Pyritization of iron in tropical coastal sediments: Implications for the development of iron, sulfur, and carbon diagenetic properties, Saint Lucia, Lesser Antilles

Timothy C.W. Ku a,⁎, Jenna Kay a, Evan Brownea, Anna M. Martinib, Stephen C. Petersc, Mary D. Chenb

a Department of Earth and Environmental Sciences, Wesleyan University, Middletown, CT 06459 USA
b Department of Geology, Amherst College, MA 01002-5000 USA
c Department of Earth and Environmental Sciences, Lehigh University, PA 18015 USA

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Abstract

Pore water chemistries and rates of pyritization in tropical coastal sediments were investigated in two semi-protected bays, Praslin Bay and Savannes Bay, along the eastern side of the Caribbean island of Saint Lucia. Sediments were collected from deltaic, nearshore non-deltaic, and offshore environments and 210Pb-derived sedimentation rates ranged between 0.1 and 1.7 g/cm²/yr. Sediments were mixed carbonate-siliciclastic (2–44% CaCO₃) and had higher average FeHR/FeT ratios (0.4–0.6) than either global averaged continental margin sediments (0.28) or local bedrock and soils (0.11–0.15). Organic carbon concentrations, C/N ratios, and δ¹³COC measurements demonstrated that the organic carbon in offshore Savannes Bay sediments was dominantly marine in origin while the nearshore Savannes Bay and offshore Praslin Bay sediments contained organic carbon from both marine and terrestrial sources. Organic matter in Praslin Bay deltaic sediments and in organic-rich storm deposits was mainly (61–100%) terrestrial in origin.

In most sediments, Spy concentrations and DOP values increased from zero to 0.4–1.5 wt.% and 0.18–0.56, respectively, as FeD/FeT and C/S ratios decreased with depth despite limited net sulfate reduction, as marked by lower pore water SO₄/Cl ratios and higher alkalinity values relative to overlying seawater. In the upper 15 cm of sediment, average DGT (diffusive gradients in thin-films)-sulfide fluxes were similar for all environments (5–8 nmol/cm²/d), except for Savannes Bay nearshore sediments, which had a much higher average flux (76 nmol/cm²/d). Average DGT-iron fluxes were 5–13 times average DGT-sulfide fluxes except in Savannes Bay nearshore sediments where the rates were comparable. Savannes Bay nearshore sediments were also notable for possessing the greatest organic carbon (22 mg/cm²/yr) and pyrite sulfur (9.7 mg/cm²/yr) burial rates and represented the only environment where FeDGT- and SDGT-based pore water compositions reached saturation with amorphous FeS or mackinawite. In all other environments, sulfide production and likely iron-sulfide formation preferentially occurred in microniche environments. Most δ³⁴Spy values (−22 and −34‰ VCDT) indicated that the supply of sulfate was not limited during sulfate reduction, though much higher values (up to −7.8‰) identified pyrite formed in relatively closed system conditions. Sediment burial time vs. ln (FeD/FeT) and C/S values showed that half-lives of FeD sulfidation were 71–159 years and that a normal marine C/S ratio of 2.8 was attained after 22–79 years. A comparison of net rates of pyritization with DGT-iron fluxes demonstrated that iron was recycled less than 1.9 times before final burial. Overall, pyrite sulfur burial rates correlated linearly with organic carbon burial rates, providing further evidence that pyrite formation was primarily controlled by the deposition of organic carbon.

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Keywords: pyrite; iron; sulfide; diffusive gradients in thin-films; diagenesis; Saint Lucia

⁎ Corresponding author. Tel.: +1 860 685 2265; fax: +1 860 685 3651.
E-mail address: tcku@wesleyan.edu (T.C.W. Ku).

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1. Introduction

Pyrite (FeS$_2$) forms when bacteria couple organic carbon oxidation with the reduction of sulfate to produce sulfide, which then reacts with dissolved or mineral iron to produce iron-sulfide minerals that undergo a series of reactions to eventually form pyrite (Canfield and Raiswell, 1991; Schoonen, 2004). Pyrite burial in marine sediments is the primary pathway by which reduced sulfur is removed from Earth’s exogenic cycle; thus the rate and extent of its formation strongly influences the concentration of atmospheric oxygen over geologic time and links the global cycles of iron, sulfur, and carbon (Bernier, 1982; Berner and Canfield, 1989). The abundance of pyrite in marine sediments is controlled by the availability of sulfate, reactive iron, or labile organic carbon (e.g. Goldhaber, 2004). In typical coastal sediments overlain by oxic seawater, aerobic respiration and sulfate reduction are the two most important organic matter decomposition pathways and it is generally thought that the availability of labile organic carbon is the primary control on pyrite abundance by limiting the production of sulfide (Jørgensen, 1982; Canfield, 1989; Goldhaber, 2004). The close coupling of organic matter and sulfur in normal marine sediments causes increasing organic carbon burial rates to correspond with increasing sulfate reduction rates and pyrite burial rates and results in relatively constant $C_{\text{org}}/S_{\text{py}}$ weight ratios of 2.8±0.8 (Bernier, 1982; Berner and Canfield, 1989; Lin and Morse, 1991; Lin et al., 2002).

While the deposition of organic matter certainly has a great influence on sediment pyrite concentrations, factors other than sulfide production play key roles in controlling pyrite formation. Sulfur burial efficiency, defined as reduced sulfur burial at depth divided by the integrated sulfate reduction rate, is typically <10–20% (Jørgensen, 1977; Chanton et al., 1987; see Burdige, 2006 for review). Thus, most of the produced sulfide is re-oxidized or transported away and not retained as iron-sulfides in the sediment. Also, since “highly reactive” iron (iron that can be pyritized over early diagenetic timescales) averages only 25–28% of the total iron in marine sediments, highly reactive iron concentrations may be the limiting factor in low Fe, siliciclastic sediments as well as in carbonate and opaline-rich sediments (Raiswell and Canfield, 1998). Finally, pore water sulfide concentrations remain below ~1 μM if highly reactive iron phases are present and only increase to higher concentrations if the highly reactive iron is converted into iron-sulfide phases. Therefore, it is the rate at which these iron phases react with dissolved sulfide that controls sulfide mineral formation, not the rate of sulfide production (Canfield, 1989; Canfield et al., 1992; Raiswell and Canfield, 1996; Morse et al., 2002).

