Transformations of carbon in anoxic marine sediments: Implications from $\Delta^{14}C$ and $\delta^{13}C$ signatures

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Abstract

Organic-rich nearshore sediment was incubated in sealed vessels under sulfate-reducing conditions to investigate the mechanism of dissolved organic carbon (DOC) production in marine sediments. Concentrations and isotopic signatures ($\delta^{13}C$ and $\Delta^{14}C$) of particulate organic carbon (POC), DOC, dissolved inorganic carbon (DIC), and particulate inorganic carbon (PIC) were monitored for 130 d. POC solubilization was largely counterbalanced by respiration, resulting in a net increase in DIC of $>35$ mmol L$^{-1}$. Net accumulation of DOC was relatively muted, yet significant, at $\sim 0.04$ mmol L$^{-1}$. All carbon pools exhibited distinct $\delta^{13}C$ and $\Delta^{14}C$ signatures prior to the incubation. Once the incubation began, these isotopic values varied with time, reflecting exchanges of isotonically distinct moieties across carbon pools. The $^{14}C$-enriched (modern) component of bulk POC was selectively solubilized into DOC, and the majority of this DOC was rapidly respired to DIC. However, net accumulation of DOC was accompanied by a drop in $\Delta^{14}C$, suggesting that during selective solubilization of the younger component of bulk POC, there was concomitant solubilization of pre-aged organic matter that subsequently accumulated as DOC. PIC was minor in terms of pool size, but likely played a critical role in determining the $\delta^{13}C$ signature of pore-water DIC through isotope exchange.

A large fraction of global sediment organic carbon (OC) remineralization and burial takes place in coastal sediments, many of which are organic-rich and anaerobic (Canfield 1993; Middelburg et al. 1997). Under such conditions, OC is remineralized by the microbial community through a sequence of processes (Fig. 1; Megonigal et al. 2003; Canfield et al. 2005). Particulate organic carbon (POC) is first solubilized into high-molecular-weight dissolved organic carbon (DOC) by extracellular enzymatic hydrolysis, and DOC thus produced is further transformed through fermentation into low-molecular-weight compounds, such as short-chain fatty acids and alcohols. These low-molecular-weight products are eventually oxidized into dissolved inorganic carbon (DIC) by terminal respiration, with $\text{SO}_4^{2-}$ being the primary electron acceptor in many coastal depositional environments (Canfield et al. 2005). Clearly, DOC is a key intermediate in the overall process of POC degradation in anaerobic sediments, and as such, the composition and turnover of pore-water DOC should hold important clues regarding the factors that control the rates of anaerobic OC degradation.

There is evidence for rapid turnover of the majority of pore-water DOC due to close coupling between DOC production and terminal respiration (Alperin et al. 1994; Arnosti et al. 1998). Yet organic-rich anaerobic sediments are also significant sources of DOC to the overlying water column (Burdige et al. 1999; Holcombe et al. 2001). For sediments to export DOC, there must be an excess of DOC production over consumption, resulting in DOC accumulation and efflux out of the sediments. Studies show that reactive constituents, such as short-chain fatty acids and amino acids, typically make up a minor fraction of the pore-water DOC standing stock (Sansone and Martens 1982; Burdige and Martens 1990), and that DOC accumulation is largely supported by net production of moieties that are not readily amenable to characterization at the molecular level (Lomstein et al. 1998; Burdige 2001). Application of high-resolution mass spectrometry to pore-water dissolved organic matter has so far underscored the complexity of this material, and led to the identification of what could be a recalcitrant component of the DOC pool that is common to both sediments and the water column (Koch et al. 2005; Tremblay et al. 2007).

The pathway through which recalcitrant DOC is produced in sediments is unclear. Traditionally, condensation and polymerization of labile monomers were considered to generate complex macromolecules that subsequently accumulate in the pore waters (Nissenbaum et al. 1971). This model was later revised by Burdige and Gardner (1998), who determined the molecular weight distribution of pore-water DOC, and proposed that DOC in sediments is mostly of low-molecular-weight material that is produced as a result of internal transformations of otherwise labile DOC (pore-water size reactivity [PWSR] model; Fig. 1). More recently, Robador et al. (2010) proposed another model where DOC accumulates because of inherent recalcitrance of DOC that is produced during POC hydrolysis (Weston and Joye 2005; Fig. 1). A key difference between these two hypotheses is that while the PWSR model predicts that all hydrolysis products are labile, the latter states that hydrolyzable POC partly consists of OC that is inherently recalcitrant once in solution.

To better understand the mechanism of pore-water DOC accumulation, we conducted an incubation experiment to constrain the pathway of recalcitrant DOC production using natural $^{14}C$ as a proxy for OC reactivity. Studies conducted in a number of soils and marine environments show a general pattern of rapid recycling of organic matter...
with high $^{14}$C values (young radiocarbon age), and slow turnover of components with lower $^{14}$C values (older radiocarbon age; Trumbore 2000; Mayorga et al. 2005; Repeta and Aluwihare 2006). To the best of our knowledge, systems that show clear exceptions to this trend are to date limited to glaciated watersheds (Hood et al. 2009) and an urbanized estuary receiving large quantities of treated wastewater (Griffith and Raymond 2011). Hence, in the context of the current study, if the dominant pathway for DOC production is described by the PWSR model where originally labile monomers are transformed into recalcitrant components, then the DOC accumulating in the pore water is expected to have isotopic values that are indistinguishable from DOC that is respired to DIC. On the other hand, if recalcitrant DOC is produced directly from hydrolysis of POC, then the DOC accumulating in the pore water is expected to be depleted in $^{14}$C relative to that supporting terminal metabolism.

We examined the controls on OC remineralization and DOC accumulation in an organic-rich nearshore sediment by monitoring the fractional abundances of natural $^{14}$C and $^{13}$C in POC, DOC, DIC, and carbonates (particulate inorganic carbon [PIC]) during a 130-d anaerobic incubation experiment. From these values, the isotopic composition of POC and DOC that were subject to degradation during the incubation were calculated. Results show that the isotopic value of the OC that underwent degradation was distinct from that of the bulk parent material, and that both POC hydrolysis and DOC respiration were selective processes. The data also indicate that recalcitrant pore-water DOC was derived from $^{14}$C-depleted components of the bulk POC pool. Furthermore, we show that although PIC was a minor component of the total carbon standing stock, it likely played a critical role in defining the $^{13}$C signature of DIC, possibly through recrystallization.

