GEOCHEMISTRY

Mineralogical control on the fate of continentally derived organic matter in the ocean

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First-order relationships between organic matter content and mineral surface area have been widely reported and are implicated in stabilization and long-term preservation of organic matter. However, the nature and stability of organomineral interactions and their connection with mineralogical composition have remained uncertain. In this study, we find that continentally derived organic matter of pedogenic origin is stripped from smectite mineral surfaces upon discharge, dispersal, and sedimentation in distal ocean settings. In contrast, organic matter sourced from ancient rocks that is tightly associated with mica and chlorite endures in the marine realm. These results imply that the persistence of continentally derived organic matter in ocean sediments is controlled to a first order by phyllosilicate mineralogy.

Phyllosilicates are dispersed across the ocean floor with their terrestrial provenance manifested in spatial gradients of abundance and composition, the latter of which is controlled by regional climate and bedrock lithology (1). The major phyllosilicates in ocean sediments (smectite, chlorite, mica, and kaolinite) differ in the configuration of their tetrahedral and octahedral sheets, giving rise to differences in physicochemical properties such as interlayer expansion ability, mineral surface area (MSA), and cation exchange capacity (CEC) (1, 2). Because of the high reactivity of phyllosilicates, much research has focused on their interactions with organic matter (OM) in order to understand their influence on OM stabilization in soils and preservation in both recent and geologically ancient sediments (3–5). Mineral ballast is a key mechanism by which OM is exported to the deep ocean by accelerating sinking velocity and increasing export efficiency of particulate matter from surface waters (6, 7), while MSA is considered to provide physical protection of mineral-associated OM (8) against microbial (9) and oxidative attack (10, 11). OM-mineral interactions exert a primary control on OM preservation in modern and ancient continental margin sediments, which account for ~90% of organic carbon (OC) burial in the ocean, as evidenced by strong coupling of sedimentary OC content with MSA (12–14). The loss of terrestrial OM sorbed on mineral surfaces, and its exchange with marine OM as sediments are exported via rivers from land to ocean, varies markedly between fluvio-deltaic systems, suggesting that MSA is not the only control (15). The precise nature and dynamics of these interactions, including the significance of high–surface area phyllosilicates as agents for OM sequestration, raise questions concerning the influence of mineralogy on the biogeochemical cycling of carbon and associated elements in the modern ocean, as well as its role in modulating OM burial over geologic time.

To investigate mineralogical controls on OC stabilization, this study exploits the distinct mineral end-member characteristics of the northeastern South China Sea (SCS), which serves as a natural laboratory for examining OM-mineral interactions. Sediments in this region, which are characterized by high aluminum content (16) indicative of high terrigenous mineral content, exhibit one of the most pronounced spatial gradients in phyllosilicate composition in the world's oceans. This gradient results from a binary mixing of detrital minerals primarily from two source terrains: volcanic bedrock on the island of Luzon (Philippines), where chemical weathering gives rise to pedogenic smectite (17), and the Taiwan orogen, where rapid physical weathering releases bedrock-derived mica and chlorite-rich phyllosilicate assemblages to the surrounding ocean (18). Deep-sea phyllosilicate assemblages of sediments in the northeastern SCS are dominated by these two source terrains (19), providing the bulk of the mineral substrate. These uniformly high inputs of terrigenous minerals (e.g., aluminosilicates such as feldspars and phyllosilicates; see data S1) are manifested in deep-sea settling particles intercepted at water depths between 1900 and 3800 m by sediment traps deployed in this region (fig. S1). Mineralogical composition and mineral reactivity (20) (the latter defined here as the expression of MSA and CEC) of sediment trap samples is visualized in Fig. 1. Mineral reactivity is highest for sediments intercepted at traps TJ-C-MID and TJ-C-DOWN owing to the high smectite content, which reflects the mooring's proximity to Luzon. In contrast, mineral reactivity is lowest in TJ-G-DOWN, where mica and chlorite content are highest as a result of sedimentary input predominantly from Taiwan. For sediment trap TJ-A-DOWN, the phyllosilicate composition and mineral reactivity lie intermediate to those of moorings at station TJ-G and TJ-C (see figs. S2 to S6 for representative x-ray diffraction patterns). OC content ranges from 0.6 to 6.1 weight % (wt %) OC, with stable carbon isotopic compositions (δ^{13}C values) between −24.2 and −21.6 per mil (‰), and radiocarbon isotopic compositions from 0.33 to 1.03 Fm (fraction modern) (20). On the basis of these signatures, we find that the OC comprises a binary mixture of petrogenic and marine biospheric OC with end-member stable carbon isotopic and radiocarbon signatures of −25.4 and −22.0‰, and of 0 and 1.04 Fm, respectively, and lacks discernible additions of soil OC (see supplementary text).