While the factors controlling sediment pyrite concentrations are now fairly well understood, most of the field studies have investigated temperate coastal or continental slope sediments with few studies focusing on tropical coastal sediments that often contain much higher iron concentrations, presumably due to the deposition of highly weathered terrestrial materials (Alongi et al., 1993; Aller et al., 2004a; Goldhaber, 2004). In mobile mudbelt environments found down drift of large tropical deltaic complexes associated with the Amazon River and Fly River, high sediment iron concentrations coupled with rapid sediment reworking cause the dominant non-oxic organic matter decomposition pathway to be metal reduction rather than sulfate reduction (Aller et al., 1986; Aller, 1998; Aller et al., 2004a,b). These mobile mudbelts are characterized by non-sulfidic diagenesis and the sediments retain chemical properties such as high total reactive iron, high proportions of non-pyrite Fe$^{2+}$, high C:S ratios, low degree of pyritization (DOP) values, and low organic carbon particle loading values (Aller and Blair, 1996; Aller et al., 2004a,b). The high sediment mixing rates appear to be the determining factor in separating mostly Fe–Mn reduction from $\text{O}_2$–$\text{SO}_4$ reduction environments, but the few studies in more quiescent tropical coastal settings have also suggested that sulfate reduction plays a lesser role in organic carbon decomposition relative to coastal temperate sediments (Alongi et al., 1993; Alongi, 1995; Ku et al., in preparation). The differences in organic matter decomposition pathways and sediment iron concentrations between coastal tropical sediments and temperate sediments may result in different iron, sulfur, and carbon diagenetic properties (Fe$_{\text{HR}}$/Fe$_T$, DOP, C/S) and/or the time required to achieve the chemical properties preserved in the rock record. Quantifying the magnitude and rate of iron pyritization in coastal tropical sediments will help to better establish the global budgets of reactive iron, organic carbon, and reduced sulfur, which provide insights into the geochemical controls on atmospheric oxygen levels and the bioavailability of oceanic iron (Bernier, 1982; Berner and Canfield, 1989; Poulsen and Raiswell, 2002; Raiswell et al., 2006). Nearshore areas surrounding high-standing tropical islands may be particularly important since these depositional environments account for a high proportion of the sediment and particulate organic carbon delivered to the oceans (Milliman and Syvitski, 1992). For example, six islands in the southwest Pacific contribute 17–35% of the total particulate organic carbon input and ~32% of the total sediment flux to the world’s oceans, despite covering only ~3% of Earth’s land area (Lyons et al., 2002 and references therein).

This study focuses on pore water and sediment chemistry from two bays along the eastern coast of the Caribbean island of Saint Lucia. A number of pore water sampling techniques were employed (centrifugation, “peepers”, DET — diffusive equilibration technique, and DGT — diffusive gradients in thin-films) to characterize the diagenetic environment and estimate ferrous iron and reduced sulfur fluxes. These results were then combined with $^{210}$Pb-derived sedimentation rates and sediment chemistry to examine the extent and controls of pyritization in these environments and to quantify the rate at which iron, sulfur, and carbon sediment properties change during early diagenesis.

2. Study area

St. Lucia covers 616 km$^2$ and is part of the Lesser Antilles island arc on the eastern margin of the Caribbean plate, located at 13°54’N and 61°50’W (Fig. 1). Here, the Atlantic Ocean crust is underthrusting the Caribbean plate at about 2 cm/yr (Maury et al., 1990). The Lesser Antilles island arc is 850 km long and stretches from Trinidad in the south to the Virgin Islands and Anegada Passage in the north (Fig. 1). The Lesser Antilles is a double island arc, splitting north of Martinique into
Fig. 1. Map of the Lesser Antilles and island of Saint Lucia. Insets show the geology and sampling locations in the Praslin Bay (PB) and Savannes Bay (SB) areas. Sites sampled in 2001 are marked with circles and triangles represent sites sampled in 2004. Geological units from Tomblin (1979).
a younger inner and older outer arc (Tomblin, 1979; Maury et al., 1990). St. Lucia is in the presently quiescent inner arc and has bedrock composed of Miocene volcanic rocks with overlying Pliocene and Quaternary andesitic and rhyolitic ash layers (Fig. 1; Tomblin, 1979; Maury et al., 1990).

This study focuses on two semi-protected bays, Praslin Bay and Savannes Bay, which are located along the eastern St. Lucian coast and are surrounded by dominantly andesitic Miocene or Pliocene bedrock (Fig. 1; Maury et al., 1990). Praslin Bay receives direct fluvial sediments with the Mamiku River being the primary source (Fig. 1). Savannes Bay mostly receives sediments from direct coastal erosion and all existing streambeds were dry during the 2001 and 2004 wet seasons. A detailed bathymetric survey was not done, but maximum water depths were ~3 m in Praslin Bay and ~5 m in Savannes Bay. Salinities ranged from estuarine (209 mM Cl\(^{-}\)) at the mouth of the Mamiku River to normal marine (559 mM Cl\(^{-}\)) with most bay waters having salinities diluted by freshwater (427-518 mM Cl\(^{-}\); Table 1). The average tidal range in nearby Vieux Fortes Bay is 27 cm (NOAA.org, 2006).

