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Sedimentary rocks as sources of ancient organic carbon to the ocean: An investigation through $\Delta^{14}C$ and $\delta^{13}C$ 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 (~50% of POC), while lipids and acid hydrolyzable moieties were relatively minor (≤22 and ≤13%, respectively). The $\Delta^{14}C$ and $\delta^{13}C$ signatures of the isolated fractions varied dramatically, not only across different sample types, but also for a given sample. At the shale exposure, low $\Delta^{14}C$ values (<−760‰) indicated dominance of ancient C in all three organic compound classes. In downstream samples, the extractable lipids displayed the lowest $\Delta^{14}C$ values (<−500‰), while the acid hydrolyzable fraction was predominantly modern ($\Delta^{14}C > −30\%$). The nonhydrolyzable fraction displayed intermediate $\Delta^{14}C$ values (<−190‰) that increased steadily downstream with decreasing $\delta^{13}C$ 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 $\delta^{13}C$ 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.


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 Tg C yr$^{-1}$ where Tg = 10$^{12}$ 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 $\Delta^{14}C$ and $\delta^{13}C$ 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:
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.

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 km²; 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
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].

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 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].

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 Δ¹³C 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.

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 subsampled 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

All samples were lyophilized and powdered prior to analysis. For determination of weight-% OC (%OC) and δ¹³C (per mil deviation of ¹³C/¹²C ratio from PDB-1) of bulk POC, pre-weighed samples were exposed to HCl vapor in Ag capsules for 120 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 δ¹³C values of OC that agreed within error with those obtained using the sulfuric acid method [Verardo et al., 1990; T. Komada, unpublished]...

### Table 1. Underlying Lithology of the Santa Clara Basin

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

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].
The evolved CO₂ was cryogenically purified, with CuO and elemental silver as described by capsules) into quartz tubes, dried, sealed, and combusted silver capsules as described above, transferred (with the bulk POC, samples were decarbonated with HCl vapor in silver capsules were transferred quantitatively into combustion tubes, and lyophilized. The residual nonhydrolyzable solids were transferred to quartz combustion tubes, concentrated by rotary evaporation, quantitatively transferred to quartz combustion tubes, loss of volatile compounds under combustion tubes, and oxidation during acid digestion. The observed yield was lower than those reported previously 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 ≤13% of the bulk POC, respectively. The observed yield was lower than those reported previously for abyssal sediments using this method (≥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 ~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.

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.,

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk POC, %</th>
<th>Extractable Lipid, %</th>
<th>Acid Hydrolyzable, %</th>
<th>NonHydrolyzable, %</th>
<th>Total Recovered, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pico</td>
<td>1.19</td>
<td>5</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Monterey-1</td>
<td>4.29</td>
<td>21</td>
<td>48</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>Monterey-2</td>
<td>0.40</td>
<td>1</td>
<td>31b</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>Lower Monterey</td>
<td>0.50</td>
<td>22</td>
<td>n/a</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>24 Feb. 1998</td>
<td>0.94</td>
<td>6</td>
<td>n/a</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>25 March 1998</td>
<td>1.11</td>
<td>11</td>
<td>43</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>15 March 2003</td>
<td>1.01</td>
<td>10</td>
<td>48</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>0–0.5 cm</td>
<td>1.26</td>
<td>7</td>
<td>49</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>18–20 cm</td>
<td>1.15</td>
<td>5</td>
<td>58</td>
<td>74</td>
<td></td>
</tr>
</tbody>
</table>

3.1. Relative Yields of Organic Compound Classes

[11] 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 (≤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 ≤13% of the bulk POC, respectively. The observed yield was lower than those reported previously for abyssal sediments using this method (≥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 ~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.

[13] For determination of δ¹³C and Δ¹⁴C signatures, the isolated organic fractions were combusted in sealed quartz tubes as described above for bulk samples. The evolved CO₂ was purified and quantified manometrically for C yield, then split for δ¹³C and Δ¹⁴C analyses. The samples for δ¹³C determination were analyzed using a Finnigan Delta Plus isotope ratio mass spectrometer operated in dual inlet mode. The samples for Δ¹⁴C 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 ±0.3‰ for Δ¹⁴C and δ¹³C signatures, respectively [Hwang and Druffel, 2005].
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

The $\Delta^{14}C$ signatures of organic compound classes varied systematically both within and across sample types (Figure 3a, Table 3). Shales showed uniformly low $\Delta^{14}C$ values, and did not exceed $-940\%$ except for an acid hydrolyzable isolate whose signature was $-764\%$. The $\Delta^{14}C$ values of river and coastal marine samples were more variable, and ranged from $<-850\%$ to $>0\%$. In all samples, the acid hydrolyzable fraction was most enriched in $\Delta^{14}C$, while lipids were most depleted. The $\Delta^{14}C$ 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).

