Iron promotes the preservation of organic matter in sediments

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The biogeochemical cycles of iron and organic carbon are strongly interlinked. In oceanic waters organic ligands have been shown to control the concentration of dissolved iron\(^1\). In soils, solid iron phases provide a sheltering and preservative effect for organic carbon\(^2\), but the role of iron in the preservation of organic matter in sediments has not been clearly established. Here, we determine the amount of organic carbon, associated with reactive iron phases in sediments of various mineralogies collected from a wide range of depositional environments, using an iron reduction method previously applied to soils\(^3\). Our findings suggest that 21.5 ± 8.6 per cent of the organic carbon in sediments is directly bound to reactive iron phases, representing a global mass of 19 to 45 x 10\(^{15}\) g of organic carbon in surface marine sediments\(^4\). We propose that these organic carbon-iron associations, formed primarily through co-precipitation and/or direct chelation, promote the preservation of organic carbon in sediments. Since reactive iron phases are metastable over geological timescales, they serve as an efficient “rusty sink” for OC, a key factor in the long-term storage of organic carbon and thus contributing to the global cycles of carbon, oxygen and sulphur\(^5\).
Evidence of interactions between Fe and OC in marine sediments was reported nearly 40 years ago, where concentrations of Fe and OC were found to co-vary. Since both Fe and OC are commonly associated with clay mineral surfaces, it was simply stated that “where there is more deposited fine-grained material with high surface area for adsorption, we find more organic matter and more Fe.” It is still not clear whether this correlation stems from the strong affinity of both species for solid surfaces or if it reflects enhanced OC preservation by Fe. Iron’s preservative effect on organic matter was previously demonstrated in laboratory studies, which report that the presence of iron-rich solid substrates or the formation of organo-ferric complexes hampers microbial degradation of simple organic compounds. Iron also imparts a protective effect to OC in soil systems, but this preservation mechanism has never been explored in sediments.

In modern sediments, reactive Fe phases (operationally defined here as the solid iron phases that are reductively dissolved by sodium dithionite) are typically found as nano-spheres of goethite of <10 nm in diameter. These phases accumulate or are formed within the oxic sediment layer through oxidation and precipitation of dissolved Fe(II) produced during weathering and diagenetic recycling within the sediment. Over time, reactive Fe phases become more crystalline, resulting in reduced surface reactivity/area and solubility. Crystallization is, however, hindered by the active diagenetic recycling of iron, and by organic matter coating of Fe phases. Accordingly, reactive Fe phases have been shown to survive in sediments for hundreds of thousands of years.
We examined sediments collected from a wide range of environments, including freshwaters, estuaries, river deltas, continental margins and the deep-sea, encompassing various depositional environments and mineralogies. These samples include OC-rich sulphidic Black Sea sediments and OC-rich sediments from O₂-deficient zones along the Indian and Mexican (Stn. 306) margins. Also included are sediments from the Arabian Sea, the Saanish Inlet and a boreal lake (Lake Brock) which exhibit a productivity-driven seasonal pattern of O₂-deficient waters. Estuarine, deltaic and margin deposits accumulating below well-oxygenated waters of the Arctic margin, the St. Lawrence Estuary and Gulf, the Mexican margin (Stns. 303-305), the Eel River Basin and the Washington coast and adjacent Columbia River delta are also examined along with pelagic sediments from the Southern Ocean, the Santa Barbara Basin (Stn. M) and Equatorial Pacific Ocean. This sample set comprises freshwater, estuarine and marine clastic sediments, carbonate and siliceous oozes, as well as pelagic red clay sediments. We focused on determining the amount of OC associated with reactive Fe phases by applying the citrate-dithionite iron reduction method of Mehra and Jackson\textsuperscript{15}, which simultaneously dissolves all solid reactive Fe phases and the OC associated to these phases (OC-Fe) from the sediment matrix. The reduction reaction is conducted at circumneutral pH using sodium bicarbonate as a buffer, thus preventing the hydrolysis of organic matter as well as its protonation and readsorption onto sediment particles which occur under acidic conditions. Whereas the extraction of the same samples with artificial seawater released a negligible fraction of the total OC (less than 3%; results not shown), samples treated under the same experimental conditions after substituting trisodium citrate (complexing agent) and sodium
dithionite (reducing agent) for sodium chloride (equivalent ionic strength) released on average 7.2 ± 5.4% of the total OC (Supplementary Table 2). Because the OC released in these control experiments is not associated with Fe, results of individual control experiments were subtracted from the amount of OC released from the dithionite extractions (see Supplementary method for results and discussion on contamination and specificity for the OC-Fe fraction).