3. Methods

3.1. Sampling sites and field collection

Marine sediment, seawater, river sediment, soil, and bedrock samples were collected from Praslin Bay, Savannes Bay, and the surrounding watersheds in June 2001 and August 2004. Seventeen sediment cores were taken from four depositional environments: Mamiku River deltaic sediments in Praslin Bay, offshore Praslin Bay, nearshore Savannes Bay, and offshore Savannes Bay (Table 1; Fig. 1). Water depths ranged from 0.6–4.6 m. Cores PB1, PB2, PB3, SB1, and SB2 were collected in 2001 and multiple cores from sites PB3, PB4, PB6, SB3, SB4, and SB5 were collected in 2004.

Sediment cores were taken in polycarbonate tubes using a gravity core or driven in by hand. Overlying seawater samples were collected above the sediment–water interface and field temperature, pH, and titration alkalinity were measured within hours of sample retrieval. Titration alkalinity was determined by the Gran method (Gieskes and Rogers, 1973). All water samples were filtered through a 0.45 μm nylon filter and aliquots for cation analyses were acidified with trace metal grade nitric acid and stored in acid-washed bottles.

Thirty-eight rock, soil, and river sediment samples were collected from eleven locations along the southeastern St. Lucian coast. Most of the samples lie within the watersheds that drain into Praslin Bay and Savannes Bay (Fig. 1). Soil and weathered bedrock samples were collected from exposed outcrops or by using a soil auger. Nearly all of the rocks were highly weathered as samples disaggregated easily when struck by a hammer.

3.2. Pore water techniques: centrifugation, “peeper”, and DET

Pore water solute concentrations collected in 2001 were obtained by the “peeper” or dialysis method and those sampled

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Saint Lucia site summaries</th>
<th>Water depth</th>
<th>Overlying seawater Cl(^{-})</th>
<th>(^{4})CaCO(_{3})</th>
<th>(^{4})Organic C</th>
<th>(^{4})Total Fe</th>
<th>(^{4})Total Al</th>
<th>(^{4})Linear sedimentation rate</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial samples</td>
<td></td>
<td>(m)</td>
<td>(mM)</td>
<td>(wt.% )</td>
<td>(wt.% )</td>
<td>(wt.% )</td>
<td>(wt.% )</td>
<td>(cm/yr)</td>
<td></td>
</tr>
<tr>
<td>Soils</td>
<td></td>
<td>–</td>
<td>–</td>
<td>Trace</td>
<td>0.9</td>
<td>6.1</td>
<td>11.3</td>
<td>–</td>
<td>Developed on volcanic rocks along the coast</td>
</tr>
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<td>Rocks</td>
<td></td>
<td>–</td>
<td>–</td>
<td>0</td>
<td>0.2</td>
<td>4.7</td>
<td>10.6</td>
<td>–</td>
<td>Within the Praslin Bay and Savannes Bay watersheds</td>
</tr>
<tr>
<td>Mamiku River sediment</td>
<td></td>
<td>–</td>
<td>–</td>
<td>0</td>
<td>0.3</td>
<td>9.0</td>
<td>8.0</td>
<td>–</td>
<td>Shallow river discharging into Praslin Bay</td>
</tr>
<tr>
<td>Marine sediments</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Mamiku River Delta in Praslin Bay</td>
<td></td>
<td>0.6</td>
<td>341–559</td>
<td>5</td>
<td>1.3</td>
<td>6.1(^{e})</td>
<td>9.6(^{e})</td>
<td>–</td>
<td>Deltaic sediments</td>
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<tr>
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<td>0.8</td>
<td>209</td>
<td>2</td>
<td>0.5</td>
<td>7.7</td>
<td>8.1</td>
<td>1.17(^{d})</td>
<td>Silty sands</td>
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<tr>
<td>Savannes Bay nearshore</td>
<td></td>
<td>2.4</td>
<td>427</td>
<td>30</td>
<td>1.4</td>
<td>3.6</td>
<td>6.1</td>
<td>1.75</td>
<td>Semi-protected bay, direct fluvial input</td>
</tr>
<tr>
<td>Savannes Bay offshore</td>
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<td>2.1</td>
<td>448</td>
<td>32</td>
<td>1.0</td>
<td>3.7</td>
<td>6.3</td>
<td>1.08</td>
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<td>SB1((SB2)^{e})</td>
<td></td>
<td>0.6</td>
<td>515</td>
<td>44</td>
<td>0.7</td>
<td>3.9</td>
<td>4.6</td>
<td>–</td>
<td>Semi-protected bay, little fluvial input</td>
</tr>
<tr>
<td>SB4</td>
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<td>510</td>
<td>44</td>
<td>1.1</td>
<td>2.1</td>
<td>4.6</td>
<td>1.74</td>
<td>Semi-protected bay, seagrass beds</td>
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<tr>
<td>SB3</td>
<td></td>
<td>3.0</td>
<td>484</td>
<td>28</td>
<td>2.2</td>
<td>3.7</td>
<td>6.5</td>
<td>0.17</td>
<td>Gray muds, seagrass beds</td>
</tr>
<tr>
<td>SB5</td>
<td></td>
<td>4.6</td>
<td>518</td>
<td>36</td>
<td>2.3</td>
<td>3.3</td>
<td>5.5</td>
<td>0.18</td>
<td>Gray muds</td>
</tr>
</tbody>
</table>

\(^{a}\) Entire core or sample type averages.
\(^{b}\) Calculated from sediment depth and excess \(^{210}\)Pb.
\(^{c}\) Averages of cores PB1 and PB3.
\(^{d}\) Estimate (see text).
\(^{e}\) Data for site SB1 (site SB2 pore waters collected from a similar location).
in 2004 were collected by centrifugation and diffusive equilibration in thin-films (DET) (see Davison et al. (2000) for review on all three methods). The peeper and DET methods were used in addition to centrifugation to obtain higher spatial resolutions and because pore water could not be obtained by centrifugation from sandy, deltaic sediments in Praslin Bay. Pore water samples were collected by centrifugation sampled at 2.5–5.0 cm sediment intervals, filtered, and preserved as seawaters described above. Each aliquot was processed in ambient atmosphere, so oxidation of dissolved H₂S may have occurred but this amount was likely minor given the presence of reactive sediment iron phases and lack of sulfide odor.

