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Authors

Drenzek, Nicholas J
Hughen, Konrad A
Montluçon, Daniel B
et al.

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A new look at old carbon in active margin sediments

Nicholas J. Drenzek^{1*}, Konrad A. Hughen¹, Daniel B. Montluçon¹, John R. Southon²,
Guaciara M. dos Santos², Ellen R.M. Druffel², Liviu Giosan³, and Timothy I. Eglinton¹

¹Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, USA

²Department of Earth System Science, University of California–Irvine, Irvine, California 92697, USA

³Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, USA

ABSTRACT

Recent studies suggest that as much as half of the organic carbon (OC) undergoing burial in the sediments of tectonically active continental margins may be the product of fossil shale weathering. These estimates rely on the assumption that vascular plant detritus spends little time sequestered in intermediate reservoirs such as soils, freshwater sediments, and river deltas, and thus only minimally contributes to the extraneously old ¹⁴C ages of total organic matter often observed on adjacent shelves. Here we test this paradigm by measuring the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of individual higher plant wax fatty acids as well as the $\delta^{13}\text{C}$ values of extractable alkanes isolated from the Eel River margin (California). The isotopic signatures of the long chain fatty acids indicate that vascular plant material has been sequestered for several thousand years before deposition. A coupled molecular isotope mass balance used to reassess the sedimentary carbon budget indicates that the fossil component is less abundant than previously estimated, with pre-aged terrestrial material instead composing a considerable proportion of all organic matter. If these findings are characteristic of other continental margins proximal to small mountainous rivers, then the importance of petrogenic OC burial in marine sediments may need to be reevaluated.

INTRODUCTION

The transfer of terrigenous organic carbon (OC) from continents to the sea and its ultimate fate therein play an important role in regulating global carbon and oxygen cycles and hence past and future climate (Bernier, 1989; Burdige, 2005; Petsch, 2003). The ability of some of this OC to survive early diagenesis and the effect of its sedimentary burial on the oxidation state of the atmosphere may likewise be influenced by its molecular composition, mineral association, and the conditions under which it is deposited (Blair et al., 2003, 2004; Hedges and Keil, 1995; Keil et al., 1997; Leithold and Blair, 2001; Leithold et al., 2005).

Recent studies, primarily based on carbon isotopic measurements of total organic carbon (TOC) and its component compound classes, have suggested that petrogenic material ($\Delta^{14}\text{C} = -1000\text{‰}$) weathered from uplifted shales might contribute a significant portion of the recalcitrant organic matter delivered to the oceans (Blair et al., 2003, 2004; Dickens et al., 2004; Goñi et al., 2005; Hwang et al., 2005; Komada et al., 2004, 2005). The persistence of noncontemporary radiocarbon compositions of fluvial dissolved and particulate organic carbon phases, certain lipid fractions, and shallow sedimentary OC in an array of margin systems imply that some fossil material is able to evade complete remineralization (Goñi et al., 2005; Hwang et al., 2005; Komada et al., 2004, 2005; Raymond and Bauer, 2001a, 2001b; Yunker et al., 2005). While bacterial assimilation of petrogenic carbon has been demonstrated (Petsch et al., 2001, 2003), a significant portion might be efficiently recycled through the modern environment and undergo reburial in shelf sediments. Rapid delivery by small mountainous rivers that drain many shale-rich, tectonically active margins likely further aids in its overall preservation by effectively bypassing the efficient diagenetic machinery of many larger estuarine/deltaic systems (Blair et al., 2003, 2004).

Bulk level ¹⁴C depletions are not uniquely diagnostic of petrogenic inputs, however, and may also result from the incorporation of vascular plant detritus that has been pre-aged in an array of terrestrial reservoirs such as soils, wetlands, and freshwater sediments. Although previous

studies have provided indirect evidence of this process (Alin et al., 2008; Aller et al., 2008; Druffel et al., 1986; Goñi et al., 1997, 1998, 2005, 2008; Gordon and Goñi, 2004; Masiello and Druffel, 2001; McCallister et al., 2004; Perruchoud et al., 1999; Rethemeyer et al., 2004a, 2004b; Townsend-Small et al., 2005), isotopic measurement of attendant higher plant biomarkers can yield direct new information on the age, abundance, and preservation of such material independent of truly fossil counterparts. Here we utilize these molecular signatures in a coupled isotope mass balance to apportion the sources of OC in coastal sediments receiving large amounts of both petrogenic and vascular plant input from the episodic flooding of an adjacent small, mountainous river system.