Increasing proportions of marine OM, despite uniformly high aluminum content of sinking particulate matter, reveal that the provenance of sedimentary OM and minerals is
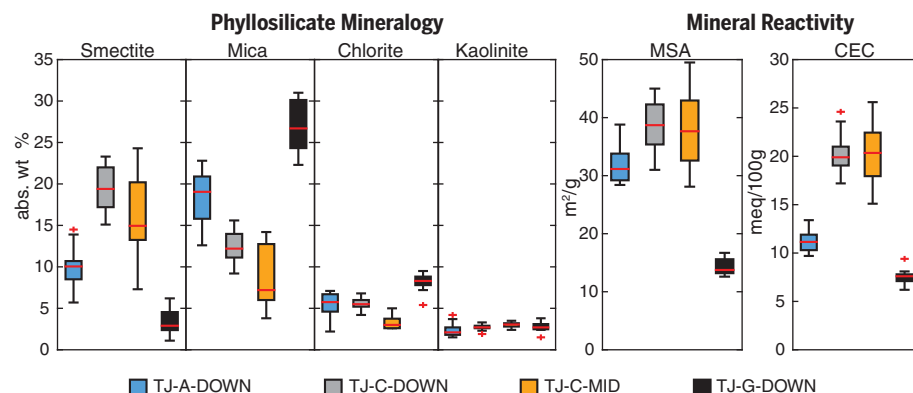
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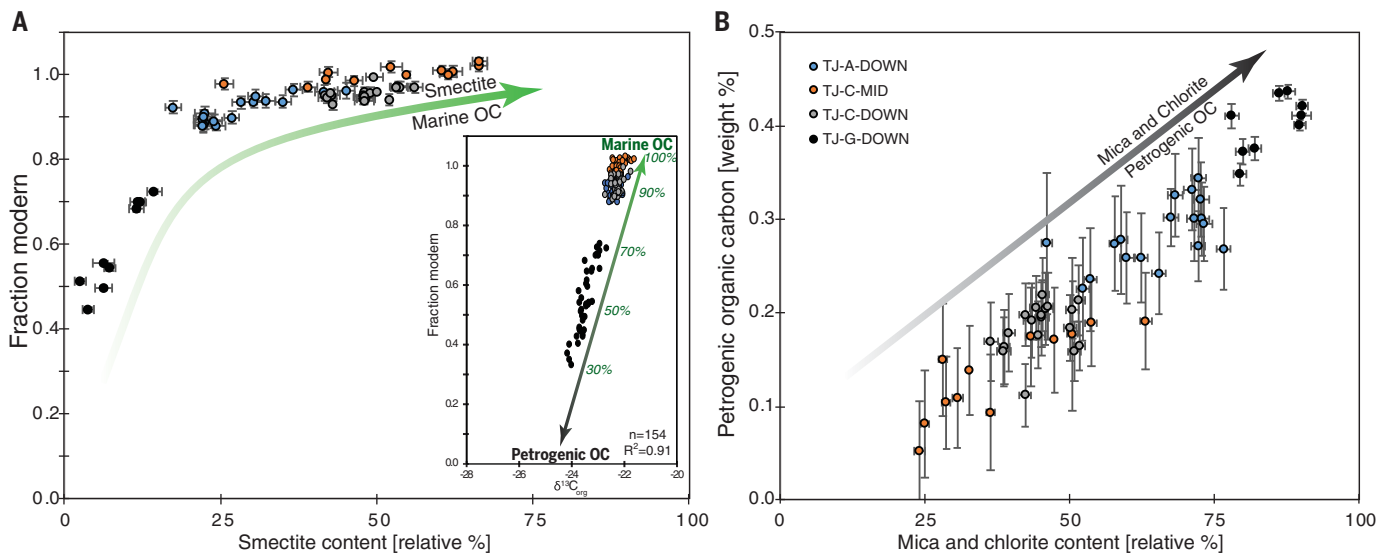