The peeper and DET methods estimate pore water concentrations by allowing solutes in ambient pore water to equilibrate with water or water-based gels after passing through diffusional and/or filtration membranes. Plexiglass peelers were similar to the design described by Hesslein (1976) and by Teasdale et al. (1995) and consisted of 50 3-ml collection ports spaced at 1 cm intervals and covered with a 0.45 μm filter membrane. Collection ports were filled with DI water and the devices were driven vertically into the sediment and allowed to equilibrate in situ for at least 72 h. Upon retrieval, four consecutive collection ports were commingled into a single sample, filtered, and preserved for subsequent analyses.

Fifteen-cm long constrained DET probes (DGT Research, Lancaster, UK) were used according to sampling protocols described by Davison et al. (1991) and Krom et al. (1994). Each of the 75 1-mm discrete intervals were loaded with an agarose gel, covered with a 0.45 μm filter sheet, and pre-equilibrated with a NaCl–MgSO₄ salt solution containing ~25% of standard seawater concentrations of chloride and sulfate. DET probes were degassed with N₂ gas for at least 24 h prior to deployment, inserted into sediment cores, and allowed to equilibrate at ambient temperatures (~29 °C) for 26–32 h. After removal, each gel slice was placed into pre-weighed micro centrifuge tubes and alternating intervals were measured for anions after back-equilibration with DI water for at least 72 h.

### 3.3. DGT methods: iron and sulfide

In diffusive gradients in thin-films (DGT) methods, solutes diffuse across an ion-permeable gel of known thickness and are effectively trapped by a binding agent impregnated in a second gel layer (Zhang and Davison, 1995; Davison et al., 2000). A diffusional gradient will develop and the solute will continue to accumulate in the binding gel as long as the binding capacity is not exceeded. By measuring the mass of the accumulated solute, the time of exposure, and the spatial dimensions of the DGT assembly, the solute flux and DGT-derived concentration (C_{DGT}) can be calculated using Fick’s first law of diffusion (Davison et al., 2000).

Two DGT probes (DGT Research, Lancaster, UK), a combined Chelex-Agl assembly and a ferricydrite unit (not discussed here), were inserted into sediment cores taken at each of the six coring locations in 2004. Chelex-Agl probe assembly and sampling protocols followed those of Motelica-Heino et al. (2003) and Naylor et al. (2004). The combined Chelex-Agl probe had an exposure area of 1.8 cm × 15 cm and consisted of a 0.45 μm filter membrane, a polyacrylamide-based diffusion gel (0.8 mm thick), a Chelex impregnated gel (0.4 mm thick), and a gel containing finely divided AgI (0.4 mm thick). The Chelex resin binds dissolved iron and other metals and the AgI fixes dissolved sulfide species (H₂S, HS⁻, and polysulfides) as Ag₂S. The presence of the Chelex layer does not impede the diffusion of sulfide species (Naylor et al., 2004). Probes were pre-equilibrated with a 0.01 M NaCl solution and degassed for approximately 24 h with N₂ prior to insertion into sediment cores. Cores remained at ambient temperature (~29°C) for at least 24 h. After extraction, the sediment–water interface was noted and the Chelex gel was separated from the diffusion gel and AgI gel and cut into 3 mm intervals using a Teflon-coated razor blade and stored in pre-weighed micro centrifuge tubes. Prior to analyses, each gel slice was treated with 200 μL of 2 M trace metal grade HNO₃ and allowed to back-equilibrate for longer than 48 h. This treatment releases 80±4% of the iron bound to the Chelex (Zhang and Davison, 1995). Calculated Fe_{DGT} concentration used the diffusion coefficient for Fe^{2+} in seawater at 29 °C, which was calculated using data from Li and Gregory (1974).

Silver iodide gels were processed using methods similar to those described by Teasdale et al. (1999), Devries and Wang (2003), Motelica-Heino et al. (2003), and Naylor et al. (2004). Each AgI gel layer was dried and preserved between two clear cellulose films (Promega Gel Drying Kit). Dried gels were scanned with a commercial scanner to create 300 dpi grayscale images. Grayscale values were converted into areal densities of sulfur (μmol Ag₂S/cm²) by comparing samples to a calibration curve created by exposing AgI gel disc probes to varying concentrations of H₂S solutions for 4 h. Calibration solutions were prepared gravimetrically using Na₂S·9H₂O in a N₂-atmosphere. Standards were best fit with a modified hyperbolic curve, \( y = \frac{a(x+b)}{x} \), where \( y \) = grayscale value, \( a = 4.9 \times 10^{-4} \) (μmol/cm²), and \( a \) and \( b \) are constants. Our constants \( (a = 2.03 \times 10^{-4}, b = 5.39 \times 10^{-3}) \) were comparable to values \( (a = 3 \times 10^{-4}, b = 4.9 \times 10^{-3}) \) reported by Naylor et al. (2004). Since sulfide must diffuse through both the diffusional gel and the Chelex gel, the combined thickness was used for \( \Delta g \). The diffusion coefficient for HS⁻ in seawater at 29 °C was calculated using data from Li and Gregory (1974). Image processing (ImageJ, National Institute of Health) and computational (MATLAB, The Mathworks) software was used to convert scanned grayscale images into two-dimensional maps and to quantify flux–area relationships.