Methods

Sample collection and processing—Sediment used for the incubation was collected in July 2007 from a bioturbated, non-vegetated tidal creek bank in Muzzi Marsh, a restored salt marsh in San Francisco Bay, California (restoration year 1976; Fig. 2). Samples were collected adjacent to a cordgrass (Spartina spp.) stand, ~ 3 m from a dike. Vegetation on and along the banks of the dike was dominated by pickleweed (Salicornia spp.) and saltgrass (Distichlis spp.). The site was accessed by foot during low tide, and ~ 6 liters of the uppermost 3 to 5 cm of sediment were collected with a trowel into plastic bags. Three sediment cores were also taken to determine DIC, $\mathrm{NH}_4^+$, and $\mathrm{SO}_4^{2-}$ concentrations in surface pore waters. Additional surface (ca. 0–5-cm) sediment sample was collected with a trowel in March 2011. All samples were placed on ice and transported 8 km to the laboratory in Tiburon for further processing.

Upon returning to the laboratory, the cores were extruded and sliced in an N$_2$ atmosphere into 1-cm intervals and centrifuged (4°C; 8.5 × 10$^4$ m s$^{-2}$). The supernatant was filtered (0.2-$\mu$m polysulfone with glass microfiber pre-filter) and split into aliquots for DIC, $\mathrm{NH}_4^+$, and $\mathrm{SO}_4^{2-}$ analyses as described below. Surface sediment collected in March 2011 was centrifuged as described above.
and processed for DOC as given below. The 6-liter aliquot for the incubation experiment was processed over the course of the next 4 d by manually removing large objects, including shell fragments and plant and animal tissue, over a stainless steel mesh (1 mm). Care was taken to remove as much benthic fauna as possible, but a significant amount of soft tissue disintegrated and was incorporated into the sediment. The sediment was exposed to laboratory air throughout this process, and chilled whenever possible. When sieving was complete, the sample was pooled and homogenized.

Leaves and stems of cordgrass and pickleweed were collected in July 2008 from the vicinity of the study site as potential OC end-members. Plant samples were rinsed with dilute HCl followed by deionized water, and frozen until further processing. Estuarine water was collected in July 2008 from the vicinity of the study site as potential OC end-members. Plant samples were rinsed with deionized water and solids. The tubes were centrifuged (4°C, 14,800 \times 10^3 \text{m s}^{-2}), and the supernatant from all tubes were pooled in a 100-mL gastight glass syringe with a stainless steel needle. The pooled supernatant was filtered (0.2-\mu m polysulfone with glass microfiber pre-filter; first 1 mL was discarded) and processed for DIC, DOC, NH$_4^+$, total dissolved Fe (SigmaFe$_{aq}$), and SO$_4^{2-}$ as described below. The solids were frozen.

Sulfate concentration was monitored to ensure that it was sufficiently high to prevent the onset of methanogenesis. At t = 39 d when SO$_4^{2-}$ concentration decreased to 19.4 mmol L$^{-1}$ (Fig. 3a), all remaining 24 tubes were spiked with 220 \mu L of saturated Na$_2$SO$_4$ by briefly opening the cap and injecting the solution into the center of the tube using a stainless steel needle. Sulfate concentration at the next sampling time point (t = 53 d) increased to 26.5 mmol L$^{-1}$, and remained above 20 mmol L$^{-1}$ for the remainder of the incubation.

Sample preservation and analytical methods—All glass-and plasticware were soaped, acid washed, and rinsed thoroughly with deionized water. Glassware was further ashed at 550°C for 4 h; quartz and CuO were pre-combusted at 850°C for 4 h. DIC samples (∼ 10 mL) were flame sealed under a stream of ultra-high-purity N$_2$ into borosilicate tubes containing HgCl$_2$. DOC samples were collected into 20-mL borosilicate scintillation vials with Teflon-lined caps and frozen. SigmaFe$_{aq}$ samples were collected into 4-mL high-density polyethylene bottles, acidified to pH 2 with 6 mol L$^{-1}$ HCl, and refrigerated. NH$_4^+$ samples were frozen in 15-mL polypropylene tubes. Sulfate samples were transferred into 1-mL plastic syringes spiked with 10 \mu L of saturated Zn acetate, filtered into 7-mL glass vials, acidified with 100 \mu L of 1 mol L$^{-1}$ HCl, and refrigerated.

DIC ampules were cracked open under vacuum in the presence of 3 mL of saturated CuSO$_4$ in 3 mol L$^{-1}$ H$_2$PO$_4$ (McCorkle et al. 1985; Aller and Blair 2006). The evolved CO$_2$ was dried, quantified, and collected into borosilicate break-seal tubes for determination of $^{13}$C by isotope ratio mass spectrometry (IRMS), and for $^{14}$C by accelerator mass spectrometry (AMS). DOC was oxidized to CO$_2$ by thermal SO$_4^{2-}$ reduction (Johnson and Komada 2011), then quantified and split for isotopic analyses as described above. The entire contents of each DOC sample vial (solution plus precipitates that formed during frozen storage) were processed to ensure accurate DOC determination. SigmaFe$_{aq}$ was determined by spectrophotometry (Stookey 1970), NH$_4^+$ by fluorometry (Holmes et al. 1999; Taylor et al. 2007), and SO$_4^{2-}$ by turbidimetry (Clesceri et al. 1998).

