

Sedimentary rocks as sources of ancient organic carbon to the ocean: An investigation through $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ signatures of organic compound classes

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[1] Chemical and isotopic variability of particulate organic carbon (POC) was examined in samples from the Santa Clara River watershed and adjacent shelf to investigate the processing of fossil POC derived from bedrock. The Santa Clara is a small coastal river that drains mountainous terrain in southern California, United States. Organic carbon in shale, river suspended sediment, and coastal marine sediment was separated into three operationally defined organic compound classes: total extractable lipids, acid hydrolyzable material, and the nonhydrolyzable residue. In all samples, the nonhydrolyzable fraction was dominant ($\sim 50\%$ of POC), while lipids and acid hydrolyzable moieties were relatively minor (≤ 22 and $\leq 13\%$, respectively). The $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ signatures of the isolated fractions varied dramatically, not only across different sample types, but also for a given sample. At the shale exposure, low $\Delta^{14}\text{C}$ values ($< -760\text{‰}$) indicated dominance of ancient C in all three organic compound classes. In downstream samples, the extractable lipids displayed the lowest $\Delta^{14}\text{C}$ values ($< -500\text{‰}$), while the acid hydrolyzable fraction was predominantly modern ($\Delta^{14}\text{C} > -30\text{‰}$). The nonhydrolyzable fraction displayed intermediate $\Delta^{14}\text{C}$ values ($< -190\text{‰}$) that increased steadily downstream with decreasing $\delta^{13}\text{C}$ values (-22.2 to -25.0‰), possibly from mixing of shale and surface soil POC. Our results indicate that most of the fossil POC discharged by the Santa Clara is composed of non-acid hydrolyzable material, but its elusive molecular structure and marine-like $\delta^{13}\text{C}$ signature may render its detection in the ocean difficult. In contrast, fossil lipids may be more amenable to detection if their resistant components (e.g., asphaltic material) are unique to crustal sources.

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1. Introduction

[2] Small mountainous rivers draining tectonically active margins have recently received attention as previously overlooked systems that export significant quantities of sediment and particulate organic carbon (POC) to the oceans [Milliman and Syvitski, 1992; Milliman *et al.*, 1999; Lyons *et al.*, 2002]. Contrary to the conventional view that rivers exclusively discharge modern POC [Hedges *et al.*, 1986], it has been recognized that small mountainous rivers discharge fossil POC derived from rapid erosion of bedrock [Kao and Liu, 1996; Masiello and Druffel, 2001; Blair *et al.*, 2003; Komada *et al.*, 2004]. Existing data further indicate efficient injection

of fossil POC into the ocean in an active margin setting as a combined result of rapid sediment transport and slow rate of fossil POC degradation [Blair *et al.*, 2003]. The estimated flux of fossil POC from rivers ($>40 \text{ Tg C yr}^{-1}$ where $\text{Tg} = 10^{12} \text{ g}$ [Blair *et al.*, 2003]) is sufficient to account for $>25\%$ of the rate of POC burial in ocean sediments (160 Tg C yr^{-1} [Hedges and Keil, 1995]) and $>40\%$ of the turnover of deep water dissolved OC (DOC) assuming an average ^{14}C -age for DOC of 6000 years under steady state conditions (100 Tg C yr^{-1} [Williams and Druffel, 1987]). However, the impact of fossil POC export by rivers on the marine organic carbon (OC) cycle remains uncertain.

[3] The present study aims to better understand the upstream processes in the overall continental export of fossil OC to the ocean. We investigate the cycling of fossil POC within a coastal drainage system by examining the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ signatures of POC at the organic compound class level along a downstream transect encompassing shale exposure to coastal marine sediment. We examine three operationally defined organic compound classes:

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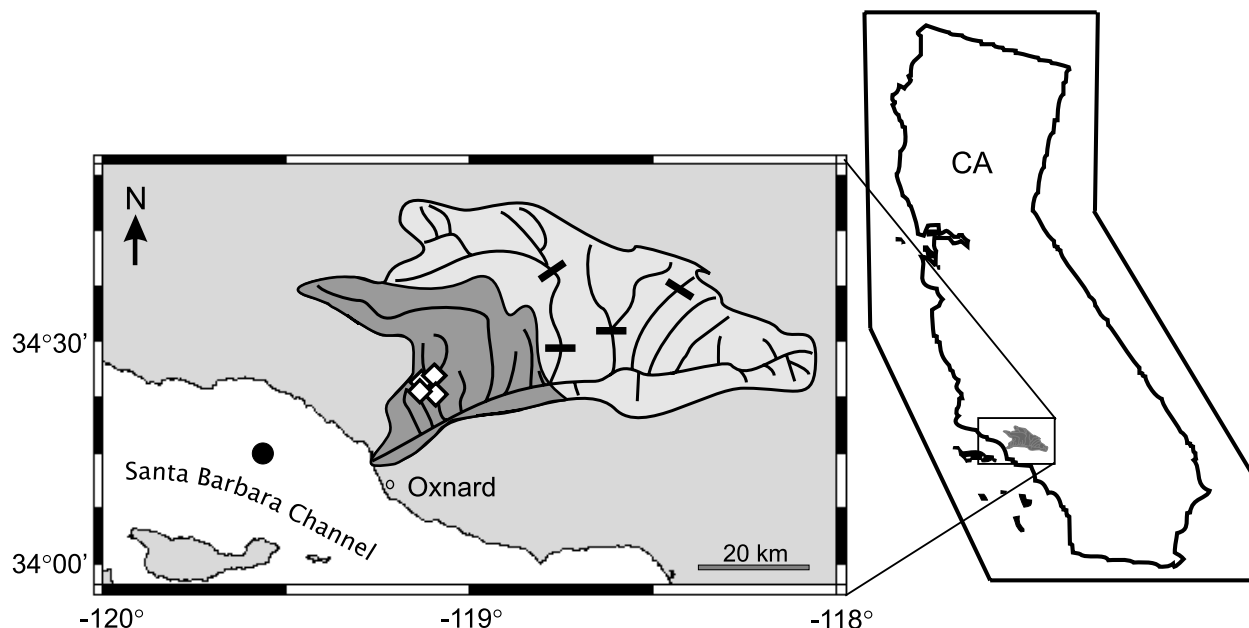