Fig. 1. Phyllosilicate composition, MSA, and CEC of sediment trap samples from the northeastern SCS. Abs. wt %, absolute weight %.

Fig. 2. Evidence for mineralogical control on the fate of sedimentary OM. (**A**) Relationship between the proportion of marine OC, as inferred from radiocarbon content (fraction modern values) and smectite abundance (relative to total phyllosilicate abundance). Inset image shows carbon isotopic composition of sediment trap–intercepted OM over a 2-year deployment period. (**B**) Relationship between the abundance of petrogenic OC and mica and chlorite abundance (relative to total phyllosilicate abundance). Error bars (±1σ) are propagated based on measurement and, for petrogenic OC, end-member uncertainties.

decoupled, implying loss and replacement of terrestrial OM initially associated with alumino-silicate mineral surfaces (*16*). This loss of terrestrial OM observed in bulk-level properties is also reflected on a molecular level by the loss of terrestrial lipids from suspended particulate matter in the northeastern SCS (*21*). Notably, increasing smectite content scales with the proportion of marine OM, implying extensive loss of soil OC from this pedogenic mineral (Fig. 2). In parallel, mineral surface properties of bulk sediment become increasingly dictated by smectite, which exhibits the highest MSA and CEC of all phyllosilicates (*2, 22*) (Fig. 2A, compare with fig. S7). Higher marine OC content thus correlates with increasing mineral reactivity (Fig. 3, A and B).

We suggest that changes in ionic composition and strength associated with freshwater-seawater transitions result in smectite being stripped of its associated pedogenic OC (see model in Fig. 4). Upon transitioning from fluvial to marine domains, the accompanying changes in salinity cause calcium-sodium exchange and delamination (*23*), the latter of which is a process unique to smectite (*24*). Although flocculation and settling of smectites occur, some smectites escape as small (partially) exfoliated particles, which subsequently may reassemble and sink (*23*), leading to differential settling and their enrichment in distal sediments (*1, 22, 23, 25*). As a result of exfoliation, we speculate that biological and chemical attack and cation exchange promote cleansing of smectite interlamellar surfaces of associated pedogenic OM before these surfaces are repopulated with fresh marine-dissolved and particulate OM. Although loss of
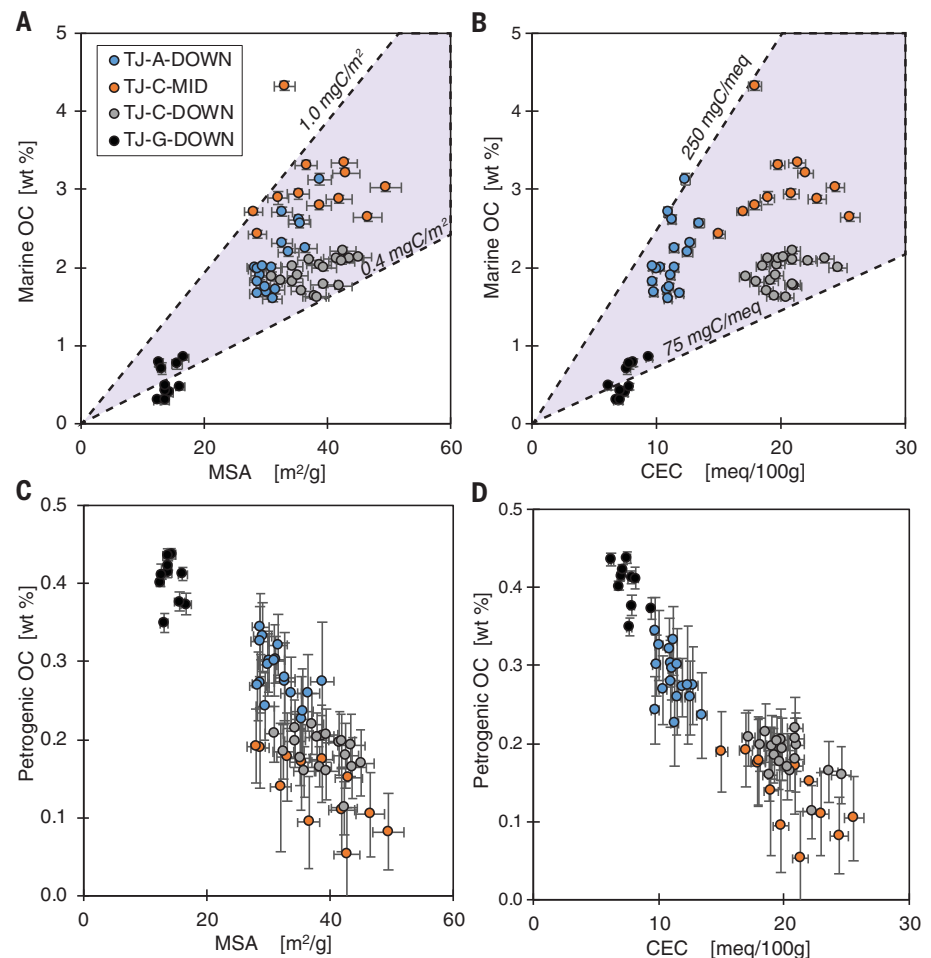

