indicated below the x-axis.
271 Molar OC:Fe ratios of the uppermost surface sediment layer are also shown (black squares).
272 The iron reduction was carried out following the method of Mehra and Jackson (1960) without
273 adding agents that promote flocculation of the dissolved organic matter after the reduction
274 step. Error bars show s.d. (n = 12-15 for the St. Lawrence samples, and n = 3 for all the others).

275

276 Figure 2: Carbon isotopic signatures ($\delta^{13}\text{C}$ normalized to VPDB) of non iron-bound organic
277 carbon (OC) (blue) and iron-bound OC (brown) for all sediment samples. The samples were
278 depth-integrated whenever possible; the number of depth intervals integrated is indicated in
279 parentheses above the sample name. Error bars show s.d. (n = 12-15 for the St. Lawrence
280 samples, and n = 3 for all the others).

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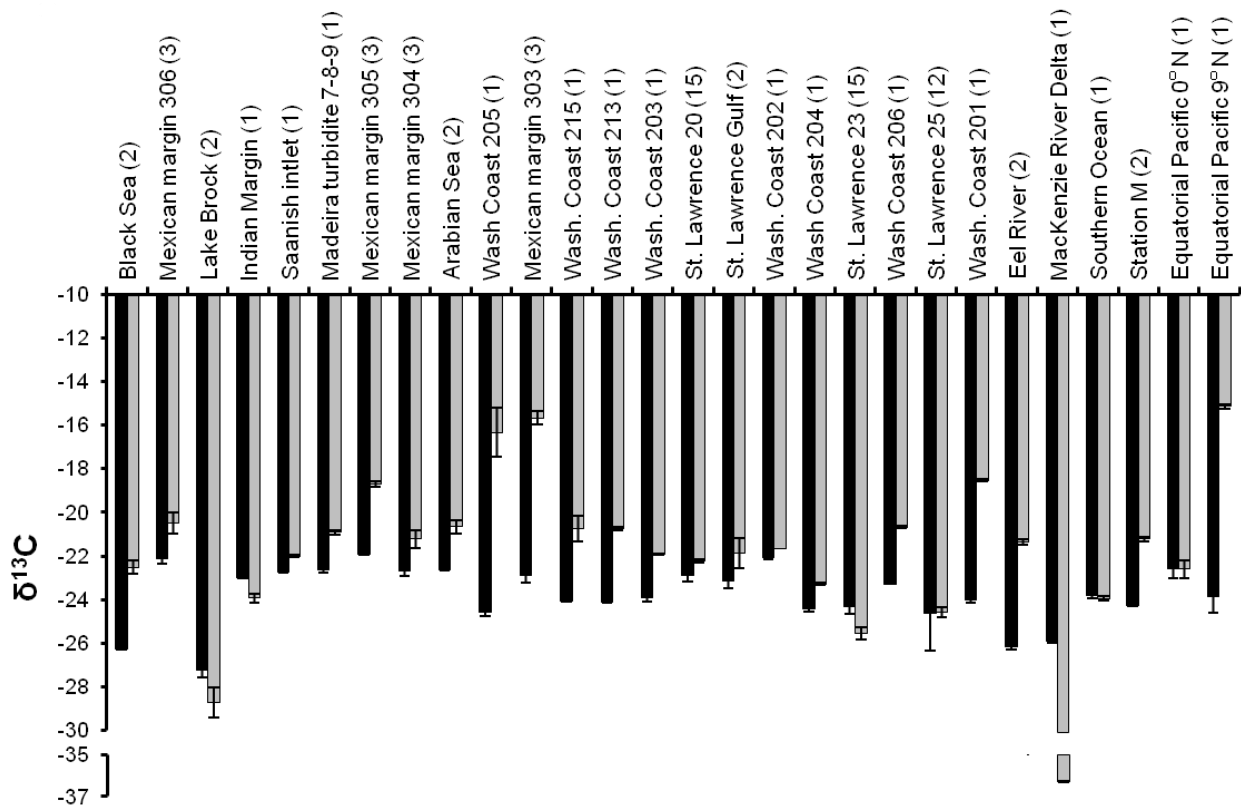
282 Figure 1



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291 Figure 2



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