Figure 1. Map of the Santa Clara drainage system showing shale (diamonds) and coastal sediment (solid circle) sampling sites. Suspended solids from the river were collected ~ 0.3 km upstream of the river mouth. Bars represent active dams. The western region of the watershed with high sediment yield ($1400\text{--}2800\text{ km}^{-2}\text{ yr}^{-1}$ compared to $\leq 410\text{ km}^{-2}\text{ yr}^{-1}$ for the rest of the watershed) is highlighted in dark shading [after Warrick, 2002].

total extractable lipids, acid hydrolyzable material, and the nonhydrolyzable residue. This fractionation scheme has been applied to contemporary organic matter as a means to separate some major forms of biochemicals (various lipids and hydrolyzable sugars and amino acids) from the bulk OC pool [Wang *et al.*, 1996, 1998]. Extractable lipids and hydrolyzable moieties include compounds that are highly biolabile [e.g., Wakeham and Lee, 1993; Wakeham *et al.*, 1997]. In contrast, the nonhydrolyzable residue is considered in this paper to approximate, but not equal, the molecularly uncharacterized POC that constitutes a significant component of resistant organic matter preserved in marine sediments [Hedges *et al.*, 2000; Lee *et al.*, 2004]. Unlike contemporary organic matter, OC preserved in ancient sediments is considered largely insoluble and non-hydrolyzable [Tissot and Welte, 1984]. When this fractionation scheme is applied to sedimentary rocks, bulk POC is separated into bitumen (the solvent-extractable pool), kerogen (the non-solvent extractable, nonhydrolyzable residue), and acid-labile moieties.

[4] We examine the isotopic evolution of these organic compound classes isolated from POC transported through the Santa Clara drainage system in southern California, United States. This study is related to work conducted in the same location that examined bulk isotopic signatures of river suspended solids and two terrestrial end-member POC sources: shale and surface soil [Komada *et al.*, 2004]. The current work reports isotopic signatures of organic compound classes isolated from an overlapping set of these samples, along with additional samples collected from nearby shelf sediments. A companion paper [Hwang *et*

al., 2005] discusses the lateral transport of riverine POC within the continental margin.

2. Materials and Methods

2.1. Study Sites and Sampling

[5] All samples were collected within the Santa Clara watershed, a small mountainous river, and nearby shelf located in southern California, United States (Figure 1). The Santa Clara River (drainage area 4210 km^2 ; headwater height 2900 m) is one of the few relatively intact drainage basins in this region, where 88% of land cover is native vegetation [Davis *et al.*, 1998] consisting mostly of mixed chaparral and sage scrub [Scott and Williams, 1978]. The remaining 12% land surface has been converted to exotic grassland (2%), agriculture (4%), urban (3%), and barren (3%) land uses [Davis *et al.*, 1998]. The climate is semi-arid with a disproportionate amount of the annual precipitation (0.4 m yr^{-1} on average) occurring in episodic storms during the winter months of November through March [Warrick, 2002]. Such events are also responsible for the annual discharge of sediment [Warrick, 2002].

[6] The Santa Clara watershed lies within one of the most prolific hydrocarbon-producing regions of California [Jeffrey *et al.*, 1991; Tennyson and Isaacs, 2001]. In 2002, Los Angeles and Ventura counties (which constitute the Santa Clara watershed) ranked second and third, respectively, in oil production in the state (http://www.dof.ca.gov/html/fs_data/stat-abs/tables/g32.xls). Underlying lithology consists mostly of Cenozoic sediments of marine origin including the Monterey Formation and Rincon Shale which

Table 1. Underlying Lithology of the Santa Clara Basin^a

| Geologic Age | Area, % | Source | Common Stratigraphic Units |
|------------------|------------|--------------------------------|--|
| Quaternary | 13 | alluvium, marine and nonmarine | |
| Plio-Pleistocene | 4 | nonmarine | Saugus |
| Pliocene | 14 | mostly nonmarine | Pico, Ridge Route |
| Miocene | 15 | mostly marine | Sisquoc, Monterey, Rincon, Vaqueros |
| Oligocene | 7 | marine, nonmarine and volcanic | Sespe |
| Eocene | 18 | marine | Coldwater, Cozy Dell |
| Tertiary | 1 | nonmarine | |
| Cretaceous | 1 | marine | Jalama |
| Mesozoic | 9 | granitic | |
| Pre-Cretaceous | 4 | metamorphic | |
| Precambrian | 15 | granitic and metamorphic | |