SETTING AND METHODS

The ~20-km-wide Eel River margin (California) is aptly characterized as a subaqueous floodplain that sequesters ~20% of the $\sim 14 \times 10^{10}$ g of terrigenous OC supplied each year by the Eel River (Sommerfield and Nittrouer, 1999; Walsh and Nittrouer, 1999). The river and its tributaries drain a small but rugged headwater terrain of ~8640 km² that is elevated ~2000 m above sea level at its maximum and largely underlain by readily erodible soils and shale mélange (Blair et al., 2003, 2004). On an inter-annual time scale, major rainfall events resulting from large, climatically driven storms have triggered the episodic deposition of clay-rich flood layers interbedded with the silts over much of the Eel shelf (Leithold and Blair, 2001; Leithold and Hope, 1999; Sommerfield and Nittrouer, 1999; Sommerfield et al., 1999, 2002; Wheatcroft et al., 1997). Elemental and isotopic studies of these flood deposits have led previous investigators to conclude that they represent the primary vehicle by which petrogenic material survives oxidation to overwhelm other sources of OC in Eel River margin sediments (Blair et al., 2003, 2004; Leithold and Blair, 2001; Leithold et al., 2005).

In order to test this hypothesis, a 1.15-m-long gravity core (GGC5) was collected in 2001 from the shelf depocenter (40°49.956'N, 124°19.068'W; 70 m water depth), split lengthwise, and scanned for the relative X-ray emission intensities of 26 transition metals with an X-ray fluorescence (XRF) microscanner. A 0.30-m-long multicore (MC36) was

*E-mail: ndrenzek@whoi.edu.

also recovered from the same location. Select sediment horizons from both cores were measured for TOC and total nitrogen (TN) content, the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ composition of TOC, and ^{210}Pb , ^{214}Pb , and ^{137}Cs activity. Sediments from a subset of GGC5 intervals were then processed to isolate individual *n*-fatty acid and *n*-alkane lipids, which were measured for abundance, $\delta^{13}\text{C}$, and $\Delta^{14}\text{C}$. See the GSA Data Repository¹ for a detailed description of all methods.

RESULTS AND DISCUSSION

Episodic flood deposition and subsequent resuspension cycles lead to abrupt changes in sedimentation rate across the Eel River margin and therefore complex downcore excess ^{210}Pb ($^{210}\text{Pb}_{\text{xs}}$) and ^{137}Cs behavior (Leithold and Hope, 1999; Sommerfield et al., 1999; Walsh and Nittrouer, 1999) (Fig. 1). Average sedimentation rates are nonetheless approximated by interpolation of $\ln(^{210}\text{Pb}_{\text{xs}})$ versus depth to be 1.1 and 0.6 cm yr^{-1} over the length of GGC5 and MC36, respectively, in broad agreement with other estimates for the mid-shelf depocenter (Leithold et al., 2005; Sommerfield and Nittrouer, 1999; Sommerfield and Wheatcroft, 2007). As gravity coring usually displaces several centimeters of surficial sediments, the depth scale for GGC5 was linked to the seafloor via comparison of its $^{210}\text{Pb}_{\text{xs}}$ and ^{137}Cs activities to those of MC36. Nominal calendar years for underlying sediments were then assigned by applying the mean accumulation rate for GGC5.

