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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 iron[1]. In soils, solid iron phases provide a sheltering and preservative effect for organic

36 carbon[2], 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 soils[3]. 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 x 10^{15} g of organic carbon in

42 surface marine sediments[4]. 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 sulphur [5].

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-vary[6]. 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 systems[2], 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 diameter[9-10]. 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 sediment[11]. 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 iron[12], and by organic

67 matter coating of Fe phases[13]. Accordingly, reactive Fe phases have been shown to survive in

68 sediments for hundreds of thousands of years[14].

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 O_2-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 O_2-

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 Jackson[15], 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 ± 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 ± 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%, respectively[17] - we estimate that the global

103   pool of OC specifically associated to Fe corresponds to 21.5 ± 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 calculations[3], 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 particles[16]. These "blebs" are consistent with

115   our proposed structure of OC-Fe, as are the findings of Mayer[17], 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 Mayer[3] 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 10 [3].

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 Zirino[18], 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 10 [19-20]. 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 Fjord[21]. 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 ($K \approx 10^{14}$ M^{-1} for natural dissolved OC to 10^{52} M^{-1}

137   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 surfaces[24], 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 ($\delta^{13}C$ and $\delta^{15}N$) 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 ^{13}C ($\delta^{13}C$ increases by 1.7 ± 2.8‰) (Fig. 2) and nitrogen

153   (C/N decreases by 1.7 ± 2.8) relative to the rest of the sedimentary OC pool whereas $\delta^{15}N$

154   displayed little or no fractionation (Supplementary Figs. 1 and 2). ^{13}C-rich natural organic

155   compounds include proteins and carbohydrates[25], 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   degraded[4].

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 ^{13}C- 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 signature[26]. 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 OC[4]), 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 OC[4]), 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

245   www.nature.com/nature.

246

256 Author Contributions: The original working hypothesis was formulated by Y.G., while K.L., Y.G.

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.

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

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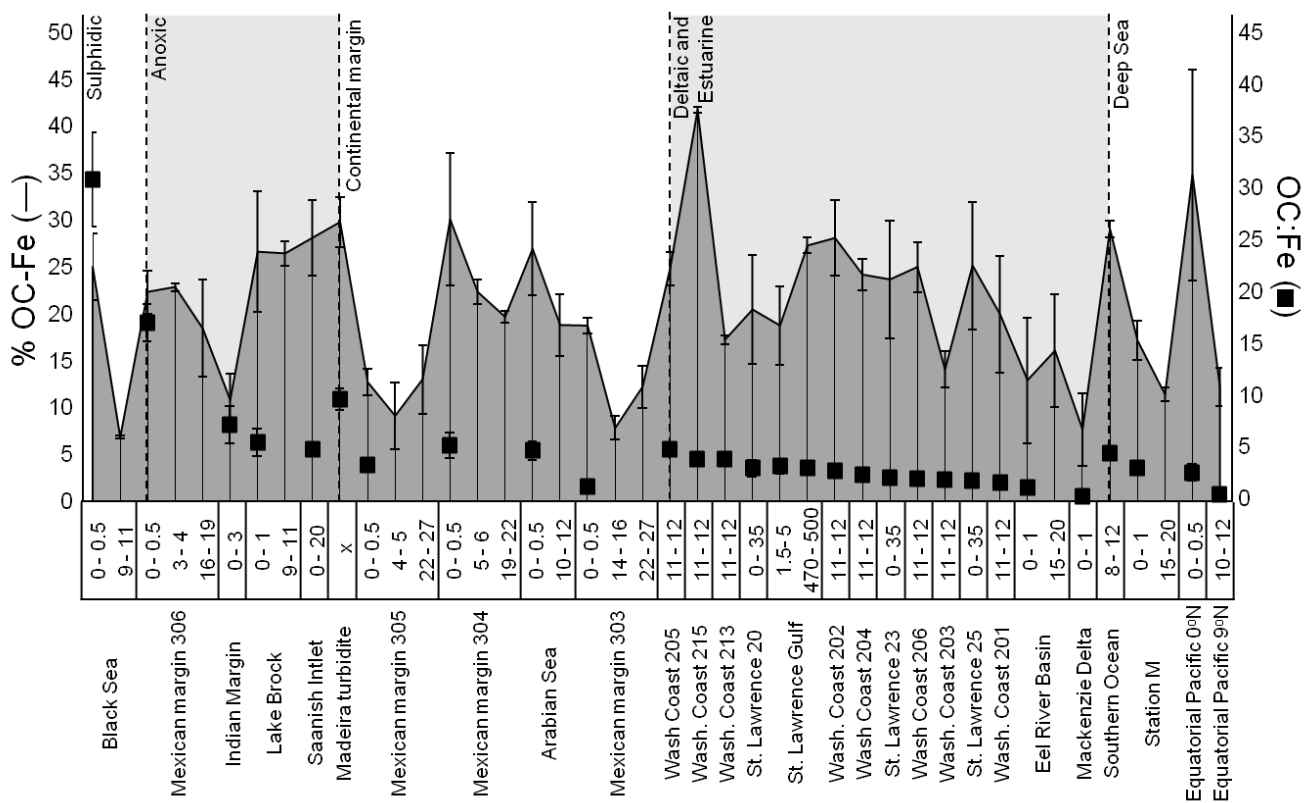
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266   *Figure captions:*