^aData from Dibblee Geological Maps (Dibblee Geological Foundation, Camarillo, Calif.), *Jennings and Strand* [1991], and *Santa Barbara County Flood Control and Water Conservation District* [1975] as compiled by *Warrick* [2002].

are potential petroleum source rocks [*Tennyson and Isaacs*, 2001] (Table 1). Soft bedrock, mountainous terrain, and tectonic uplift together promote rapid physical denudation. As a result, along with other rivers of similar morphology, the Santa Clara exhibits high sediment yield [*Milliman and Syvitski*, 1992], and exports poorly weathered bedrock material to the coastal ocean [*Masiello and Druffel*, 2001; *Komada et al.*, 2004]. Much of the sediment delivered to the river mouth originates from the western portion of the watershed where sediment yields are high (Figure 1; 1400–2800 t km⁻² yr⁻¹) relative to the remainder of the basin that is largely dammed or underlain by granitic and metamorphic rocks (≤ 410 t km⁻² yr⁻¹ [*Warrick*, 2002; *Jennings and Strand*, 1991]). Sediment production in the Santa Clara and its nearby watersheds has been found to correlate with the aerial extent of soft geologic units (in particular, the Pico Formation; see below), and grassland, agriculture, and barren land uses [*Warrick*, 2002].

[7] Of the sedimentary sequences underlying this region (Table 1), three stratigraphic units were targeted as potentially important sources of sediment and POC to the Santa Clara River: Pico (Pliocene, marine), Monterey (Miocene, marine), and lower Monterey (Miocene, marine) Formations. The Pico Formation is unique in that it is highly susceptible to mass wasting, and its presence has been found to positively correlate with the overall sediment yield of the drainage basin [*Warrick*, 2002]. The Monterey Formation was selected because of its high organic content (as high as >15% with a reported average of ~4% [*Jeffrey et al.*, 1991; *Rullkötter et al.*, 2001]). The Cozy Dell Formation was sampled as a representative Eocene unit and analyzed for bulk properties in our previous study [*Komada et al.*, 2004], but was not included in the present sample set because of low organic content (0.33% in our sample; <1% reported for a 120-m section [*Slatt and Thompson*, 1985]). Eocene rocks are considered minor sources of petroleum relative to Miocene rocks [*Jeffrey et al.*, 1991; *Tennyson and Isaacs*, 2001]. Granitic and metamorphic rocks are organic-poor, and outcrop primarily in the sediment-poor eastern portion of the watershed [*Jennings and Strand*, 1991; *Warrick*, 2002]. Shale samples were collected from road cuts after removal of 10–20 cm of overlying litter and soil. The Monterey Formation was sampled from two isolated exposures, and these are referred to as Monterey-

1 and -2. All exposures were located using 1:24,000 scale geological maps [*Dibblee*, 1987, 1990].

[8] We also report data for three suspended solid samples collected from the Santa Clara River during moderate to high flow storm events: a sample collected on 15 March 2003, and two archived samples collected on 24 February 1998 and 25 March 1998 and stored frozen [*Masiello and Druffel*, 2001]. These samples were selected from a more comprehensive sample set [*Komada et al.*, 2004] to cover low (15 March 2003), moderate (25 March 1998), and high (24 February 1998) bulk $\Delta^{14}\text{C}$ signatures. The 15 March 2003 sample was collected from the main stem ~0.3 km upstream of the river mouth following methods of *Masiello and Druffel* [2001]. River water was collected during low tide to prevent inclusion of marine POC, and immediately placed on ice and in the dark. Suspended solids were concentrated by centrifugation and frozen within 24 hours.

[9] To explore the fate of riverine POC in the coastal ocean, a box core was recovered from ~90 m water depth approximately 8 nautical miles due west of the Santa Clara River mouth (34°15'N, 119°33'W) in June 2002 (Figure 1). Our coring site lies within the region of the shelf where silt discharged by the Santa Clara during storm events is deposited [*Drake et al.*, 1972; *Thornton*, 1984]. The recovered sediment was fine-grained and bioturbated to ~5 cm depth [*Hwang et al.*, 2005]. The boxcore was subcored with a Plexiglas core liner, sectioned on board ship at intervals of 0.5 to 1.0 cm, and frozen.

2.2. Sample Processing and Analyses

[10] All samples were lyophilized and powdered prior to analysis. For determination of weight-% OC (%OC) and $\delta^{13}\text{C}$ (per mil deviation of $^{13}\text{C}/^{12}\text{C}$ ratio from PDB-1) of bulk POC, pre-weighed samples were exposed to HCl vapor in Ag capsules for 10 hours [*Hedges and Stern*, 1984], then analyzed using a Carlo Erba elemental analyzer interfaced with a Finnigan Delta Plus isotope ratio mass spectrometer. Test analyses of standard materials and samples showed that this acidification method (1) was sufficient to fully decarbonate sediments containing >20% dolomitic limestone (NIST SRM 88b), and (2) produced $\delta^{13}\text{C}$ values of OC that agreed within error with those obtained using the sulfurous acid method [*Verardo et al.*, 1990; T. Komada, unpublished