Bulk and molecular level profiles of elemental and isotopic abundance in GGC5 are displayed in Figure 1. As expected, elevated TOC/TN ratios and the generally depleted $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures of TOC relative to those characteristic of contemporary marine biomass both suggest that the OC in Eel River Margin sediments contains a large component from pre-aged and/or fossil terrigenous sources (Blair et al., 2003, 2004). This is also reflected at the molecular level, where leaf wax $\delta^{13}\text{C}$ values of approximately -30‰ and below for long chain ($\geq n\text{C}_{24}$), even carbon-numbered fatty acids and the long chain, odd carbon-numbered alkanes both point to C_3 vascular plant detritus (Collister et al., 1994; Lockheart et al., 1997). Similar ^{13}C depletions for short chain ($\leq n\text{C}_{20}$) fatty acids, whose presence in marine sediments is generally assumed to indicate algal and/or bacterial input, suggest instead that these homologues are primarily derived from terrestrial vegetation in this environment. A notable exception is the $n\text{C}_{18}$ acid, whose $\delta^{13}\text{C}$ values are consistently the most enriched, implying that it might contain a significant contribution from the fixation of surface ocean dissolved inorganic carbon by phytoplankton. The influence of thermally mature carbon weathered from outcrops of the Franciscan Complex in the Eel River watershed is reflected in a low odd-over-even carbon-number predominance of the short chain alkanes and the corresponding ^{13}C enrichment over their longer, odd carbon-numbered counterparts (Fig. 1; also see the Data Repository). Notably however, the depleted $\Delta^{14}\text{C}$ compositions of the long chain fatty acid leaf waxes and their apparent covariation with those of TOC indicate that a large portion of the terrigenous material is composed of pre-aged vascular plant detritus.

Terrigenous flood deposits are collectively identified by elevations in TOC/TN, K/Ti, and Si/Ti ratios in sediments, light-colored bands in visible and positive X-ray photographs, historical records, and previous stratigraphic investigations (Leithold and Hope, 1999; Sommerfield and Nittrouer, 1999; Yarincik et al., 2000; Zabel et al., 2001), and are thus delineated by these criteria in Figure 1. Due to the uncertainty in the age model, it is not surprising that the dates for these events given by the chronology for GGC5 do not exactly match those assigned in other studies (Leithold and Blair, 2001; Leithold et al., 2005; Sommerfield et al., 2002),

¹GSA Data Repository item 2009064, supplementary information on analytical methods, model sensitivity and end-member compositions, and individual biomarker abundance distributions and $\delta^{13}\text{C}$ signatures, is available online at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

although they do generally agree within several years. In accord with these investigations, major floods only frequent the latter half of the century. Similar to observations by Leithold and Hope (1999), the accompanying TOC $\delta^{13}\text{C}$ depletions further suggest that the majority of the OC in these deposits is derived from vascular plants as opposed to sedimentary rocks,