We determined that for all sediments tested, an average of 20.5 ± 7.8% of the total OC is directly associated to Fe, with the highest OC-Fe concentrations in the uppermost sediment layers where most of the reactive Fe phases accumulate (Fig. 1). Considering OC burial within different depositional settings - deltaic and continental margin sediments account, respectively, for 44% and 45% of global OC burial, while pelagic sediments and high productivity zones, including anoxic basins, account for 5% and 6%, respectively\textsuperscript{17} - we estimate that the global pool of OC specifically associated to Fe corresponds to 21.5 ± 8.6% of the total sedimentary OC or 19 to 45 × 10^{15} g of OC. Even in mature sediments (1000 to 1500 yrs old), 23-27% of the total OC remains bound to reactive Fe oxide phases, suggesting that the strong association between Fe and OC may inhibit microbial OC degradation and enhance OC preservation.

In agreement with Wagai and Mayer’s calculations\textsuperscript{3}, our measurements reveal that reactive Fe phases do not provide sufficient surface area (<5% of the total surface area of sediments; Supplementary Table 3) for adsorption of the entire OC-Fe pool onto Fe oxides. Alternatively, we propose the existence of largely organic OC-Fe macromolecular structures that are dissolved and dislodged from the sediment during iron reduction. Transmission
electron microscopy studies describe sedimentary organic matter as “discrete, discontinuous blebs” that adhere to the surface of sediment clay particles. These “blebs” are consistent with our proposed structure of OC-Fe, as are the findings of Mayer, who reported that sedimentary organic matter is not spread evenly over clay particles but covers only about 15% of particle surfaces. We believe that Fe or Fe oxides are critical in providing cohesion to these macromolecular structures, possibly fixing them to clay particles through strong covalent bonds.

Calculations by Wagai and Mayer indicate that simple sorption of OM on reactive Fe oxide surfaces results in a maximum molar OC:Fe ratio of 1.0 for the co-extracted organic carbon and iron, based on the maximal sorption capacity of reactive iron oxides for natural organic matter. On the other hand, co-precipitation and/or chelation of organic compounds with Fe generates low density, organic-rich structures with OC:Fe ratios between 6 and 10. According to the results of our dithionite extractions, typical continental margin sediments overlain by oxic bottom waters yield an average OC:Fe ratio of 4.0 ± 2.8 (Supplementary Table 3), greatly exceeding the maximum sorption capacity of Fe oxides but consistent with the formation of OC-Fe chelates. These chelates are predominantly organic structures which likely resemble those depicted by the ‘onion model’ of Mackay and Zirino, where organic molecules are ‘glued’ together by Fe ions or nanophases of Fe oxides. The formation of such chelates from solution is possible when the molar porewater OC to Fe ratio is approximately 10. This molar ratio is typically observed in anoxic sediment porewaters such as in the St. Lawrence Estuary (Lalonde unpubl. data) and in the nearby Saguenay Fjord. The diffusion of dissolved
Fe(II) from anoxic to surficial oxic sediments would trigger the oxidation of Fe(II) to Fe(III) and the formation of very stable organic complexes (\(K \approx 10^{14} \text{ M}^{-1}\) for natural dissolved OC to \(10^{52} \text{ M}^{-1}\) for siderophores)\(^{22-23}\).