Table 2. Bulk POC Content and Recovery of Organic Compound Classes^a

| Sample | Bulk POC, wt% | Extractable Lipid, % | Acid Hydrolyzable, % | NonHydrolyzable, % | Total Recovered, % |
|--------------------------------|---------------|----------------------|----------------------|--------------------|--------------------|
| <i>Shale</i> | | | | | |
| Pico | 0.19 | 5 | n/a | n/a | n/a |
| Monterey-1 | 4.29 | 21 | 0.2 | 48 | 69 |
| Monterey-2 | 0.40 | 1 | 10 | 31 ^b | n/a |
| Lower Monterey | 0.50 | 22 | n/a | n/a | n/a |
| <i>Suspended POC</i> | | | | | |
| 24 Feb. 1998 | 0.94 | 6 | n/a | n/a | n/a |
| 25 March 1998 | 1.11 | 11 | 10 | 43 | 64 |
| 15 March 2003 | 1.01 | 10 | 5 | 48 | 64 |
| <i>Coastal Marine Sediment</i> | | | | | |
| 0–0.5 cm | 1.26 | 7 | 13 | 49 | 69 |
| 18–20 cm | 1.15 | 5 | 11 | 58 | 74 |

^aHere n/a denotes data not available.^bThere was significant sample loss due to spillage.

data, 2003). The standard deviation of replicate measurements were $\pm 0.02\%$ and $\pm 0.1\%$ for $\%OC$ and $\delta^{13}C$ values, respectively. For determination of $\Delta^{14}C$ (per mil deviation of $^{14}C/^{12}C$ ratio from a nineteenth century wood standard normalized to $\delta^{13}C$ of -25% [Stuiver and Polach, 1977]) of bulk POC, samples were decarbonated with HCl vapor in silver capsules as described above, transferred (with the capsules) into quartz tubes, dried, sealed, and combusted with CuO and elemental silver as described by Druffel *et al.* [1992]. The evolved CO_2 was cryogenically purified, reduced to graphite with hydrogen on a Co catalyst [Vogel *et al.*, 1987], and analyzed at the Keck Carbon Cycle AMS Laboratory at the University of California, Irvine. Total uncertainty including errors arising from sample processing and AMS analysis was less than $\pm 20\%$. Blanks that were processed in parallel generated CO_2 amounting to less than 0.5% of the C content of the actual samples.

[11] Bulk samples were separated into organic compound classes following the methods of Wang *et al.* [1998], but without isolation of neutral carbohydrates and amino acids from the total acid hydrolyzable fraction. Briefly, the total extractable lipids were first isolated from the bulk sample by five sequential extractions with 2:1 (v/v) methylene chloride/methanol. Each cycle consisted of 30-s ultrasonication followed by centrifugation. Lipids were concentrated from the pooled extract by rotary evaporation, quantitatively transferred to quartz combustion tubes, and lyophilized. The non-extractable solids were hydrolyzed with 6N HCl in an N_2 atmosphere for 19 hours at $100^\circ C$. The acid hydrolyzate was separated from the residual solids by centrifugation, concentrated by rotary evaporation, quantitatively transferred to quartz combustion tubes, and lyophilized. The residual nonhydrolyzable solids were transferred quantitatively into combustion tubes and lyophilized.

[12] For determination of $\delta^{13}C$ and $\Delta^{14}C$ signatures, the isolated organic fractions were combusted in sealed quartz tubes as described above for bulk samples. The evolved CO_2 was purified and quantified manometrically for C yield, then split for $\delta^{13}C$ and $\Delta^{14}C$ analyses. The samples for $\delta^{13}C$ determination were analyzed using a Finnigan

Delta Plus isotope ratio mass spectrometer operated in dual inlet mode. The samples for $\Delta^{14}C$ determination were analyzed by AMS as described above. Because of extensive sample handling, isotopic values of organic compound classes are associated with uncertainties larger than those for bulk samples; we assign conservative values of ± 30 and $\pm 0.3\%$ for $\Delta^{14}C$ and $\delta^{13}C$ signatures, respectively [Hwang and Druffel, 2005].

3. Results

3.1. Relative Yields of Organic Compound Classes

[13] Bulk $\%OC$ varied across samples by more than an order of magnitude, with a maximum of $>4\%$ for Monterey-1, intermediate values of 0.9–1.3% for river suspended and coastal marine POC, and low values ($\leq 0.5\%$) for the remaining shales (Table 2). On average, 68% of the bulk POC was recovered from the three organic compound classes (Table 2). In all samples, the nonhydrolyzable fraction dominated, constituting 43 to 58% of the bulk POC, while the extractable lipids and the acid hydrolyzable fraction were ≤ 22 and $\leq 13\%$ of the bulk POC, respectively. The observed yield was lower than those reported previously for abyssal sediments using this method ($\geq 81\%$ [Wang *et al.*, 1998]), but comparable to more recent results from continental margin sediments [Hwang *et al.*, 2005]. At the present time, it is unclear how $\sim 30\%$ of the total OC is lost. Possibilities include incomplete transfer of samples into combustion tubes, loss of volatile compounds under vacuum, and oxidation during acid digestion.