Thawed sediment samples were mixed, subsampled, oven-dried to constant weight (80°C), and powdered using an agate mortar and pestle. Unlike the case for pore-water samples where the supernatant from all six tubes were...
Table 1. Isotopic values of end-member samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ^{13}C (%)</th>
<th>Δ^{14}C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cordgrass* leaves</td>
<td>−16.4</td>
<td>+32</td>
</tr>
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<td>Cordgrass root</td>
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<td>—</td>
</tr>
<tr>
<td>Cordgrass stem</td>
<td>−14.3</td>
<td>—</td>
</tr>
<tr>
<td>Pickleweed† leaves</td>
<td>−27.7</td>
<td>—</td>
</tr>
<tr>
<td>Pickleweed root</td>
<td>−26.7</td>
<td>—</td>
</tr>
<tr>
<td>Pickleweed stem</td>
<td>−28.1</td>
<td>—</td>
</tr>
<tr>
<td>Estuarine water DIC</td>
<td>−2</td>
<td>−1</td>
</tr>
</tbody>
</table>

* Spatina spp.
† Salicornia spp.

Results

Isotopic compositions of end-member carbon sources—The δ^{13}C values of local plants ranged from −28.1‰ (pickleweed) to −14.3‰ (cordgrass), and they fell within range of a comprehensive set of δ^{13}C values reported for these plants in San Francisco Bay (Cloern et al. 2002; Table 1; Fig. 4). The Δ^{14}C value of cordgrass had a clear bomb-^{14}C signal (+32‰), and was the highest among all Δ^{14}C values obtained in this study. Estuarine water DIC had a δ^{13}C value of −2‰ and a Δ^{14}C value of −1‰ (Table 1; Fig. 4).

Incubation results: concentrations—During the incubation, POC decreased by about 7% in an exponential fashion, from an initial value of 1.83‰ weight (wt%) to ~1.7 wt% by t = 39 d (Table 2; Fig. 5a). The loss in POC was mirrored by an increase in DIC by more than sixfold, from a starting value of 6.8 mmol L^{-1} to 44.3 mmol L^{-1} at t = 95 d (Table 2; Fig. 5d). DOC initially dropped from 1.43 mmol L^{-1} at t = 0 d to 1.31 mmol L^{-1} at t = 2 d (Table 2; Fig. 5g). It then increased by ~0.2 mmol L^{-1} from t = 5–25 d to ~1.5 mmol L^{-1} and remained largely constant for the remainder of the experiment. At t = 0 d, DOC accounted for 17% of the total dissolved carbon (DIC + DOC), but its relative importance dropped to <10% by t = 5 d, and was 3% by t = 95 d (Table 2). Similar to previous reports (Alperin et al. 1994, 1999), only <1% of the net increase in total dissolved carbon between t = 0 and 95 d could be attributed to DOC, indicating that the vast majority of DOC produced during the incubation was efficiently respired to DIC. NH_4^+ increased exponentially
from a starting value of 0.11 mmol L\(^{-1}\) to 1.81 mmol L\(^{-1}\) at the end of the incubation (Fig. 3b). PIC was very low, and fluctuated between 0.025 and 0.031 wt% (Fig. 5j).

\(\Sigma\)Fe\(_{aq}\) increased sharply at the start of the incubation indicating active Fe(III) reduction (Fig. 3a). After reaching a maximum of 0.96 mmol L\(^{-1}\) at \(t = 18\) d, it dropped to a non-detectable level by \(t = 95\) d. Sulfate showed no detectable change during the first 2 d, but decreased rapidly thereafter and reached a minimum value of 19.4 mmol L\(^{-1}\) at \(t = 39\) d (Fig. 3a). After each tube was spiked with Na\(_2\)SO\(_4\)(aq) at \(t = 39\) d (see Methods), SO\(_2\)\(^\text{4}^-\) concentration returned to values >26 mmol L\(^{-1}\), then decreased again but at a slower rate. Increases in DIC plotted against decreases in SO\(_2\)\(^\text{4}^-\) (Table 2) gave a slope (± 1 standard error [SE]) of 1.9 ± 0.3 (figure not shown), which was within error of the theoretical ratio of 1.7–1.8 for OC whose oxidation number is −0.7 to −0.5 (Burdige 2006). Sulfide was not measured in this study, but the presence of \(\Sigma\)Fe\(_{aq}\) up to \(t = 95\) d suggests that free sulfide was absent prior to this time point (Canfield 1989). Increases in DIC relative to increases in NH\(_4^+\) generated two slopes (± 1 SE): 63 ± 1 between \(t = 0\) and 5 d, and 20 ± 1 between \(t = 9\) and 95 d (figure not shown). This shift in the apparent generation ratio could reflect a change in the C:N ratio of remineralized organic matter, or bacterial NH\(_4^+\) incorporation during the early phase of the incubation (Blackburn and Henriksen 1983; Lomstein et al. 1998). Another possible explanation is that this was due to net dissolution followed by precipitation of PIC. The latter point is addressed in the Discussion section.

DIC, DOC, and NH\(_4^+\) concentrations at \(t = 0\) d were elevated relative to those measured in the surface sediment and core samples (by 30% for DIC, and by a factor of 5.5 and 2.5 for NH\(_4^+\) and DOC, respectively; Table 2), likely due to extensive disturbance during sieving and homogenization. The rapid drop in DOC observed between \(t = 0\) and \(t = 2\) d suggests that elevated DOC at \(t = 0\) d reflected a transient buildup of labile DOC that leached from fresh substrate (Arnosti et al. 2005). Below, we present \(\Delta^{14}\)C values of DOC that further support this suggestion. In contrast, the ingrowth of DOC observed after \(t = 5\) d was clearly from net solubilization of POC that occurred during the incubation (Fig. 5g). While the experimental system was highly artificial, given the realistic DIC production rate (see Time-dependent models) and the low net DOC:DIC production ratio discussed above, the key properties of DOC dynamics presented below are most likely to be applicable to other similar benthic systems.

### Table 2. Solute concentrations in incubated and non-incubated sediment samples. Estimated measurement uncertainties are: POC < 3%; PIC 5%; NH\(_4^+\) 2%; DOC 5%; DIC = 2%; \(\Sigma\)Fe\(_{aq}\) 20%; SO\(_2\)\(^\text{4}^-\) 5%. nd, not detected.