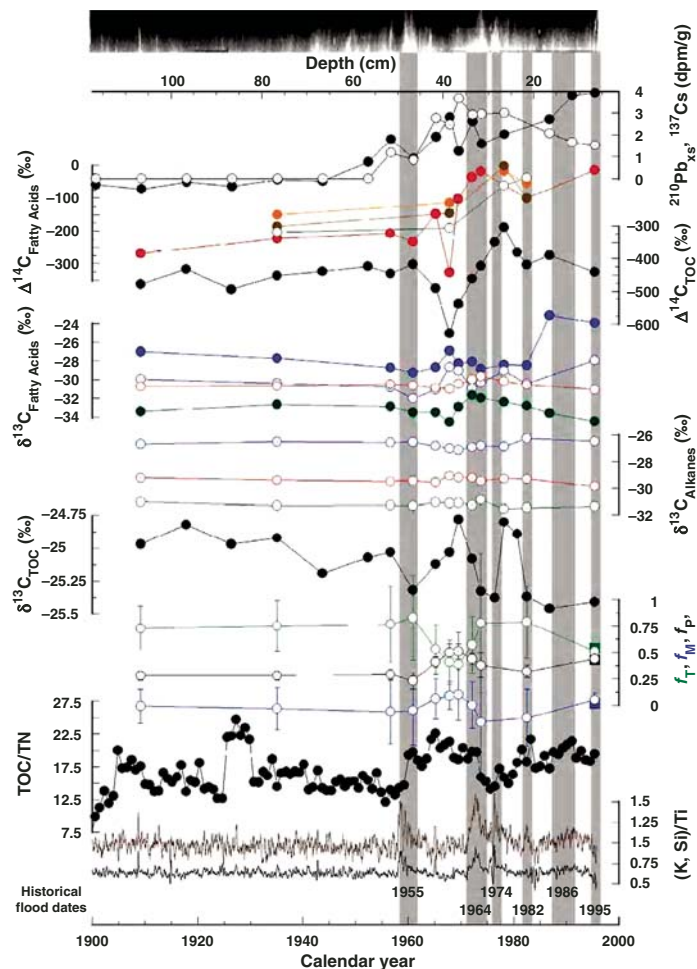


Figure 1. Downcore profiles for various bulk and molecular parameters in GGC5, as well as coupled molecular isotope mass-balance solutions (open circles) for fractions of terrestrial (f_T), marine (f_M), and petrogenic (f_P) organic carbon (those in which the surface sediment end-member $\delta^{13}\text{C}$ compositions of Blair et al. [2003] were substituted are given as closed squares; see the Data Repository [see footnote 1]). Depths are relative to the seafloor after accounting for the displacement of 6 cm of surficial sediments during the gravity coring process. Unsupported $^{210}\text{Pb}_{\text{xs}}$ activity is shown as closed symbols, ^{137}Cs activity (multiplied by a factor of 10) as open symbols. Colors for even carbon-numbered individual fatty acid homologues (closed symbols) and homologue combinations (open symbols) are as follows: $n\text{C}_{18}$ (blue), $n\text{C}_{24}$ (red), $n\text{C}_{26}$ (orange), $n\text{C}_{28}$ (olive), $n\text{C}_{32}$ (green), $n\text{C}_{14-20}$ (blue), $n\text{C}_{24-32}$ (red), and $n\text{C}_{30-32}$ (green). Colors for alkane combinations (all open symbols) are as follows: even-numbered homologues $n\text{C}_{16-20}$ (blue) and $n\text{C}_{24-32}$ (red), and odd-numbered homologues $n\text{C}_{25-33}$ (green). Analytical uncertainties are not shown for clarity, except for mass-balance solutions where they integrate the 1σ deviation in solutions across 7‰ – 9‰ $\delta^{13}\text{C}_{\text{biomass}} - \delta^{13}\text{C}_{\text{lipid}}$ offset for terrestrial and marine end members and 0‰ – 2‰ offset for petrogenic material. Profiles for K/Ti and Si/Ti are shown as 10 point running averages. TOC—total organic carbon; TN—total nitrogen. Positive X-ray radiograph of GGC5 is shown above the plot; light regions reflect clay-rich deposits. Gray bars denote flood layers (see text for assignment criteria); historical (calendar) emplacement dates are given at bottom.

considering that the isotopic compositions for these end members are estimated as $-26.5‰$ and $-24.3‰$, respectively, in the Eel catchment (Blair et al., 2003). In addition, noticeable depletions in the $\Delta^{14}\text{C}$ composition of TOC expected from the fossil signature of petrogenic carbon are absent in these layers. In fact, the most depleted bulk $\Delta^{14}\text{C}$ interval occurs between flood layers and is coeval with some of the largest variations in $^{210}\text{Pb}_{\text{xs}}$, possibly reflecting physical scouring and/or redeposition from fast moving currents on the shelf (Leithold and Hope, 1999; Sommerfield et al., 1999; Walsh and Nittrouer, 1999).

The proportion of pre-aged vascular plant OC in Eel River margin sediments relative to those from petrogenic and marine sources can be more quantitatively estimated by incorporating their corresponding biomarker $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures as end members in the following dual isotope mass balance:

$$f_T(\Delta^{14}\text{C}_T) + f_M(\Delta^{14}\text{C}_M) + f_P(\Delta^{14}\text{C}_P) = \Delta^{14}\text{C}_S, \quad (1)$$

$$f_T(\delta^{13}\text{C}_T) + f_M(\delta^{13}\text{C}_M) + f_P(\delta^{13}\text{C}_P) = \delta^{13}\text{C}_S, \quad (2)$$