[14] The four shale samples exhibited more than an order of magnitude variability in the abundance of the lipid and acid hydrolyzable fractions, while only a factor of 2 variability was observed among river suspended and coastal marine POC (Table 2). The high bulk $\%OC$ and lipid yield observed in Monterey-1 and Lower Monterey samples may reflect the high oil source potential of this formation [Philippi, 1965; Jeffrey *et al.*, 1991]. The bulk $\%OC$ and lipid yields for all three Monterey samples fell within range, or slightly below, previously reported values (0.7–16% bulk OC, 3–35% solvent extractable [Rullkötter *et al.*,

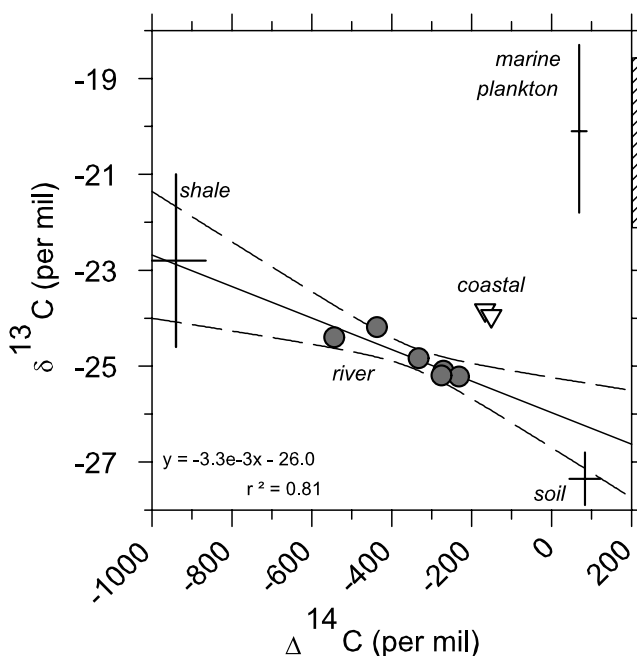


Figure 2. The $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures of bulk river suspended solids (shaded circles [Komada *et al.*, 2004]), and coastal marine sediment (triangles; Table 3). Total uncertainties for both $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ are smaller than the size of the symbols. Crosses indicate the total ranges (plus uncertainty) of bulk isotopic values observed for (in order of increasing $\Delta^{14}\text{C}$): shale ($n = 5$), oceanic surface water plankton ($n = 2$), and surface soil ($n = 4$ [Wang *et al.*, 1998; Komada *et al.*, 2004]). The range of $\delta^{13}\text{C}$ values reported for zooplankton in coastal waters of southern California (as compiled by Williams *et al.* [1992]; $n = 39$) is also indicated with a shaded box adjacent to the y axis. Diagonal line is linear regression through the bulk isotopic values of river suspended solids with 95% confidence intervals [Komada *et al.*, 2004]. The $\Delta^{14}\text{C}$ signature of the 18–20 cm sample from the coastal site has been age corrected to the estimated time of deposition (see Table 3).

2001)). Our limited results of acid hydrolysis yields showed a 50-fold difference between Monterey-1 and -2. While the low acid hydrolysis yield as observed for Monterey-1 (0.2%; Table 2) is expected based on the resistant nature of ancient organic matter [Tissot and Welte, 1984; De Leeuw and Largeau, 1993], the higher yield from Monterey-2 (10%; Table 2) is surprising, and may have been caused by weathering. This point is discussed further in section 4.1.

3.2. Isotopic Signatures of Bulk POC

[15] A wide range of $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures were observed for bulk watershed samples (shales, river suspended solids, and surface soils reported previously by Komada *et al.* [2004]), and bulk coastal marine sediments (Table 3; Figure 2). The isotopic signatures of bulk river-suspended POC are indicative of bimodal mixing of ^{13}C -enriched rock-derived POC, and ^{13}C -poor modern surface soil POC (Figure 2). The bulk coastal marine

sediment POC, on the other hand, exhibited isotopic values intermediate of river-suspended POC and marine plankton, suggesting strong influence of river discharge at our study site.

3.3. Isotopic Signatures of Organic Compound Classes

[16] The $\Delta^{14}\text{C}$ signatures of organic compound classes varied systematically both within and across sample types (Figure 3a, Table 3). Shales showed uniformly low $\Delta^{14}\text{C}$ values, and did not exceed -940‰ except for an acid hydrolyzable isolate whose signature was -764‰ . The $\Delta^{14}\text{C}$ values of river and coastal marine samples were more variable, and ranged from $<-850\text{‰}$ to $>0\text{‰}$. In all samples, the acid hydrolyzable fraction was most enriched in $\Delta^{14}\text{C}$, while lipids were most depleted. The $\Delta^{14}\text{C}$ values of the nonhydrolyzable fraction were intermediate and correlated well with the bulk values, as expected given the dominance of this fraction in the total POC pool (Table 2).

[17] The $\delta^{13}\text{C}$ values of organic compound classes overlapped across samples without obvious trends (Figure 3b, Table 3). Shale $\delta^{13}\text{C}$ values ranged by 3‰ , from -25.0 to -21.9‰ . The $\delta^{13}\text{C}$ values of river and coastal sediment samples were similar, between -25.0 and -23.3‰ , except for the acid hydrolyzable isolates from the coastal site which had higher values (-20.8 and -21.4‰).

[18] The isotopic signature of bulk POC calculated as the weighted means of the isotopic values of the three organic compound classes agreed reasonably well, to within 80 and 1‰ of the observed bulk $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values, respectively (Table 3). However, the recovered pool was systematically depleted in ^{14}C relative to the bulk (Table 3), which may be due to preferential loss of the ^{14}C -enriched moieties during the separation process, or incomplete removal of organic solvents used during lipid extraction.