<table>
<thead>
<tr>
<th>t (d)</th>
<th>POC (wt% C)</th>
<th>PIC (wt% C)</th>
<th>TN (wt% N)</th>
<th>SO(_4)(^{2-}) (mmol L(^{-1}))</th>
<th>(\Sigma)Fe(_{aq}) (mmol L(^{-1}))</th>
<th>DIC (mmol L(^{-1}))</th>
<th>NH(_4^+) (mmol L(^{-1}))</th>
<th>DOC (mmol L(^{-1}))</th>
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<tbody>
<tr>
<td>0</td>
<td>1.83</td>
<td>0.030</td>
<td>0.211</td>
<td>27.5</td>
<td>0.17</td>
<td>6.8</td>
<td>0.11</td>
<td>1.43</td>
</tr>
<tr>
<td>2</td>
<td>1.80</td>
<td>—</td>
<td>0.209</td>
<td>27.5</td>
<td>0.42</td>
<td>11.3</td>
<td>0.18</td>
<td>1.31</td>
</tr>
<tr>
<td>5</td>
<td>1.79</td>
<td>0.031</td>
<td>0.208</td>
<td>—</td>
<td>0.72</td>
<td>15.9</td>
<td>0.25</td>
<td>1.30</td>
</tr>
<tr>
<td>9</td>
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<td>—</td>
<td>0.202</td>
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<td>0.89</td>
<td>20.5</td>
<td>0.52</td>
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<tr>
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<td>24.3</td>
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<tr>
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<td>32.2</td>
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<td>53</td>
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<td>39.4</td>
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<td>0.198</td>
<td>24.2</td>
<td>0.06</td>
<td>42.7</td>
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<tr>
<td>Core samples</td>
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<td>—</td>
<td>24±1†</td>
<td>—</td>
<td>5.2±0.1†</td>
<td>0.02±0.02†</td>
<td>0.58±0.02§</td>
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</table>

* Immediately prior to spiking with saturated Na\(_2\)SO\(_4\). Post-spike concentration is not available.

† Average and standard deviation of four to eight pore-water samples from the uppermost 3 cm of three sediment cores.

‡ Average and absolute range of two pore-water samples from 1–2- and 2–3-cm-depth intervals of one sediment core.

§ Average and standard deviation of four pore-water samples obtained by centrifuging a bulk surface sediment sample (ca. 0–3 cm) collected in March 2011.

Incubation results: isotopic composition—At \(t = 0\) d, \(\delta^{13}\)C\(_{POC}\) was −22.2‰ (Table 3; Fig. 5b), which was within the range of \(\delta^{13}\)C values reported for soils and sediments in the Sacramento–San Joaquin River delta (−28.1‰ to −19.8‰) and seston in San Francisco Bay (−28.2‰ to −17.4‰; Cloern et al. 2002). This value was also intermediate between \(\delta^{13}\)C of local cordgrass and pickleweed, and within range of \(\delta^{13}\)C values reported for benthic diatoms and phytoplankton (Cloern et al. 2002; Fig. 4).

\(\Delta^{14}\)C\(_{POC}\) at \(t = 0\) d was −159‰ (Table 3; Fig. 5c), which was significantly depleted relative to all other organic sources analyzed (Fig. 4). The overall low \(\Delta^{14}\)C\(_{POC}\) value was expected because OC can have prolonged residence in the soil profile (Trumbore 2000), and fossil C input from bedrock erosion (Blair et al. 2004) and anthropogenic contamination is highly likely at this site. As the incubation progressed and POC concentration decreased, \(\delta^{13}\)C\(_{POC}\) and \(\Delta^{14}\)C\(_{POC}\) decreased by ~ 0.3‰ and 10‰, respectively, indicating net loss of isotopically enriched OC from bulk POC (Fig. 5a–c). There was an apparent increase in \(\Delta^{14}\)C\(_{POC}\) from \(t = 0\) to \(t = 5\) d (Table 3; Fig. 5c), which...
was likely an artifact of analyzing only a small fraction of the incubated sediment. If there were large differences in the $^{14}$C content of ambient sediment POC and organic detritus, then patchy distribution of such solids could cause significant noise in $\Delta^{14}$C$_{POC}$.

$\delta^{13}$C$_{DIC}$ at $t = 0$ d was $-7.0\%$ (Table 3; Fig. 5e). This value was similar to those observed in the core samples (Table 3) and intermediate between $\delta^{13}$C of estuarine DIC and cordgrass (Fig. 4). As the incubation progressed and DIC concentration increased, $\delta^{13}$C$_{DIC}$ decreased, indicating net production of $^{13}$C-depleted DIC (Fig. 5d,e). $\delta^{13}$C$_{DIC}$ appeared to asymptote by $t = 75$ d at about $-11.4\%$, which was low relative to that of estuarine DIC, but higher than $\delta^{13}$C of local cordgrass and other primary
Table 3. Isotopic values of the incubated and non-incubated sediment samples in %. Where duplicate samples were processed, the results for both samples are listed. Estimated uncertainties are: $\delta^{13}$CPoC, $\delta^{13}$CDIC, and $\delta^{13}$C PIC, $\pm 0.1\%$; $\delta^{13}$CDOC $\leq \pm 0.4\%$; $\Delta^{14}$C PoC and $\Delta^{14}$C DIC $\leq \pm 3\%$; $\Delta^{14}$C PIC $\leq \pm 1\%$.

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<th>DIC</th>
<th>DOC</th>
<th>PIC</th>
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<td>Core samples†</td>
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* Internal sample identification number.
† Two pore-water samples taken from 1–2- and 2–3-cm-depth intervals.

Producers reported for San Francisco Bay (Fig. 4; Cloern et al. 2002). $\Delta^{14}$DIC was $+22\%$ at t = 0 d (Table 3; Fig. 5f), which was higher than that observed in the core samples by $\sim 10\%$ (Table 3). It is possible that extensive sample handling prior to the experiment caused rapid degradation and oxidation of $^{14}$C-enriched organic matter. Additionally, sieving likely enhanced gas exchange with atmospheric CO$_2$, which is elevated in $^{14}$C. Once the incubation started and DIC concentration increased, $\Delta^{14}$DIC dropped rapidly and reached $+14\%$ by t = 2 d, and remained largely constant for the rest of the incubation. Clearly, DIC that was depleted in $^{14}$C relative to that present at t = 0 d was produced during the incubation (Fig. 5d,f).