To evaluate pore water saturation with amorphous FeS and mackinawite (FeS), IAPs (ion activity products) were calculated for the equation \( \text{FeS} + H^+ \rightarrow \text{Fe}^{2+} + \text{HS}^- \). Activities for Fe^{2+} and HS⁻ were calculated from Fe_{DGT} and S_{DGT} concentrations using the chemical speciation program Solmientos88 and sediment pH values at each depth-core interval (Kharaka et al., 1988). The average concentration of pore water major cations and anions in the upper 15 cm were used for each core, except for core PB6 (no pore water) where the overlying seawater concentration was used. A temperature of 29 °C and an alkalinity of 2.2 meq/L were used for all
calculations and saturation IAPs for amorphous FeS and mackinawite were from Huerta-Diaz et al. (1998).

3.4. Water and gel analyses

Anion (Cl\(^-\), SO\(_4\)^{2-}, NO\(_3\), PO\(_4\)^{3-}\) concentrations of seawater, pore water, DET, and peeper samples were measured at Amherst College with a Dionex IC-500 ion chromatograph using a AS14 column. IAPSO was used as a check standard and the precision was ±4% (2\(\sigma\)). Concentrations of Na, Ca, Mg, K, Sr, B, and Si were measured on a Leeman Labs Profile Plus ICP-OES at Amherst College and were used for ionic strength and activity coefficient modeling purposes only. Iron concentrations extracted from the Chexel gels were determined at Lehigh University on a Thermo XSeries II ICP-MS with a precision of ±5% (2\(\sigma\)). Procedural blanks using DGT-Chelex assemblies immersed in DI water showed no iron contamination. Sediment pH was measured by direct insertion of a pH electrode.

3.5. Sediment geochemistry

Rock, soil and sediment samples were oven-dried at ~80 °C. Total C and total N concentrations were determined on a Thermo Flash 1112 elemental analyzer with precisions better than 5% (1\(\sigma\)). Inorganic carbon was determined on a UIC Carbon Coulometer and organic carbon by subtraction of inorganic carbon from total carbon. All inorganic carbon was assumed to be calcium carbonate. Carbon isotope analysis of organic carbon was determined by CF-IRMS at the Saskatchewan Isotope Laboratory at the University of Saskatchewan after removal of carbonate with 10% HCl. Carbon isotope results are reported relative to the VPDB standard and the precision was ±0.1‰.

Dithionite-extractable iron (FeD) and boiling HCl-extractable iron (FeH) were determined using the methods of Canfield (1998) and Berner (1970), respectively. Extractant iron from these techniques have been reviewed by Raiswell et al. (1994) and are divided into three operationally defined iron pools based on their reactivity towards sulfide (Raiswell and Canfield, 1998): highly reactive iron (Fe\(_{HR}\)=pyrite S/2. FeD is mainly composed of iron oxides and oxyhydroxides, which have half-lives with respect to 1 mM H\(_2\)S of minutes to 182 days, though the technique also extracts a small amount of iron from sheet silicates with a half-life of 84,000 years (Canfield et al., 1992; Poulton et al., 2004). The Fe\(_{HR}\) pool thus represents the iron that may be readily converted into iron-sulfides plus the iron already present as iron-sulfides (Raiswell and Canfield, 1998; Poulton and Raiswell, 2002).

Sediment bulk densities (g dry sed/ml wet sed) were determined by measuring the weight and volume of wet sediment, then reweighing the sediment after drying. Homogenized sediments collected in 2004 were analyzed for \(^{210}\)Pb, \(^{137}\)Cs, and \(^{226}\)Ra at OceanChem Laboratories (Narragansett, Rhode Island) via gamma counting techniques using a well-type pure Ge detector (Cutshall et al., 1983; Moore, 1984). Sediment mass accumulation rates and \(^{210}\)Pb chronologies were determined by graphing the cumulative dry sediment mass (no salt correction) vs. excess \(^{210}\)Pb activities and applying the constant flux constant rate model (e.g. Appleby and Oldfield, 1992). Clay separates (<2 μm) of selected samples were obtained by repeated centrifugation following the techniques of Jackson (1969) and Moore and Reynolds (1997).

4. Results and discussion

4.1. Calcium carbonate, organic carbon, and iron/aluminum

Sediment-depth profiles of CaCO\(_3\) concentration, organic carbon geochemistry (wt.%, C/N, \(\delta^{13}\)C) and FeT/Al ratios are shown in Fig. 2. Praslin Bay deltaic sediments had low average calcium carbonate concentrations (2–5 wt.%), and variable organic carbon concentrations between 0 and 4 wt.%. The other three depositional environments (Praslin Bay offshore, Savannes Bay nearshore, and Savannes Bay offshore) were composed of mixed carbonate-siliclastic sediments (average CaCO\(_3\)=28–44 wt.%) that averaged between 0.7 and 2.3 wt.% organic carbon. The offshore Savannes Bay sediments contained the highest average organic carbon concentration (Table 1, Fig. 2).