4. Discussion

[19] The goal of this study was to better understand how key organic compound classes of fossil OC are processed within a drainage system, and to evaluate their potential fate upon oceanic export. To achieve this goal, we find it useful to define the organic fractions extracted from the rock samples using petroleum geochemistry terminology. Organic C in sedimentary rocks are separated into two major fractions: bitumen and kerogen. Bitumen, defined as the fraction of sedimentary organic matter extractable with carbon disulfide [Hunt, 1996], is operationally similar to the total lipid extract examined in this study. In our fractionation scheme, the nonhydrolyzable component is operationally similar to kerogen [Hunt, 1996]. Below, we discuss the potential fate of fossil OC by examining the dynamics of kerogen (non-extractable, nonhydrolyzable OC), bitumen (total extractable lipids), and the acid hydrolyzable fraction, as they are exported into the aquatic environment.

4.1. Fossil OC Processing in the Drainage System

[20] Throughout the transect, the acid hydrolyzable fraction was consistently enriched in ^{14}C relative to the bulk pool (Figure 3a), indicating enrichment of recently photo-

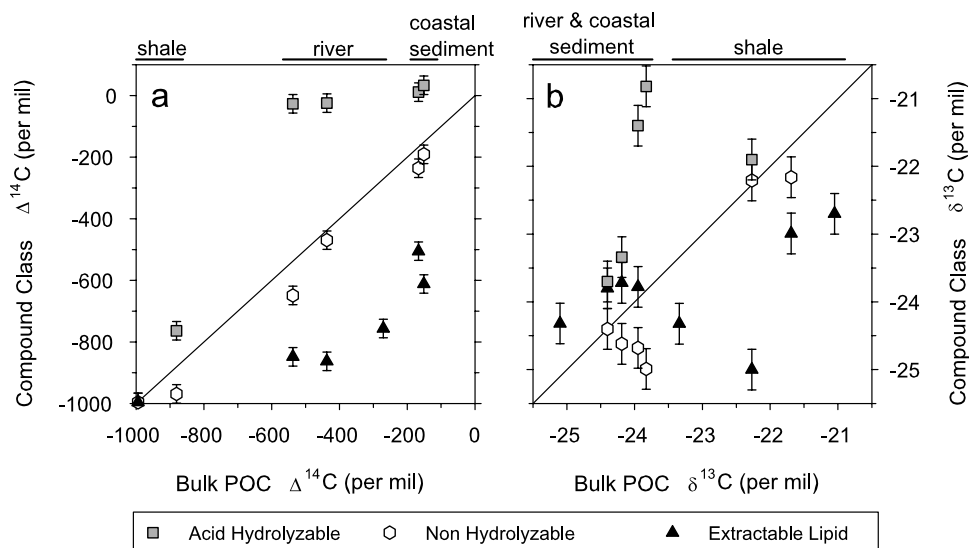


Figure 3. $\Delta^{14}\text{C}$ (a) and $\delta^{13}\text{C}$ (b) signatures of organic compound classes as a function of corresponding bulk values. Shaded square, acid hydrolyzable; white hexagon, nonhydrolyzable; black triangle, total extractable lipids. Error bars for organic compound classes are $\pm 30\%$ and $\pm 0.3\%$ for $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$, respectively. Solid diagonal line indicates a 1:1 relationship. The $\Delta^{14}\text{C}$ signature of the 18–20 cm sample from the coastal site has been age corrected to the estimated time of deposition (see Table 3).

synthesized material in this fraction. The high $\delta^{13}\text{C}$ values of acid hydrolyzable OC relative to bulk POC in coastal marine samples are also consistent with enrichment of carbohydrates and amino acids in this isolate (Figure 3b [Degens *et al.*, 1968]). However, in the case of Monterey-2, the acid hydrolyzable fraction was dominated by ancient C ($\Delta^{14}\text{C} = -764\%$) despite a 121‰ enrichment relative to the bulk (Table 3, Figure 3a). Therefore it appears that the acid hydrolyzable fraction of this shale sample consisted largely of acid-labile moieties of kerogen with little modern C. This suggestion is supported by the similarity in the $\delta^{13}\text{C}$ values of the acid hydrolyzable fraction and kerogen (Table 3). It is unknown how the acid-labile fossil OC was produced, but may have been a result of weathering processes. The predominantly modern $\Delta^{14}\text{C}$ signatures of the acid hydrolyzable fraction isolated from downstream samples further suggest that the basement rocks of this watershed are insignificant sources of acid hydrolyzable fossil OC to the river POC load (Figure 3a). This is also discerned from the relationship between $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures of the acid hydrolyzable fraction that shows clear deviation from the shale-soil mixing curve inferred from bulk isotopic data (Figure 4a).

[21] Relative to the acid hydrolyzable fraction, the nonhydrolyzable material showed greater retention of its fossil counterpart, kerogen, throughout the transect (Figure 4b). The $\delta^{13}\text{C}$ signatures of the nonhydrolyzable fraction decreased with increasing $\Delta^{14}\text{C}$, forming a trend that fell close to the mixing line between shale and surface soil inferred from the bulk data. Therefore kerogen, along with surface soil OC, appears to persist in the nonhydrolyzable fraction of the river and coastal marine POC.