$\delta^{13}$CDOC at t = 0 d was $-20.5\%$ (Table 3; Fig. 5f). In the first 9 d, $\delta^{13}$CDOC dropped by $\sim 2\%$ to $-22.6\%$, and it remained largely constant for the rest of the incubation (Fig. 5f). $\Delta^{14}$CDOC at t = 0 d was $-20\%$ (Table 3; Fig. 5f). During the first 14 d of the incubation, $\Delta^{14}$CDOC dropped sharply to $-79\%$, and remained low until t = 25 d (Fig. 5i). Therefore, the rapid drop in DOC observed between t = 0 and 2 d involved consumption of $^{14}$C-enriched DOC, while the increase in DOC observed between t = 5–25 d was due in part to net production of $^{14}$C-depleted DOC. After t = 25 d, $\Delta^{14}$CDOC increased by $\sim 30\%$, then decreased again after t = 74 d by $\sim 15\%$ (Fig. 5i), indicating variation in DOC composition despite minimum changes in DIC concentration. At the end of the incubation, $\Delta^{14}$CDOC was lower than the starting value by ca. 40%. Because DOC concentration increased by $\sim 0.1$ mmol L$^{-1}$ over this time period, these results show that $^{14}$C-depleted DOC was produced during the incubation.

$\delta^{13}$C PIC at t = 0 d was $-7.1\%$, and showed no clear trend during the remainder of the incubation (Table 3; Fig. 5k). $\Delta^{14}$C PIC values were notably low, at about $-480\%$ (Fig. 5k). PIC content, $\delta^{13}$C PIC, and $\Delta^{14}$C PIC all appeared to oscillate randomly with time, but they were positively correlated with each other such that samples with higher PIC content were also isotopically enriched (Figs. 4, 5j–l; Tables 2, 3). These trends were consistent with PIC being an admixture of $^{14}$C-depleted carbonates from fossil sources (bedrock), and $^{14}$C-enriched carbonates from recent sources (shells).

**Discussion**

**Carbon mass balance**—Prior to determining the isotopic values of carbon transformed during the incubation, we evaluate the degree to which carbon mass balance was achieved. Assuming that net dissolution or precipitation of PIC was negligible, the decrease in POC should be largely balanced by increase in DIC because net production of DOC was small. Methane can be ignored because SO$_2$ concentrations were sufficiently high to inhibit methanogenesis (Canfield et al. 2005; Fig. 3a). Based on these assumptions, and using a measured porosity ($\phi$) of 0.85 (estimated error 3%) and an assumed dry sediment density of 2.6 (Burdige 2006), the observed increase in DIC predicted a loss in POC of approximately 0.1 wt% by t = 130 d (Fig. 5d), which agreed to within analytical error of the observed POC loss ($\sim 0.13$ wt%; Fig. 5a). However, POC loss calculated from DIC gain was systematically lower than the observed POC loss by $\sim 20\%$ throughout the incubation, suggesting the presence of a determinate
error. While the exact source(s) of such an error is unknown, the offset can be explained if $\varphi$ was underestimated by 4%. Therefore, in the modeling work shown below, we use an adjusted $\varphi$ of 0.88 to correct for this offset.

**Isotopic values of carbon transformed during the incubation**—The isotopic values of OC that was transformed during the incubation were evaluated in two independent ways: Through the use of two-component isotope mixing plots, and by modeling the data as time-dependent variables. In the first approach, the isotopic value of the carbon that was added to, or removed from, the carbon reservoir over the corresponding time interval was determined graphically. The product of the concentration and isotopic value of a given sample was plotted against concentration, and the slopes of the linear portions of these plots were taken to represent the isotopic value of the component added or removed (Sayles and Curry 1988; Hu and Burdige 2007; Aller et al. 2008). This approach does not require a priori knowledge of the mechanisms of carbon transformations. In the second approach, a model that prescribes the carbon transformation reactions was constructed, then fit to the observed data to constrain the rates of these reactions and the isotopic values of the carbon transformed.

Isotope mixing plots were used to analyze POC, DIC, and DOC data. PIC was excluded from this exercise because the measured data reflected only a subset of the total carbonate pool that was present in the incubated sediment (see Methods). Time-dependent models were constructed for POC, DIC, and PIC. DOC was not modeled because it clearly underwent compositional changes through the incubation (Fig. 5i). Variation in DOC isotopic composition observed in the present study is consistent with the results from flow-cell and sediment incubation experiments that demonstrated temporary accumulation of hydrolysis and fermentation products due to lagged consumption (Brüchert and Arnosti 2003; Arnosti et al. 2005). It is therefore possible that the apparent transient buildup of $^{14}$C-enriched DOC between $t = 25$ d and $t = 53$ d was due to short-term imbalances among hydrolysis, fermentation, and $\text{SO}_4^{2-}$ reduction rates. In the absence of chemical compositional data, there was insufficient information to parameterize such changes without introducing a large number of unknowns into the model. The net reaction rates of DOC were small relative to those of POC and DIC (< 1%; Table 2), hence the error incurred from omitting DOC from the carbon and isotope budgets is likely small relative to the uncertainty associated with the model itself.

Isotope mixing plots: With the exception of $\Delta^14C_{\text{POC}}$, all sets of isotopic values showed at least one linear region in the mixing plot (Fig. 6). $\delta^{13}C_{\text{POC}}$ gave one straight line with a slope of $-18.5 \pm 0.7\%$ (± 1 SE); $\Delta^14C_{\text{POC}}$ showed considerable noise, with a slope of $+30 \pm 50\%$. These values were higher than the $\delta^{13}C$ and $\Delta^14C$ of the bulk pool by $-4\%$ and $190\%$, respectively (Table 3), indicating that POC degradation was biased toward contemporary OC that was also $^{13}C$-enriched, possibly reflecting cordgrass degradation (Table 1). Preferential loss and biological uptake of $^{14}$C-enriched POC during diagenesis have been reported in a number of studies with offsets between the $\Delta^14C$ of the parent OC and the utilized or degraded OC on the order of 10–20% (Cherrier et al. 1999; Aller and Blair 2004; Purinton et al. 2008).