Sediments bathed by oxygen-depleted bottom waters, such as in the Black Sea, the Mexican margin (Stn. 306) and the Indian margin, host high OC:Fe ratio structures (7 to 32). These organo-metallic structures appear to be particularly stable under anaerobic conditions and survive degradation. In contrast, in oxic environments, the organic lining of these structures is progressively degraded, reducing the OC:Fe ratio to levels observed in typical continental margin sediments (Fig. 1). Long periods of exposure to oxic conditions increase the fraction of the total sedimentary OC pool that is tightly adsorbed to particle surfaces\(^ {24}\), owing to the preferential degradation of organic structures that are more loosely attached to the clay mineral matrix, such as the OC-Fe chelates. Very long exposure to oxic conditions results in the very low OC:Fe observed at the deep-sea Equatorial Pacific site (0.36; Fig.1).

We also analyzed the isotopic (\(\delta^{13}C\) and \(\delta^{15}N\)) and elemental composition (C:N molar ratio) of the bulk OM and the Fe-associated OC fractions of all sediment samples. In most cases, we find that the OC-Fe is enriched in \(^{13}C\) (\(\delta^{13}C\) increases by 1.7 ± 2.8‰) (Fig. 2) and nitrogen (C/N decreases by 1.7 ± 2.8) relative to the rest of the sedimentary OC pool whereas \(\delta^{15}N\) displayed little or no fractionation (Supplementary Figs. 1 and 2). \(^{13}C\)-rich natural organic compounds include proteins and carbohydrates\(^ {25}\), which are rich in nitrogen and/or oxygen functionalities that favour the formation of inner-sphere complexes with Fe. The preferential
binding of such highly labile organic compounds to Fe may explain why reactive organic compounds can be preserved in sediments while other, more recalcitrant molecules, are degraded\textsuperscript{4}.

Our findings have far-reaching implications on our understanding of organic matter cycling in sediments. First, the protection mechanism described above, which preferentially shields \textsuperscript{13}C- and nitrogen-rich organic compounds from microbial degradation, could help explain a phenomenon that has puzzled organic geochemists for decades: the replacement, seaward of river mouths, of terrigenous organic matter from sediments by compounds bearing a more marine isotopic and elemental signature\textsuperscript{26}. Our data also show that the traditional sorptive stabilization mechanism, which hypothesizes that clay particles have a preservative effect on organic matter through direct adsorption on their surfaces\textsuperscript{4,27-28}, does not describe accurately the mode of stabilization for all organic compounds in sediments. Although more work is needed to elucidate the exact nature of OC-Fe interactions, our data suggest that direct chelation or co-precipitation of macromolecular OC-Fe structures also plays a significant role.

Finally and most importantly, our results reveal that 21.5 ± 8.6\% of the OC buried in surface marine sediments (150 × 10\textsuperscript{15} g of OC\textsuperscript{4}), or a global mass of 19 to 45 × 10\textsuperscript{15} g of OC, is preserved as a result of its intimate association with reactive Fe phases. Assuming that our estimate also applies to OC locked in the sedimentary rock reservoir (150,000 × 10\textsuperscript{18} g of OC\textsuperscript{4}), Fe-associated OC would account for 1900 to 4500 × 10\textsuperscript{18} g of OC, or roughly 2900 to 6800 times the size of the atmospheric carbon pool. Hence, reactive Fe phases serve as an extremely efficient “rusty sink”
for OC, a key factor in the long-term storage of organic carbon and the global cycles of carbon, oxygen and sulphur.
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238 Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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Figure captions:

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

Figure 2: Carbon isotopic signatures ($\delta^{13}$C normalized to VPDB) of non iron-bound organic carbon (OC) (blue) and iron-bound OC (brown) for all sediment samples. The samples were depth-integrated whenever possible; the number of depth intervals integrated is indicated in parentheses above the sample name. Error bars show s.d. (n = 12-15 for the St. Lawrence samples, and n = 3 for all the others).
Figure 1