[22] Of the three organic fractions examined, total extractable lipids were consistently depleted in ^{14}C and showed relatively small variation in $\delta^{13}\text{C}$ signature (Figures 3a

and 4c), suggesting preponderance of bitumen throughout the transect. It is most likely that fossil OC from anthropogenic sources was present in the lipid fraction, but there are several reasons to believe that it was minor relative to fossil OC derived from natural sources. First, the urban landscape constitutes a minor fraction of the total drainage area (3%) relative to native land cover (88% [Davis *et al.*, 1998]), and yields lower runoff (2.6 cm yr^{-1}) than the steep headlands that receive greater precipitation (up to 22 cm yr^{-1} [Warrick, 2002]). Second, anthropogenic pollutants that accumulate on urban surfaces and roadways during the dry months have been found to undergo seasonal flushing at the beginning of the wet season [Svejkovsky and Jones, 2001; Tiefenthaler *et al.*, 2001]. The river suspended samples examined in the present study were collected in February and March (Table 2) toward the end of the wet season, and hence are least likely to have been impacted by the seasonal flushing effect. Last, the $\delta^{13}\text{C}$ signatures of our lipid extracts are 1–3‰ enriched relative to those reported for urban runoff in the nearby Los Angeles watershed that was found to be contaminated by anthropogenic petroleum residues [Eganhouse *et al.*, 1981; Eganhouse, 1982]. We conclude that the low $\Delta^{14}\text{C}$ signatures of the extractable lipid fraction were most likely due to the persistence of bitumen originating from natural fossil sources within the drainage basin.

4.2. Oceanic Fluxes of Kerogen and Bitumen and Their Possible Impact on the Marine OC Pool

[23] Kerogen consists of complex macromolecules that survived and were altered by diagenesis and varying degrees of catagenesis [Tissot and Welte, 1984]. As such, kerogen is considered one of the more degradation-resistant forms of OC on Earth [Hedges, 1992]. Bitumen, on the

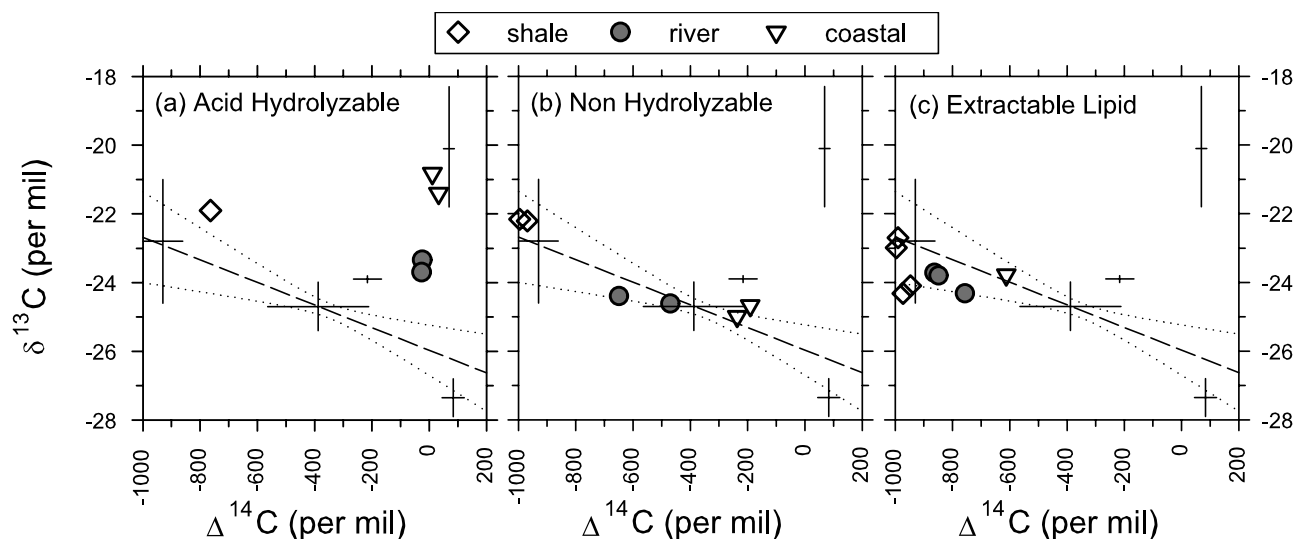


Figure 4. The $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures of (a) acid hydrolyzable, (b) nonhydrolyzable, and (c) total extractable lipid fractions isolated from shale (diamonds), river suspended solids (shaded circles), and coastal marine sediment (triangles; Table 3). Total uncertainties for both $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ are smaller than the size of the symbols. The crosses in the background are total observed ranges (plus uncertainties) of bulk isotopic data as shown in Figure 2 (in order of increasing $\Delta^{14}\text{C}$: shale, river sediment, coastal marine sediment, marine plankton, surface soil).

other hand, consists of a spectrum of compounds of variable reactivity that range from labile low-molecular-weight alkanes to resistant macromolecules such as asphaltenes, the latter being considered small analogues of kerogen [Tissot and Welte, 1984]. Although the factors affecting the rate of fossil OC weathering are currently under investigation [Petsch *et al.*, 2000, 2001], many biogeochemical models aimed at understanding the controls on atmospheric oxygen concentrations over geologic time assume complete oxidation of fossil OC on the continents [e.g., Garrels and Lerman, 1984; Berner and Canfield, 1989; van Cappellen and Ingall, 1996]. Current data from the Santa Clara River and other drainage basins of similar morphologies [Kao and Liu, 1996; Blair *et al.*, 2003] indicate export of fossil OC to the coastal ocean likely as a result of rapid physical denudation and sediment transport.