The mixing plot for $\delta^{13}C_{\text{DOC}}$ from $t = 9$ d onward generated a slope of $-22 \pm 4\%$, which was similar to the $\delta^{13}C$ value of bulk POC, suggesting little to no selection with respect to $^{13}C$ during DOC production (Fig. 6c; Table 3). The $t = 0$ d datum could not be included in this analysis because $\delta^{13}C$ values are not available for $t = 2$ and 5 d when DOC concentration was at a minimum. Nonetheless, it is clear from Fig. 6c that the DOC consumed during the first 2 d of the incubation had on average a $\delta^{13}C$ signature that was different from (and likely more positive than) $\delta^{13}C$ of DOC that was produced from $t = 9$ d onward. The $\Delta^14C_{\text{DOC}}$ mixing plot exhibited greater variability (Fig. 6d). Between $t = 0$ and $t = 2$ d, when DOC concentration initially decreased (Table 2), the slope was positive ($+154\%$), although the specific $\Delta^14C$ value is tenuous given that it was derived from only two data points. Between $t = 2$ and 25 d when DOC concentration increased, the slope was strongly negative at $-400 \pm 60\%$. This value was $> 200\%$ lower than $\Delta^14C_{\text{POC}}$ (Table 3), and $\sim 400\%$ lower than the $\Delta^14C$ of the POC that was solubilized (compare the slopes in Fig. 6b,d). Data points after $t = 25$ d showed considerable scatter. Linear regression including all data points excluding $t = 0$ d gave a slope of $-200 \pm 90\%$, which overlapped with $\Delta^14C_{\text{POC}}$ values, but was still significantly lower than the $\Delta^14C$ of POC that was solubilized.

These results show that following net consumption of $^{14}$C-enriched DOC during the first 2 d of the incubation (which was likely associated with labile DOC from dead biomass introduced by sample manipulation), the increase in DOC observed after $t = 5$ d was driven by production of DOC that was depleted in both $^{14}$C and $^{13}$C relative to DOC that was present at the start of the incubation. The data also show that although the solubilizable component of bulk POC was on average enriched in $^{14}$C (Fig. 6b), it was isotopically heterogeneous, and included a small fraction (< 1%) of $^{14}$C-depleted moieties that accumulated as DOC.

The $\Delta^{14C}_{\text{DIC}}$ mixing plot gave a slope of $+12.0 \pm 0.7\%$, indicating input of bomb-$^{14}$C into the DIC pool (Fig. 6f). This value also fell within range of $\Delta^14C$ of POC that was solubilized (Fig. 6b), consistent with the concentration data showing that the vast majority of degraded POC was respired to DIC. Local plant production was unlikely to have been the sole DIC source because the slope was lower than the $\Delta^14C$ of cordgrass (Table 1).

The $\delta^{13}C_{\text{DIC}}$ mixing plot gave two linear regions with slopes of $-10.3\%$ ($t = 0$–5 d) and $-12.8\%$ ($t = 14$–95 d; Fig. 6e), which were higher than any other organic sample analyzed in this study (Fig. 4). These values overlapped with the highest $\delta^{13}C$ value reported for *Spartina foliosa* by Cloern et al. (2002), but as stated above, the $\Delta^14C_{\text{DIC}}$ values were inconsistent with local plant production being the sole DIC source. In addition, these slopes were 6–8% higher...
than the $\delta^{13}C$ of POC that was solubilized (Fig. 6a). These data indicate the presence of additional process(es) not considered thus far that was either a sink for $^{13}C$-depleted carbon or a source for $^{13}C$-enriched carbon. DOC functioned as a sink for relatively $^{13}C$-depleted carbon (Fig. 6c), but because the net reaction rate of DOC was low, this sink was insufficient to explain the high $\delta^{13}C_{\text{DIC}}$. Anomalously high $\delta^{13}C$ values have been reported for
pore-water DIC for a number of systems (Walter et al. 2007 and references therein), including nearshore terrigenous sediments (McNichol et al. 1991). Walter et al. (2007) propose that this is due to equilibrium $^{13}$C exchange between DIC and PIC. Hu and Burdige (2008) and Burdige et al. (2010) provide a different mechanism where $^{13}$CDIC increases due to a combined effect of pore-water DIC precipitation and dissolution of $^{13}$C-enriched metastable carbonates. The latter mechanism is explored in the next section using a time-dependent model.

Time-dependent models: In this section, time-dependent models are used to constrain the isotopic values of the carbon that was transformed during the incubation, as well as to assess the rates of these reactions. Two models are presented: Model-A considers POC remineralization as the sole source for DIC; Model-B includes POC remineralization and coupled dissolution–precipitation of PIC. Model-A was used to check for internal consistency with the isotope mixing plots, and Model-B was used to evaluate $^{13}$C exchange through PIC re-crystallization as a possible explanation for the high $^{13}$CDIC values.

Model-A: POC remineralization only: POC, DIC, and NH$_4^+$ were simulated assuming there was one pool of metabolizable POC ($G_m$) that degraded following first-order kinetics (Fig. 7). Because the incubation was only 130 d long, only one pool of $G_m$ was considered (Westrich and Berner 1984). Hence, POC was modeled as the sum of $G_m$ and a nonreactive component ($G_{nr}$, set to 1.70 wt%), each with its characteristic bulk $^{13}$C and $^{14}$C values (Fig. 7). Respiration of $G_m$ was assumed to proceed without isotopic fractionation. This led to the following equations:

$$G = G_m + G_{nr}$$

$$\frac{dG}{dt} = -k_{Gm}G_m$$

$$\frac{dC_{pm}}{dt} = Fk_{Gm}G_m$$

$$\frac{dN_{pw}}{dt} = \left(\frac{1}{r_{CN}}Fk_{Gm}G_m\right) \times (K_N + 1)^{-1}$$