Throughout the transect, the acid hydrolyzable fraction varied systematically both within and across sample types (Figure 3a, Table 3). Shale $\delta^{13}C$ values ranged from $-25.0$ to $-21.9\%$. The $\delta^{13}C$ 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 $-21.4\%$).

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 $\Delta^{14}C$ and $\delta^{13}C$ 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

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

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-
<table>
<thead>
<tr>
<th>Sample</th>
<th>UCID Number</th>
<th>$\Delta^{14}$C, %o</th>
<th>$\delta^{13}$C, %o</th>
<th>UCID No.</th>
<th>$\Delta^{14}$C, %o</th>
<th>$\delta^{13}$C, %o</th>
<th>UCID No.</th>
<th>$\Delta^{14}$C, %o</th>
<th>$\delta^{13}$C, %o</th>
<th>UCID Number</th>
<th>$\Delta^{14}$C, %o</th>
<th>$\delta^{13}$C, %o</th>
<th>UCID Number</th>
<th>$\Delta^{14}$C, %o</th>
<th>$\delta^{13}$C, %o</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shale</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Pico</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monterey-1</td>
<td>5334</td>
<td>-995</td>
<td>-21.7</td>
<td></td>
<td>n/a</td>
<td>n/a</td>
<td></td>
<td>5804</td>
<td>-996</td>
<td>-22.2</td>
<td>5796</td>
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<td>-23.0</td>
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<td>Monterey-2</td>
<td>5336</td>
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<td>-764</td>
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<tr>
<td>Lower Monterey</td>
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<td>5527</td>
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<tr>
<td>Santa Clara Suspended Sediment</td>
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<td>5528</td>
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<td>-22.7</td>
<td>5796</td>
<td>-996</td>
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<td>-996</td>
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<tr>
<td>24 Feb. 1998</td>
<td>6863</td>
<td>-271</td>
<td>-25.1</td>
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<td>Coastal Marine Sediment</td>
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<td></td>
</tr>
<tr>
<td>0–0.5 cm</td>
<td>6832</td>
<td>-167</td>
<td>-23.8</td>
<td>6271</td>
<td>11</td>
<td>-20.8</td>
<td>5803</td>
<td>-236</td>
<td>-25.0</td>
<td>5798</td>
<td>-506</td>
<td>n/a</td>
<td>-217</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>18–20 cm (age-corrected $\Delta^{14}$C)$^d$</td>
<td>6833</td>
<td>-265 (-151)</td>
<td>-24.0</td>
<td>6269</td>
<td>-105 (33)</td>
<td>-21.4</td>
<td>5802</td>
<td>-299 (-191)</td>
<td>-24.7</td>
<td>5799</td>
<td>-664 (-612)</td>
<td>-23.8</td>
<td>-295</td>
<td>-24</td>
<td>-24</td>
</tr>
</tbody>
</table>

$^a$Here n/a denotes data not available.

$^b$Isotopic signatures of the total recovered fraction calculated by mass balance using isotopic data of organic fractions and their corresponding yields presented in Table 2 ($\pm 2$ standard deviations) for $\Delta^{14}$C and $\delta^{13}$C estimates, respectively).

$^c$CO2 yield was insufficient for isotopic analyses.

$^d$This is hydrolyzable fraction that was separated into total hydrolyzable amino acids and neutral carbohydrates [Hwang et al., 2005]. The reported values are for the carbohydrate isolate only; amino acid yield was too low for reliable isotopic analyses.

$^e$This $\Delta^{14}$C values reported in parentheses have been corrected for decay since the estimated time of deposition [Stuiver and Polach, 1977] using a sedimentation rate of 16 cm kyr$^{-1}$ determined from the $\Delta^{14}$C gradient below the zone of bioturbation [Hwang et al., 2005]. Because this correction assumes absence of diagenetic alteration, the corrected values are considered minimum estimates if labile; $^{13}$C-rich moieties are preferentially lost during diagenesis.
synthesized material in this fraction. The high $\delta^{13}C$ 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 ($\Delta^{14}C = -764$) 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 $\delta^{13}C$ 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 $\Delta^{14}C$ 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 $\delta^{13}C$ and $\Delta^{14}C$ 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 $\delta^{13}C$ signatures of the nonhydrolyzable fraction decreased with increasing $\Delta^{14}C$, 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 $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\Delta^{14}C$ 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
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 $\Delta^{14}C$ 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 $\Delta^{14}C$-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 $\Delta^{14}C$ signatures (Tables 2 and 3). Assigning $\Delta^{14}C$ values of +80% and $\delta^{13}C_{OC}$ 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 \( \Delta^{13}C \) 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 \( \delta^{13}C \) 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 asphaltites 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 \( \Delta^{14}C \) signatures observed in lipids extracted from open ocean environments [Hwang and Druiffel, 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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