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Diverse origins and pre-depositional histories of organic matter in contemporary Chinese marginal sea sediments

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Abstract

Marginal seas are estimated to account for up to 90% of organic carbon (OC) burial in marine sediments, and thus play an important role in global carbon cycle. However, comprehensive assessments of carbon budgets for marginal sea systems are challenging due to their inherent complexity, with spatial and temporal variability in carbon inputs and dispersal processes. We examine the Bohai Sea and Yellow Sea (BS–YS) in order to further our understanding of sedimentary OC delivery, translocation and accumulation in a shallow marginal sea system. Bulk properties and the content and isotopic compositions ($\Delta^{14}C$, $\delta^{13}C$) of source-specific plant wax *n*-alkyl lipid biomarkers were determined for a suite of surficial sediment samples. Variable $\delta^{13}C$ values (−25.1‰ to −28.5‰) and contemporary radiocarbon ages of short-chain *n*-fatty acids (FAs; C_{16}, C_{18}) reflect modern autochthonous marine and/or fresh terrestrial plant input. In contrast, extremely depleted $\Delta^{14}C$ values (−932‰ to −979‰) of short-chain *n*-alkanes (C_{16}, C_{18}) suggest a predominant input from sedimentary rocks (petrogenic OC) or petroleum. Abundance-weighted average $\delta^{13}C$ and $\Delta^{14}C$ values of long-chain leaf wax lipids ($C_{26+28+30}$ *n*-FAs, $C_{24+26+28}$ *n*-alkanols, $C_{27+29+31}$ *n*-alkanes) are -29.1 ± 1.1‰ to -30.2 ± 0.3‰, and -286 ± 150‰ to -442 ± 119‰, respectively, illustrating that terrestrial OC delivery is dominated by pre-aged (~3000–5000 ^{14}C yrs) C_3 vegetation sources.

A coupled carbon-isotopic mixing model, based on the bulk and compound-specific biomarker $\delta^{13}C$ and $\Delta^{14}C$ values, is used to partition the BS–YS sedimentary OC into three components that reflect both origins and transport processes. For all sampling sites, 31–64% is modern/contemporary OC, 24–49% is pre-aged terrestrial OC, and 7–26% is fossil OC, the latter likely derived from both physical erosion of ancient sedimentary rocks and fossil fuel sources. Pre-aged soil OC is most prominent in front of the modern and old Huanghe (Yellow River) delta (48% and 49%), and fossil OC is most significant north of the old Huanghe mouth (26%). Significant pre-aged soil contributions (33%) are also evident for sites further offshore, where transport and deposition of eolian dust supply may be important. For the three major deposition areas of the BS–YS system (Bohai Basin, sub-aqueous Huanghe delta and central south YS basin), we estimate that about 3.02 Mt/yr of refractory, plant-derived pre-aged soil OC and 0.98 Mt/yr of ^{14}C-depleted fossil OC accumulates in surface sediments, corresponding

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to 35% and 11% of sediment TOC, respectively. Compared with estimates for fluxes from corresponding sources, the burial efficiency is close to 100% for pre-aged soil OC and 70% for fossil OC, implying efficient OC burial in delta and shelf environments. Re-burial of these two pools of terrigenous OC only affects carbon cycling on millennial and longer timescales respectively, and exerts little influence on the modern carbon cycle (<100 yr). Carbon isotopic compositions of source specific biomarkers are a useful tool not only for constraining OC sources and transport vectors, but also for delineating their impact on the contemporary carbon cycling in marginal sea systems.

Keywords: Organic carbon; The Bohai and Yellow Sea; Terrestrial; Pre-aged soil; Fossil; Radiocarbon; Compound-specific isotopes (^{14}C and ^{13}C)