where $G$, $C_{pm}$, and $N_{pw}$ are POC, DIC, and NH$_4^+$, respectively, $F$ is a factor that converts wt% to mmol L$^{-1}$, $k_{Gm}$ is the degradation rate constant for $G_m$, $r_{CN}$ is the molar C:N ratio of $G_m$, and $K_N$ is the dimensionless adsorption coefficient for NH$_4^+$ in anoxic sediments (Table 4). To model the isotopic values of POC and DIC, four more equations for $^{13}$C and $^{14}$C were written:

$$\frac{dG_i}{dt} = -R_{Gm}^{i}k_{Gm}G_m$$

$$\frac{dC_{pm}^{i}}{dt} = R_{Gm}^{i}Fk_{Gm}G_m$$

In Eqs. 5 and 6, $i$ is the mass of the rare carbon isotope (13 or 14), and $R_j$ is the ratio of the rare isotope to total carbon ($^{12}$C + $^{13}$C + $^{14}$C) for the carbon-containing species $j$:

$$R_j^{13} = \left[1 + \frac{1000}{(\delta_j + 1000)R_{VPDB}}\right]^{-1}$$

$$R_j^{14} \approx \left(\frac{\Delta_j}{1000} + 1\right)R_{abs}$$

where $\delta_j$ and $\Delta_j$ are the $^{13}$C and $^{14}$C values of $j$, $R_{VPDB}$ is the $^{13}$C/$^{12}$C ratio of the VPDB standard, and $R_{abs}$ is the $^{14}$C/(total C) ratio of the absolute radiocarbon standard (Stuiver 1980). $^{14}$C loss to radioactive decay was ignored given the short incubation time relative to the half-life of $^{14}$C (5730 yr). These equations were solved analytically, and the unknown parameters (Table 4) were constrained by simultaneously fitting all model equations to the data and minimizing the sum of the square of the residuals using the Solver routine in Microsoft Excel®. $^{63}$CDIC was calculated, but excluded from the fitting procedure.

With the exclusion of $^{13}$CDIC, it was possible to simulate the data reasonably well using Model-A (Fig. 5, solid lines). The model slightly overestimated DIC between ca. t = 20 d and 70 d, and tended to overestimate $^{14}$CPOC later in the incubation. However, good fits were obtained for POC, $^{13}$CPOC, and $^{14}$CDIC. The model gave $-18.0\%$ and $+11\%$ for $^{13}$C and $^{14}$C values of $G_m$, respectively, both of which were within error of those obtained from the mixing plots (Table 4). The best-fit value for $k_{Gm}$ was 0.05 d$^{-1}$, which was somewhat high relative to those reported for surface sediments and fresh detritus (0.02–0.03 d$^{-1}$; Westrich and Berner 1984; Roden and Tuttle 1996). This could have been due to introduction of animal...
tissue during initial sediment homogenization; sediment homogenization itself has also been reported to enhance microbial activity (Hansen et al. 2000; Arnosti et al. 2005). DIC production rate at t = 0 d (obtained by evaluating Eq. 3 at t = 0 d) was 1.64 mmol (L sediment)^{-1} d^{-1}. Assuming that this rate applied to 0–5 cm of the sediment column at the study site, the estimated benthic flux for this site is 82 mmol m^{-2} d^{-1}, which is within range of fluxes reported for coastal marine sediments (Burdige 2006).

Similar to the isotope mixing plots, Model-A gave δ\(^{13}\)C\(_{\text{DIC}}\) values that were consistently lower than the measured values by ~ 5\% (Fig. 5e). These results imply that while total carbon and \(^{14}\)C mass balances could be explained simply by taking \(G_m\) remineralization into account, additional process(es) were affecting δ\(^{13}\)C\(_{\text{DIC}}\) and shifting them to more positive values. The model fit to the NH\(^+_4\) data (Fig. 3b) also suggests the occurrence of reactions other than remineralization of \(G_m\). The \(r_{\text{C:N}}\) predicted by the model was similar to the observed bulk POC : TN ratios (Table 4), but the fit to the NH\(^+_4\) data was poor; the model underestimated \(r_{\text{C:N}}\) between t = 0 to ~ 50 d, and overestimated it for the rest of the incubation. In the next section, we discuss the possibility of net carbonate dissolution and precipitation, which can alter the apparent DIC : NH\(^+_4\) regeneration ratio independently of \(G_m\) remineralization.

Model-B: POC remineralization and PIC recrystallization: The sediment was aerated during sieving and homogenization, and SO\(^-\)\(^+_4\) did not show clear signs of decrease until after t = 2 d (Table 2). Therefore, it is likely that there was oxic respiration or oxidation of reduced metabolites during the first few days of the incubation, which would have promoted carbonate dissolution (Green and Aller 2001) and contributed to raising δ\(^{13}\)C\(_{\text{DIC}}\). The high apparent DIC : NH\(^+_4\) regeneration ratio observed between t = 0–5 d (63 ± 1; see Results) is also consistent with the occurrence of net carbonate dissolution early in the incubation. However, modeling the data according to this scenario creates two problems: The δ\(^{13}\)C\(_{\text{DIC}}\) data can only be simulated if there was dissolution throughout the first half of the incubation, which is unlikely given that both Fe(III) reduction and SO\(^-\)\(^+_4\) reduction became active early in the incubation (Fig. 3a), and both of these processes increase alkalinity (Berner et al. 1970; Burdige 2006); and even using an assumed δ\(^{13}\)C\(_{\text{PIC}}\) of +1\%, PIC dissolution required to simulate δ\(^{13}\)C\(_{\text{DIC}}\) results in an overestimation of DIC by as much as 5 mmol L^{-1} (results not shown).

A more plausible explanation is that there was coupled dissolution and re-precipitation, or recrystallization of carbonates. It has been shown through both field measurements and incubation experiments that isotope exchange between DIC and carbonates can occur under anaerobic conditions with limited or no net dissolution (Burdige et al. 2007; Hu and Burdige 2008). The exact mechanism of exchange is unclear, but proposed explanations include isotope exchange between CO\(_2\)(aq) and carbonates with high specific surface areas (Burdige et al. 2007), and dissolution of metastable phases coupled with precipitation of more stable secondary phases (Hu and Burdige 2008; Burdige et al. 2010). Here we adopt the coupled dissolution re-precipitation model of Hu and Burdige (2008; Fig. 7) to test whether isotope exchange between DIC and PIC can explain the observed δ\(^{13}\)C\(_{\text{PIC}}\) values.