Fig. 3. Evidence for contrasting behavior of OM-mineral associations. Loadings of marine (**A** and **B**) and petrogenic (**C** and **D**) OC on mineral surfaces, as related to MSA [(A) and (C)] and CEC [(B) and (D)]. Error bars (±1σ) are propagated based on measurement and, for marine and petrogenic OC, end-member uncertainties.

Fig. 4. Evolving OM-phyllosilicate associations across the fluvial-marine transition. Loss and replacement of pedogenic OM (orange ellipses) with marine OM (green ellipses) occurring parallel to cation exchange of calcium ions (blue circles) with sodium ions (small red circles). The sediment traps TJ-A, TJ-C, and TJ-G are schematically pictured, showing the points of observation with their superimposed qualitative phyllosilicate and OM compositions.
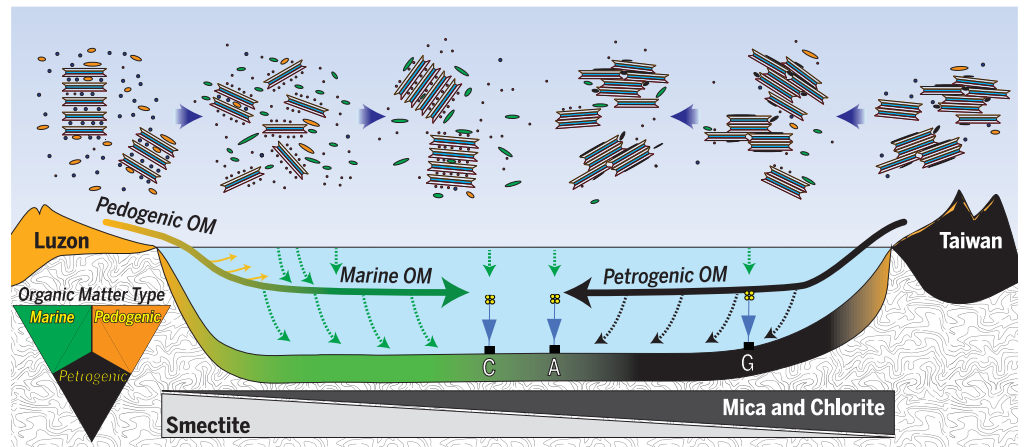
pedogenic OC from smectite-rich sediments may not be complete in marginal settings (*26*), presumably owing to dilution of marine OM near large river mouths, at least partial repopulation of smectite mineral surfaces appears to occur in these settings (*4*). This same process may also have operated in the Cretaceous, when OM predominantly of marine origin is associated with smectite-rich deep-sea sedimentary deposits (*13, 27*). Smectite-rich sediments, which are most prevalent at tropical latitudes and around point sources of volcanic bedrock, have waxed and waned over geologic time in response to climate and volcanism (*1, 27*), with Earth system evolution leading to a general increase in the abundance of smectite over the Phanerozoic (*28*). A corollary of this loss-and-replacement hypothesis is that terrestrial biospheric activity becomes decoupled from the geological carbon sink, rendering marine primary productivity and the oceanic biological pump as the main mechanisms for sequestration of atmospheric CO_2. This corresponds to a rerouting of the primary locus of CO_2 drawdown from land to ocean for marine basins receiving inputs from smectite-rich hinterlands.