$$f_T + f_M + f_P = 1, \quad (3)$$

where f is the fractional abundance and the subscripts T, M, P, and S are terrestrial (vascular plant), marine, petrogenic, and bulk sedimentary carbon, respectively. The limitations of this approach, such as the low constituency of lipid biomarkers in TOC and the uncertainties associated with the magnitude of their ^{13}C depletion from the bulk biomass they represent ($\delta^{13}\text{C}_{\text{biomass}} - \delta^{13}\text{C}_{\text{lipid}}$), should be carefully noted (Drenzek et al., 2007; also see the Data Repository for sensitivity analyses). However, based on the source assignments discussed above, the stable carbon isotopic compositions of the $n\text{C}_{18}$ and $n\text{C}_{32}$ acids are employed for $\delta^{13}\text{C}_M$ and $\delta^{13}\text{C}_T$, respectively, after accounting for a $\delta^{13}\text{C}_{\text{biomass}} - \delta^{13}\text{C}_{\text{lipid}}$ difference of $7‰$ – $9‰$ (Drenzek et al., 2007, and references therein). Following correction for natural decay in the sedimentary column, the $\Delta^{14}\text{C}$ values of $n\text{C}_{24}$ are equated to $\Delta^{14}\text{C}_T$ since they are similar in value to those for the longer homologues but available in greater quantity. The $\Delta^{14}\text{C}_M$ values are calculated from an annual resampling of the $\Delta^{14}\text{C}$ record of mixed-layer DIC compiled by Pearson (1999) for the southern California Bight. The mean values of the $n\text{C}_{16}$ – $n\text{C}_{20}$ alkanes are used to constrain $\delta^{13}\text{C}_P$ after accounting for a $0‰$ – $2‰$ depletion from bulk kerogen (Eglinton, 1994), while $\Delta^{14}\text{C}_P$ is assumed to be $-1000‰$.

Results are shown in Figure 1. In agreement with the qualitative assessment given above, pre-aged vascular plant material dominates the OC budget at most depths in the sediment column, with petrogenic debris largely composing the remainder and marine carbon virtually absent. Moreover, these fractional abundances do not appreciably change in flood deposits, suggesting that while floods increase the flux of pre-aged vascular plant and petrogenic OC to the shelf, their relative proportions remain similar. Rather, the largest shifts are synchronous with the period of ^{14}C depletion and ^{13}C enrichment in TOC around 40 cm depth, when both f_P and f_M increase at the expense of f_T . $^{210}\text{Pb}_{\text{xs}}$ and ^{137}Cs activities are also considerably variable in this interval, which may again imply local redeposition of fine-grained sediments scoured from shallower regions during energetic storm events (Leithold and Hope, 1999; Sommerfield and Nittrouer, 1999; Sommerfield et al., 1999; Walsh and Nittrouer, 1999). Indeed, petrogenic OC has been shown to be concentrated in the clay-sized sediment fraction on the Eel River margin (Blair et al., 2003, 2004; Leithold and Blair, 2001; Leithold et al., 2005), consistent with depleted $\Delta^{14}\text{C}$ and enriched $\delta^{13}\text{C}$ signatures exhibited by the $<63\ \mu\text{m}$ component relative to bulk sediment in GGC5 (A. Dickens, 2008, personal commun.). No other systematic downcore trends are observed for f_T or f_P , indicating that both forms of terrigenous OC are resistant to diagenetic processes transpiring within the first ~ 1 m of the sedimentary column.

Small mountainous rivers draining the world's tectonically active margins have been inferred to deliver more than 40×10^{12} g of fossil organic carbon to the oceans annually, based on the model that depleted $\Delta^{14}\text{C}$ values for organic matter in their suspended loads and adjacent shelf sediments primarily reflect a large petrogenic component (Blair et al., 2003, 2004; Komada et al., 2004, 2005). When incorporated into a coupled isotope mass balance, the molecular ^{14}C data presented here indicate that, even in highly erodible watersheds with thinly developed soils, significant inputs of some pre-aged vascular plant detritus from terrestrial reservoirs and/or intermediate floodplains may account for the majority of these $\Delta^{14}\text{C}$ depletions. As different river systems are likely to exhibit significant heterogeneity in OC sources and depositional dynamics, further application of coupled molecular isotope mass balances in a variety of margin settings should help to refine our understanding of the age composition and burial of organic matter in marine sediments on a global basis.

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