267

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 (δ^{13}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

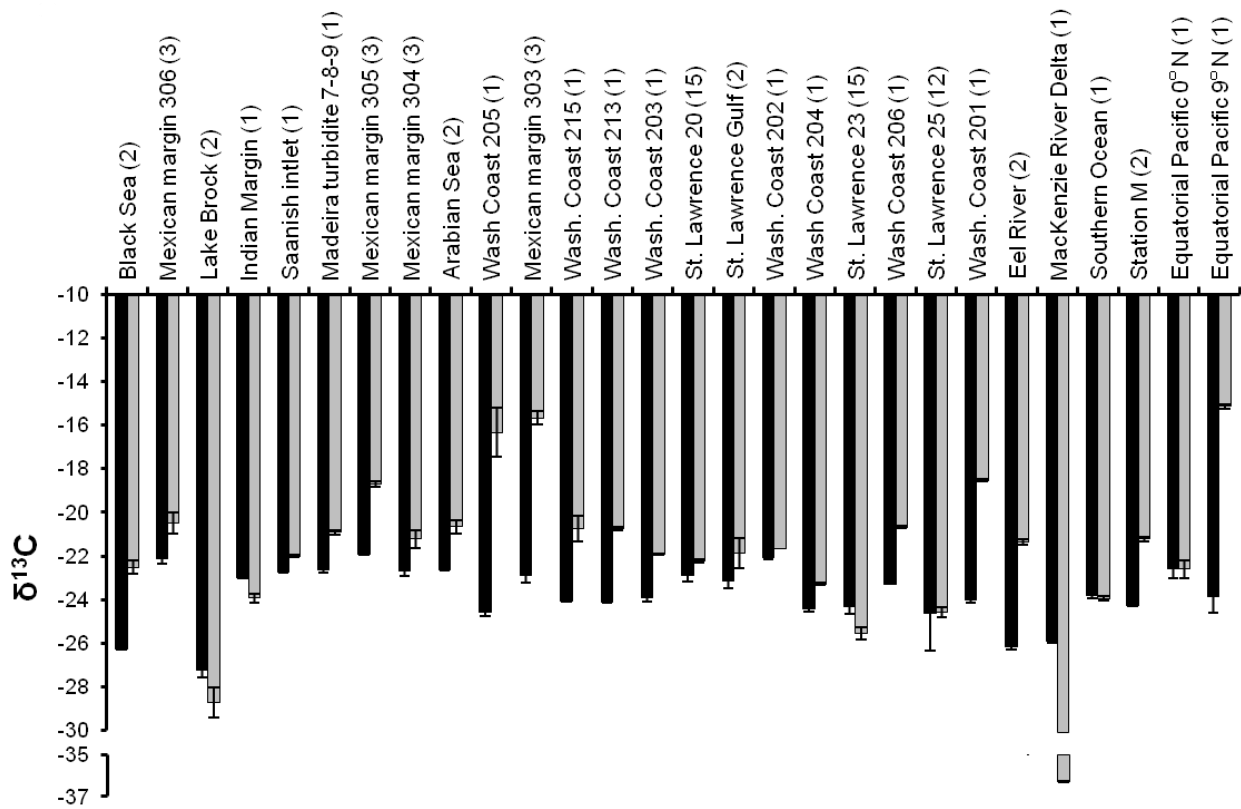280   samples, and n = 3 for all the others).

281

282   Figure 1

290

291   Figure 2

292