In stark contrast, continentally derived OC of petrogenic origin associated with mica and chlorite is efficiently transferred to the abyssal ocean (*16, 29, 30*). Taiwan is characterized by poorly developed, thin soils, the formation of which is undermined by rapid physical erosion. This leads to strong dilution of pedogenic OC by bedrock-derived petrogenic OC in sediments exported to the ocean (*18, 30, 31*). Additionally, pedogenic OC is efficiently segregated from petrogenic OC during downslope transport (*29*) and trapped on the Taiwanese margin, resulting in its diminished occurrence in deep-sea sediments (*16*). The negative relationship between petrogenic OC abundance and mineral reactivity indicates that ion exchange does not lead to desorption of this type of OC. This inverse relationship stands counter

to the commonly observed positive OC-MSA relationships (*5, 12–14, 32*), including the one observed between marine biospheric OC and MSA in this study (Fig. 3). Close physical association between petrogenic OC and these lithogenic phyllosilicates is evident because differential hydrodynamic sorting processes would otherwise undermine the observed strong basin-wide correlation (Fig. 2B). However, whereas shielding of lithoclast-embedded petrogenic OC from exchange with seawater may be important for coarser sediments, the fine silt and clayey nature of distal sediments increases the exposure of mineral surfaces to seawater, thereby minimizing the effect of this textural overlay. Advanced phases of orogeny increase the supply of mica and chlorite to the oceans as a consequence of enhanced erosion of metamorphosed bedrock (*27*), which, as we demonstrate, is tightly coupled with petrogenic OC supply. Ultimately, this OM-mineral association appears to facilitate the reburial of petrogenic OC, which, in contrast to the burial of biospheric OC, exerts no influence on atmospheric CO_2 and O_2 (*33, 34*).

In addition to influencing OC burial in modern and past oceans, phyllosilicate composition has been invoked as a critical determinant for the preservation, and hence detection, of OM in sedimentary deposits on Mars. In particular, lacustrine deposits draining smectite-rich catchments are considered to generate conditions conducive to long-term preservation of mineral-protected OM (*35*); as such, processes discussed here may prove crucial for interpreting potential geochemical vestiges of life in Martian sediments. Overall, it is increasingly apparent that phyllosilicates, or "clays," are not only key agents driving OC sequestration (*5*), but phyllosilicate mineralogy also plays a crucial role in governing the type of OM ultimately preserved in ocean sediments and, potentially, on extraterrestrial bodies.

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SUPPLEMENTARY MATERIALS

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Materials and Methods
Supplementary Text
Figs. S1 to S7
References (*36–48*)
Data S1 and S2

Science

Mineralogical control on the fate of continentally derived organic matter in the ocean

T. M. Blattmann, Z. Liu, Y. Zhang, Y. Zhao, N. Haghipour, D. B. Montluçon, M. Plötze and T. I. Eglinton

Bound to rock

Organic matter binds to phyllosilicates, a process which affects both its transport and chemical stability. How does that affect the fate of terrestrial organic carbon that enters the ocean? Blattmann *et al.* show that organic carbon derived from soils is stripped from mineral surfaces upon discharge and dispersal into the ocean, whereas organic matter derived from ancient rocks is preserved there. Their results show that preservation of continentally derived organic matter in marine sediments is controlled largely by phyllosilicate mineralogy.
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