1. INTRODUCTION

OC burial in marine and terrestrial sedimentary basins comprises the second largest long-term sink for atmospheric CO_2 on geological time-scales (Burdige, 2005; Galy et al., 2007). Due to high biological productivity, supply of allochthonous materials and sedimentation rates, marginal seas are regionally and globally significant sites of both carbon sequestration and remineralization. Despite occupying less than 10% of the global ocean area, continental shelves, including marginal seas, have been proposed to account for up to 90% of organic matter burial in the modern ocean (Hedges and Keil, 1995) and 20% of the net ocean CO_2 uptake (2.0 ± 0.6 Gt C) (Battle et al., 2000). However, considerable uncertainties persist regarding the nature and magnitude of carbon burial because marginal seas reside at the land–ocean continuum, and are inherently dynamic and spatially heterogeneous systems. OC supplied from adjacent continents via fluvial and eolian processes is augmented by marine OC produced in overlying waters, (Bianchi, 2011; Blair and Aller, 2012), resulting in diverse fluxes, reactivities and ages of organic matter deposited in marginal sea sediments. The extent to which OC burial constitutes a net carbon source or sink, strongly depends upon the origin of sedimentary OC.

OC in marginal sea sediments can be considered to comprise of three components: marine OC, terrestrial biospheric OC, and petrogenic OC from erosion of sedimentary rocks or from anthropogenic activities (Goñi et al., 2005; Drenzek et al., 2007; Galy et al., 2008; Kusch et al., 2010b; Blair and Aller, 2012). These different OC pools can influence the carbon cycle over varying timescales. Recent marine and terrestrial OC can be reactive and hence fully or partially degraded during transport and sedimentation processes, resulting in recycling of carbon to the atmosphere (Aller and Blair, 2004; Bianchi, 2011). On the other hand, burial of this recently synthesized "biospheric" OC in sediments reflects sequestration of modern C. Temporary storage or protracted translocation of biospheric OC within and between intermediate reservoirs (e.g., soils, floodplain deposits, mobile mudbelts) can influence remineralization/burial timescales. In contrast, recycling and reburial of "fossil OC" without significant alteration exerts a minimal net influence on atmospheric CO_2 (Galy et al., 2008; Galy and Eglinton, 2011). Anthropogenic activity has also contributed to the burial of fossil OC in marine sediments (Eglinton et al., 1997; Hedges et al., 1997; Pearson and Eglinton, 2000). Overall, the difference between oxidation and burial of the biospheric OC governs the net sink of atmospheric CO_2 over shorter timescales (decades to thousands years) whereas exhumation and re-burial of fossil OC has no net effect on atmospheric CO_2 (Galy et al., 2008; Galy and Eglinton, 2011).

Terrestrial OC discharged by large rivers (e.g., Brahmaputra-Ganga, Huanghe) is usually thought to be relatively refractory as a consequence of long-term storage and exposure to biological degradation in continental reservoirs (Eglinton et al., 1996; Kusch et al., 2010b; Galy and Eglinton, 2011; Feng et al., 2013a). In contrast, extensive loss of terrestrial OC in some estuarine and deltaic environments (Hedges et al., 1997; Keil et al., 1997; Aller et al., 2008; Bianchi, 2011) suggests that terrestrial OC can be reactive. In addition, dynamics associated with windborne and fluvial transport of terrestrial OC are quite distinct, with significant implications for the physicochemical characteristics of terrestrial OC supplied to the adjacent marginal seas. Shallow marginal seas are characterized by extensive horizontal material transport by coastal currents, storm and tidal activity, each affecting the fate of terrestrial and marine OC.

Association with mineral surfaces exerts strong influence not only on the reactivity of OC (Meyers, 1994; Keil et al., 1997; Blair and Aller, 2012; Bouchez et al., 2014), but also on its susceptibility to redistribution (Goñi et al., 1998). OC content generally positively correlates with mineral-specific surface area (SA), and is inferred to reflect organic matter association with, and protection by, fine-grained minerals (Keil et al., 1997; Goni et al., 2008; Blair and Aller, 2012). Moreover, hydrodynamic particle sorting processes in the benthic boundary layer promote resuspension, lateral transport and redistribution of OC (Kusch et al., 2010a; Xu et al., 2012). These complex patterns of OC supply and dispersal render it challenging to assess controls on the nature and burial efficiency of organic matter in marginal sea sediments (Ohkouchi et al., 1997; Kusch et al., 2010b). Nevertheless, constraining the various sources and ages of sedimentary OC components is essential for improved understanding of the various sedimentological and biogeochemical processes.

The BS–YS is a large river-influenced marginal sea system and is considered an important sink for atmospheric CO_2 (Oh et al., 2000; Chen and Borges, 2009). Only ~5% of the sediment derives from marine production or from