Recrystallization is modeled by setting the precipitation rate equal to the rate of dissolution such that net carbonate reaction rate is zero at any given time. This gave the
following equations for DIC:
\[
\frac{dC_{pw}}{dt} = F\left[k_{Gm}G_m + k_{PICm}PIC_m\right] - r_{precip} \tag{9}
\]
\[
\frac{dC_{pw}}{dt} = F\left[R_{Gm}^{i}k_{Gm}G_m + R_{PICm}^{i}k_{PICm}PIC_m\right] - R_{C_{pw}}^{i}r_{precip} \tag{10}
\]

where PIC\textsubscript{m} is metastable carbonate that underwent dissolution, k\textsubscript{PICm} is the dissolution rate constant for PIC\textsubscript{m}, and r\textsubscript{precip} is the precipitation rate in units of mmol L\textsuperscript{-1} d\textsuperscript{-1}. Equation 10 was written for \(i = 13\) and \(14\), as described above for Eq. 6. \(^{13}\)C fractionation associated with carbonate precipitation was ignored (ca. 1\%\textsubscript{oo}; Zeebe and Wolf-Gladrow 2001). The equations for \(G\) and \(N_{pw}\) were identical to those in Model-A. Equations 2, 4, 5, 9, and 10 were solved numerically using the fourth-order Runge-Kutta method in Stella\textsuperscript{R} (High Performance Systems, Inc.) with a time interval of 0.25 d. The fitting parameters were constrained by visually inspecting the model fit to the data. To reduce the number of fitting parameters, results from Model-A were assigned to all but \(k_{PICm}\) and the size and isotopic composition of PIC\textsubscript{m} (Table 4).

It was possible to simulate the data including \(^{13}\)C\textsubscript{DIC} by invoking PIC\textsubscript{m} that was distinct from the PIC detected in the samples in two key aspects (Fig. 5j–l; Table 4). First, PIC\textsubscript{m} at \(t = 0\) d was roughly a factor of 2 more abundant than PIC detected in the samples. Second, in contrast to the observed \(^{14}\)C\textsubscript{PIC} values which were notably depleted, the model-derived \(\Delta_{PICm}\) was enriched (+14\%), suggesting a modern biogenic origin. Walter et al. (2007) proposed that isotope exchange occurs between pore-water DIC and biogenic carbonates with high specific surface areas. As outlined in the Methods section, shell fragments were present in the incubated sediment, but were removed prior to powdering the samples for analyses to prevent bias. We therefore propose that isotope exchange occurred between pore-water DIC and small shell fragments that were present during the incubation, but were not reflected in the PIC data.

**Possible origin and fate of recalcitrant DOC in sediment pore waters**—Results from both isotope mixing plots and time-dependent modeling show unequivocally that the \(^{14}\)C-enriched component of POC was remineralized to DIC (Fig. 8). More importantly, the results also show that the DOC that accumulated in the pore water was notably depleted in \(^{14}\)C, by \(\approx 200\%\textsubscript{oo}\) or more, relative to OC that supported terminal respiration (Fig. 8). Given the short incubation time period relative to the half-life of \(^{14}\)C, this observation can only be explained if net DOC production and terminal metabolism were supported by different “parts” of the POC pool with distinct isotopic signatures and susceptibility toward microbial breakdown.

It has been suggested that the degree to which a given substrate is amenable to microbial breakdown is determined by substrate structure more so than by chemical composition or size (Arnosti and Repeta 1994; Arnosti et al. 2005). The results of this study corroborate this notion in the sense that \(^{14}\)C-depleted organic matter resisted degradation regardless of whether it was part of a solid or in solution. In shelf sediments in the Gulf of Mexico off the Atchafalaya River, Mead and Goñi (2008) found that the fraction of bulk POC that resisted base hydrolysis was most diagenetically altered and depleted in \(^{14}\)C, while the base hydrolyzable fraction was less degraded and had higher \(^{14}\)C values. In the present study, it is unclear whether the \(^{14}\)C-depleted DOC originated from a diagenetically altered, mineral-bound POC, or from other sources, such as anthropogenic petroleum contaminants that were adsorbed or occluded in natural POC. Investigation into the chemical composition of pore-water DIC in conjunction with isotopic determination should provide further insight into the occurrence of aged DOC in sediments.

The mechanism for recalcitrant DOC production can be gleaned from the timing of net DOC production. Net DOC reaction was most pronounced during the first 25 d of the incubation, where a decrease in DOC (\(t = 0–2\) d) was followed by an increase in DOC (\(t = 5–25\) d; Fig. 5g). This period also coincided with an acute drop in \(\Delta^{14}\)C\textsubscript{DOC}, reflecting consumption of highly labile, \(^{14}\)C-enriched DOC (\(t = 0–2\) d), and ingrowth of \(^{14}\)C-depleted DOC (\(t = 5–25\) d; Fig. 5i). Hence, while internal transformations of DOC within the pore water cannot be refuted, DOC accumulation appears better explained if DOC solubilization includes production of DOC that resists further processing by the fermentative microbial community (pathway [b] in Fig. 1; Weston and Joye 2005; Robador et al. 2010).
Based on the high Δ14C value of bulk pore-water DOC, Bauer et al. (1995) concluded that marine sediments are unlikely to be sources of pre-aged DOC to the water column. One implication from the present study is that even if the average Δ14C signature of pore-water DOC is high, the enriched component is selectively respired, potentially leaving behind 14C-depleted DOC for export. However, it should be noted that the present study was conducted in an artificial environment where metabolites were allowed to accumulate over time. Hence, although DIC production rate was high, and net DOC production was low (i.e., OC oxidation appeared efficient), it is possible that the imposed conditions resulted in inefficient oxidation of aged OC relative to natural conditions. The fate of any pre-aged pore-water DOC in the oxic water column is also unknown and requires investigation.

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