The primary autochthonous and allochthonous sources of sedimentary organic carbon can be distinguished on the basis of C/N (organic C/total N) ratios and carbon isotope compositions (\(\delta^{13}\)C\(_{OC}\)) (e.g. Lamb et al., 2006). Differences in cellulose and protein compositions and in the source and isotopic fractionation of carbon during photosynthesis causes organic carbon from terrestrial C\(_3\) vascular plants to have higher C/N ratios (19) and lower \(\delta^{13}\)C values (~25 to ~28‰) than marine phytoplankton (C/N: 5–10, \(\delta^{13}\)C\(_{OC}\): −17 to −22‰) and terrestrial soils that contain C\(_3\) plant material (C/N: 8–15, \(\delta^{13}\)C\(_{OC}\): approximately −25 to −28‰) (Meyers, 1994; Hedges and Oades, 1997; Burdige, 2006). We evaluated the contribution of the terrestrial carbon by comparing C/N ratios and applying a simple isotope mixing model. The concentration of terrestrial organic carbon is given by the equation wt.% OC\(_{terr}=100\ast(\delta^{13}\)C\(_{sed}\) − \(\delta^{13}\)C\(_{mar}\))/ (\(\delta^{13}\)C\(_{terr}\) − \(\delta^{13}\)C\(_{mar}\)) where \(\delta^{13}\)C\(_{sed}\) equals the sediment value, \(\delta^{13}\)C\(_{mar}\) is the marine end member value (−19‰), and \(\delta^{13}\)C\(_{terr}\) is...
Fig. 2. Geochemistry of Praslin Bay deltaic (1st row), Praslin Bay offshore (2nd row), Savannes Bay nearshore (3rd row), and Savannes Bay offshore (4th row) sediments. Horizontal dark gray bar denotes the storm sediment intervals at sites PB4 and PB5 (see text for details). $\delta^{13}$C$_{OC}$ is the carbon isotope composition of bulk organic carbon. Vertical light gray bars indicate typical C/N and $\delta^{13}$C$_{OC}$ values of marine algae, soil organic matter (SOM), vascular land plants, and $C_3$ land plants (values from Burdige (2006) and references therein).
the terrestrial end member value (−28‰) (Faganeli et al., 1994; Martiniotti et al., 1997). δ13C values greater than −19‰ were assumed to be entirely from marine sources and δ13C values less than −28‰ are assumed to be entirely from terrestrial sources. Typical end member C/N and δ13C values for soil organic matter (SOM), marine algal, and C3 vascular land plants are shown in Fig. 2.

Most of the Praslin Bay deltaic sediments had C/N ratios > 19 and site PB6 was dominantly composed of terrestrial carbon (61–92%) based on the δ13C mixing model. Organic carbon in Praslin Bay offshore sediments were mostly derived from mixed terrestrial-marine sources (30–40% terrestrial) except for two dark, discrete ∼2 cm thick, organic-rich layers between the 20 and 35 cm depths in the PB4 and PB5 cores (Fig. 2). All four cores taken from these two locations contained pieces of blue plastic that were similar to the banana ripening bags used throughout St. Lucia. Relative to the rest of the sediment in these cores, the dark sediment layers had higher organic carbon concentrations, higher C/N ratios, and lower δ13COC values, which indicated a very high proportion of C3 vascular land plant material compared to the sediments above and below these layers (Fig. 2). The layers were not sampled separately, so some of the dark layer sediments were mixed with lighter colored sediments resulting in more uniform depth-chemistry profiles than if the layers were sampled discretely. Together with the 210Pb-derived sedimentation rates (next section), these layers are interpreted as storm sediments deposited in the 1980s, though a likely event was Tropical Storm Debbie, which hit Saint Lucia in 1994 causing 100-year flooding, landslides, and agricultural decimation (Cox, 2004). No such storm layers were found in the Savannes Bay sediments.

Savannes Bay nearshore sediments had mixed marine–terrestrial organic carbon sources though some of the variability in the C/N and δ13COC data was due to the presence of the abundant seagrass rhizomes found at this site, which typically have higher C/N ratios (~15–20) and more positive δ13COC values of −9 to −17‰ (Anderson and Fourqurean, 2003; Gonneea et al., 2004). Savannes Bay offshore site SB3 had mostly marine organic carbon (15–25% terrestrial) and the offshore site SB5 in deeper water contained entirely marine organic carbon (Fig. 2). All of the Savannes Bay offshore sediment had low C/N ratios that reflect a dominance of a marine phytoplankton derived organic matter (Fig. 2).

In normal marine sediments, those overlain by oxic seawaters, FeT/Al ratios can distinguish between different terrestrial sources since iron and aluminum are relatively immobile elements that usually occur in similar proportions in riverine particulate matter and in the source areas (Canfield, 1997; Sageman and Lyons, 2004; Poulton and Raiswell, 2005). Praslin Bay and Savannes Bay offshore sediments likely share a similar terrestrial source since molar FeT/Al ratios from both environments plotted within a narrow range of values, 0.26–0.30, which was similar to the FeT/Al value of 0.30 measured from the clay-size fraction of the Mamiku River sediment (Fig. 2). Within the Savannes Bay nearshore environment, core SB4 had constant FeT/Al values of ~0.22 while site SB1 had variable ratios, most likely due to this site’s proximity to direct coastal erosion. With a few exceptions, the Praslin Bay deltaic sediments had FeT/Al ratios between 0.35 and 0.55, which was comparable to the 0.54 value of bulk Mamiku River sediments (Table 1; Fig. 2). Overall, sites that accumulated finer-grained terrestrial sediments had lower FeT/Al ratios than deltaic or nearshore environments composed of larger size particles.

4.2. Sediment accumulation rates

Excess 210Pb activities decreased linearly with cumulative dry sediment mass in cores PB4, PB5, SB3, SB4, and SB5 (Fig. 3). Bulk sediment mass accumulation rates (MAR) for Savannes Bay offshore sites SB3 and SB5 were both 0.11 g/cm²/yr, while Savannes Bay nearshore site SB4 had the highest MAR of 1.71 g/cm²/yr. Though the storm layers in Praslin Bay offshore cores PB4 and PB5 caused slight offsets in the 210Pb activity profiles, one accumulation rate was calculated per core and ranged from 1.04 to 1.43 g/cm²/yr (Fig. 3). Except for the storm deposits in the Praslin Bay offshore sediments, the linear decreases in excess 210Pb activities with increasing sediment depth in these five cores demonstrated that the sediments have been steadily accumulating without significant bioturbation or physical mixing.