[24] According to Blair *et al.* [2003], >40 Tg of fossil OC is entering the oceans annually by river transport. Understanding the composition and oceanic fate of this material (whether it is rapidly oxidized or incorporated in to marine OC pools) is important in unraveling the question of how OC cycles and persists in the marine environment [Hedges, 1992]. For example, if there is significant input of pre-aged OC into the ocean's interior, in situ aging need not be the only mechanism to explain the low $\Delta^{14}\text{C}$ values observed in deep-water DOC [Druffel *et al.*, 1992; Loh *et al.*, 2004]. Reburial of fossil POC in marine sediments will impact the interpretation of ^{14}C -based sediment chronologies [Eglinton *et al.*, 1997], as well as our understanding of the control of OC preservation [Hedges, 1992]. Reincorporation of fossil OC into the geological cycle also has the potential to dampen long-term atmospheric oxygen fluctuations by reducing both oxygen

consumption during weathering and oxygen production during OC preservation [Hedges, 1992].

[25] Global fluxes of kerogen and bitumen to the oceans can be estimated using available data. Fossil OC discharged by the Santa Clara River on 25 March 1998 and 15 March 2003 can be apportioned into kerogen and bitumen using the % yield of the organic fractions and their $\Delta^{14}\text{C}$ signatures (Tables 2 and 3). Assigning $\Delta^{14}\text{C}$ values of +80‰ and -1000‰ for atmospheric CO_2 and fossil C, respectively [Xu *et al.*, 2004], 20–30% of the fossil OC that could be accounted for in the recovered organic fractions was transported as bitumen, and the remainder as kerogen. If one assumes that the relative abundances of kerogen and bitumen are not significantly affected during weathering and transport through the watershed, a more globally representative estimate of the fraction of bitumen in fossil OC discharged by rivers may be derived from the reported range of bitumen concentration in total OC of shales and carbonate rocks (1.5–4.5% [Hunt, 1972]). Taking the average value of 3%, >1.2 Tg of the reported >40 Tg of fossil OC discharged annually by rivers [Blair *et al.*, 2003], is derived from bitumen. Bitumen is also added to the oceans via offshore seepage and anthropogenic activity (e.g., spills, runoff) at a rate of 0.6 and 0.7 Tg petroleum per year, respectively [National Research Council, 2003], which amount to ~0.5 and 0.6 Tg C yr^{-1} , respectively, if petroleum from seeps and human activity is 85% C by weight [Hunt, 1996]. The greater oceanic flux of bitumen via continental erosion (>1.2 Tg C yr^{-1}) than via seepage (0.5 Tg C yr^{-1}) reflects the fact that >99% of bitumen is finely dispersed in the sedimentary rock matrix, leaving <1% to accumulate in petroleum reservoirs [Hunt, 1996].

[26] The dominance of kerogen in the fossil POC entering the ocean indicates that identification and quantification of

recycled, ancient OC in marine sediments may be difficult. Downstream of the shale exposure, our fractionation scheme did not allow isolation of kerogen from modern nonhydrolyzable material, which appeared to be primarily of terrigenous origin (Figure 4b). Generation of nonhydrolyzable material from modern OC is consistent with high $\Delta^{14}\text{C}$ values observed in surface soils and pelagic plankton after acid hydrolysis [Trumbore and Zheng, 1996; Wang et al., 1998]. When marine shales are eroded, kerogen has $\delta^{13}\text{C}$ values that overlap with those of contemporary marine POC [Goericke and Fry, 1994; Hayes et al., 1999]. Hence, as suggested previously [Blair et al., 2003], unless kerogen can be positively distinguished from autochthonous nonhydrolyzable material, much of land-derived fossil OC may remain undetected in the ocean, or be misinterpreted for marine OC that has undergone in situ aging.

[27] Unlike kerogen, bitumen is composed of a mixture of compounds ranging from labile low-molecular-weight *n*-alkanes to resistant asphaltic material, the latter including resins and asphaltenes rich in condensed aromatic and naphthenic rings, and N, S, and O [Peters and Moldowan, 1993; Hunt, 1996]. Upon exposure, bitumen composition is altered by biodegradation and weathering, which increases the concentration of asphaltic material as lower-molecular-weight hydrocarbons are preferentially lost [e.g., Tannenbaum et al., 1987; Müller et al., 1987; Peters and Moldowan, 1993]. The enrichment of complex, resistant moieties with increased degradation is also reflected in the increasing dominance of the unresolved complex mixture (UCM) in degraded oils [e.g., Blumer et al., 1973; Peters and Moldowan, 1993]. Therefore, upon oceanic export, the more labile fraction of bitumen may be rapidly lost, but its resistant components may survive degradation and persist in the extractable lipid pool of marine OC. Persistence of resistant fossil lipids may in part explain the low $\Delta^{14}\text{C}$ signatures observed in lipids extracted from open ocean environments [Hwang and Druffel, 2003; Loh et al., 2004]. Because asphaltic material and UCM can be isolated from the total lipid pool, investigation of their isotopic [Reddy et al., 2002] and chemical compositions [e.g., Gough and Rowland, 1990; Scotti and Montanari, 1998] may complement biomarker studies in understanding the sources and cycling of lipid-like material in the ocean.

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