At deltaic site PB6, the upper three excess 210Pb data points decreased linearly with depth, but the lower section of the core had alternating intervals of excess 210Pb activities and zero excess 210Pb (Fig. 3). Two of the lower data points with measurable excess 210Pb activities had overlapping analytical errors with 226Ra activities, but the deepest sediment interval had a measurement beyond analytical errors (Fig. 3). Sedimentation has not been continuous at this site and particles with no excess 210Pb were likely deposited very rapidly since they were not exposed to the atmosphere for a significant amount of time. However, even with likely sediment mixing and displacement, some of these sediments were deposited within the last ~150 years as excess 210Pb activities were measured. A regression line through all measurable excess 210Pb data yielded a reasonable fit (r = −0.85) and resulted in a MAR of 0.99 g/cm²/yr (Fig. 3). A rate of 0.68 g/cm²/yr was calculated using only the upper three data points. For comparative purposes, we use the rate of 0.99 g/cm²/yr and interpret the zero excess 210Pb activities as rapidly deposited sediments that physically replaced previously existing sediments through displacement. This is clearly a rough estimate, but this scenario is plausible in a small deltaic environment and the iron speciation and pyrite concentrations (see Sections 4.5–4.8) suggest that these sediments experienced early marine diagenesis on comparable timescales to the other sediments in this study.

4.3. Pore water sulfur and iron

Pyrite sulfur originates as sulfide produced from bacterial sulfate reduction: CH3O+SO42−→H2S+2HCO3−. Traditionally, sulfate reduction occurs in a time-depth sequence after the oxidants O2, NO3, Mn, and Fe are consumed (Froelich et al., 1979; Berner, 1980). In most nearshore sediments, oxygen
is completely utilized within the upper few millimeters or centimeters of sediment and the highest sulfate reduction rates occur just below this aerobic zone. Higher alkalinity values and lower $\text{SO}_4/\text{Cl}$ values than overlying seawaters mark the occurrence of net sulfate reduction. In Fig. 4, sediment-depth profiles of alkalinity concentrations and $\text{SO}_4/\text{Cl}$ ratios of pore waters are shown for entire cores (left 2 columns) and for the upper 15 cm of sediment (3rd column).

Due to their sandy texture, pore water could not be obtained by centrifugation from Praslin Bay deltaic sediments, but peeper samples from site PB1 had similar alkalinity (2 meq/kg) and $\text{SO}_4/\text{Cl}$ ($\sim 46 \text{ mM/M}$) values to overlying seawater until about 35 cm depth where alkalinity increased to 5.7 meq/kg and $\text{SO}_4/\text{Cl}$ decreased to 37 mM/M at a depth of 48 cm (Fig. 4). Peeper data from cores PB2 and PB3 showed minor increases in alkalinity in the upper 20 cm of sediment and much lower $\text{SO}_4/\text{Cl}$ ratios ( $\sim 38 \text{ mM/M}$) beginning at $\sim 8$ cm, remaining nearly constant throughout the rest of the sediment. DET $\text{SO}_4/\text{Cl}$ ratios from site PB6 were essentially equal to overlying seawater values for the upper 15 cm of sediment (Fig. 4). Higher $\text{SO}_4/\text{Cl}$ ratios than the overlying seawater in the PB4 DET probe may indicate localized net sulfide oxidation near the oxic–anoxic interface, though sampling effects such as the introduction of oxygenated overlying water during probe insertion remains a possibility.

Savannes Bay nearshore peeper sites (SB1 and SB2) had high alkalinity concentrations (8.3 meq/kg) and low $\text{SO}_4/\text{Cl}$ values (32 mM/M), signaling significant net sulfate reduction beginning a few centimeters into the sediment (Fig. 4). Compared to overlying seawater, pore waters from nearshore site SB4 had slightly lower $\text{SO}_4/\text{Cl}$ values, $\sim 43 \text{ mM/M}$, and a distinct decrease in $\text{SO}_4/\text{Cl}$ values was measured from the DET gels at $\sim 5$ cm depth. Except for one outlier data point, Savannes Bay offshore sediments (SB3 and SB5) had pore water $\text{SO}_4/\text{Cl}$ values almost equal to overlying seawater with no obvious change with depth (Fig. 4).

4.4. DGT sulfur and iron

Pore water $\text{SO}_4/\text{Cl}$ ratios can indicate the presence and vertical position of net sulfate reduction, but these ratios are poor indicators of the relative rates of sulfate reduction as solute transport and re-oxidation processes vary significantly between sediment sites and may not be distinguished by $\text{SO}_4/\text{Cl}$ ratios alone (Thamdrup et al.,...
Fig. 4. Peeper, pore water, DET, and DGT results from Praslin Bay and Savannes Bay sediment cores. Left two columns show peeper alkalinity and SO$_4$/Cl values obtained in 2001 (sites PB1a, PB1b, PB2, PB3, SB1, and SB2) and pore water and DET SO$_4$/Cl values collected in 2004 (sites PB4, PB5, PB6, SB3, SB4, and SB5). Right four columns show only the upper 15 cm of sediment (right side Y-axes labels). Symbols for SO$_4$/Cl are the same in columns 2 and 3. Overlying seawater values are shown as zero depth. $S_{\text{DGT}}$, $F_{\text{DGT}}$, and the IAP values for the equation FeS + H$^+$ → Fe$^{2+}$ + HS$^-$ are shown in the right three columns for cores collected in 2004 (note log scales for $S_{\text{DGT}}$ and $F_{\text{DGT}}$). Amorphous FeS and mackinawite (FeS) saturation values at 25 °C are from Huerta-Diaz et al. (1998) and references therein.
Bacterial sulfate reduction rates are typically determined by the $^{35}$S-radiotracer method, but the DGT-sulfide method used here measures the two-dimensional accumulation of sulfide as higher sulfide production rates produce greater Ag$_2$S concentrations in the gel. Averaged across the entire exposed gel area, five of the six Saint Lucia sites sampled in 2004 had very similar sulfide fluxes, 5.5–7.7 nmol/cm$^2$/d (Table 2). The Savannes Bay nearshore site, SB4, had a far higher sulfide flux of 76.2 nmol/cm$^2$/d (Table 2). Three-dimensional plots of the areal density of Ag$_2$S are shown for three representative cores in Fig. 5. In core PB4, there were localized “hotspots” of sulfide production, one at ∼3.8 cm depth and another at 7.8 cm depth (Fig. 5). DGT-sulfide results from cores PB3, PB6, and SB3 (not shown) had similar localized sulfide production distributions. At site SB5, low sulfide production was measured until ∼12 cm depth where greater production was observed (Fig. 5), perhaps marking the beginning of the sulfate reduction zone. Sulfide production at site SB4 increased at ∼3 cm depth and remained at much higher rates than the other sites through the upper 14 cm of sediment (Fig. 5).

The localized production of sulfide at sites PB3, PB4, PB6, SB3, and possibly SB5, revealed the presence of microniches where sulfate reduction occurred despite being surrounded by an overall oxic or suboxic environment (Jørgensen, 1977; Zhang et al., 2002). These microniches likely occurred around organic-rich particles and have been observed using DGT techniques in other wetland and freshwater sediments (Devries and Wang, 2003; Motelica-Heino et al., 2003). To evaluate the contribution of these microniches to the overall sulfide production, a grayscale threshold of 53 (equivalent to $1.4 \times 10^{-7}$ μmol/cm$^2$/s) was used to distinguish “high” production areas. High production areas covered 84.6% of the total area in site SB4 and accounted for nearly all of the sulfide production (Table 2). In all other sites, high production areas covered only 0.4–9.8% of the area, but accounted for 1.6–32.9% of the total sulfide production (Table 2). For example, at site PB4, the high production area covered only 1.6% of the area, yet contributed 8.2% of the total sulfide production (Table 2). These calculations demonstrate the importance of microniches and provide evidence for the local formation of iron-sulfide minerals in environments where sulfate reduction is not ubiquitous.

In anoxic sediments, ferrous iron is primarily released by the bacterial reduction of iron oxides and by iron oxide reaction with dissolved sulfide (Eqs. (1) and (2) below; Pyzik and Sommer, 1981; Thamdrup, 2000).

\[
\begin{align*}
4\text{FeOOH} + \text{CH}_3\text{O} + 8\text{H}^+ &\rightarrow 4\text{Fe}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \quad (1) \\
2\text{FeOOH} + \text{H}_2\text{S} &\rightarrow 2\text{Fe}^{2+} + \text{S}^0 + 4\text{OH}^- \quad (2)
\end{align*}
\]

Except for site SB4, the average DGT-iron flux was 5–13 times greater than the associated sulfide flux, thus iron reduction appears to dominate over sulfate reduction in the upper 12–14 cm of these sediments with higher sulfide production occurring in microniche environments (Table 2). Simultaneous release of iron and sulfur from areas ∼ 54 mm$^2$ or less is consistent with previous work (Motelica-Heino et al., 2003; Naylor et al., 2004) and likely occurred at site SB4 where mean iron and sulfide fluxes were similar (Fe$_{DGT}$ flux = 0.8 S$_{DGT}$ flux), though we cannot distinguish between iron produced by bacterial iron reduction and the iron released chemically by reaction with sulfide (Eqs. (1) and (2); Table 2).

It is important to note that DGT devices measure the flux or time-averaged concentration of sulfide and iron directly adjacent to the probe and may not be representative of the bulk sediment pore water due to the depletion or resupply of the solutes or due to sediment spatial heterogeneity (Davison et al., 2000; Devries and Wang, 2003; Naylor et al., 2004). If the resupply flux of a solute equals the DGT demand, then the DGT concentrations will equal the concentration in the bulk pore water. Thus, high DGT concentrations are related to both the concentration in the pore water and the resupply of the solute.

### Table 2

**DGT-Sulfide and Iron Flux Data**

<table>
<thead>
<tr>
<th>Location</th>
<th>Site ID</th>
<th>Average sulfide flux</th>
<th>%High production area</th>
<th>%Sulfide produced in high production area</th>
<th>%Average iron flux</th>
<th>%Pyrite Fe addition</th>
<th>Times cycled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Praslin Bay deltaic</td>
<td>PB6</td>
<td>5.8</td>
<td>0.4%</td>
<td>1.6%</td>
<td>75.4</td>
<td>39.7</td>
<td>1.9</td>
</tr>
<tr>
<td>Praslin Bay offshore</td>
<td>PB4</td>
<td>5.5</td>
<td>1.6%</td>
<td>8.2%</td>
<td>51.8</td>
<td>35.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Praslin Bay offshore</td>
<td>PB5</td>
<td>7.7</td>
<td>9.8%</td>
<td>20.4%</td>
<td>43.7</td>
<td>28.1</td>
<td>1.6</td>
</tr>
<tr>
<td>Savannes Bay nearshore</td>
<td>SB4</td>
<td>76.2</td>
<td>84.6%</td>
<td>99.4%</td>
<td>60.6</td>
<td>72.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Savannes Bay offshore</td>
<td>SB3</td>
<td>6.1</td>
<td>2.7%</td>
<td>8.4%</td>
<td>54.7</td>
<td>29.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Savannes Bay offshore</td>
<td>SB5</td>
<td>6.8</td>
<td>9.6%</td>
<td>32.9%</td>
<td>34.5</td>
<td>33.3</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* High production=⟩53 grayscale average (approximately $1.4 \times 10^{-7}$ μmol/cm$^2$/s).
* Calculated from slopes in Fig. 10E and Table 3 assuming average bulk densities for the upper 10 cm (see text).
With these considerations in mind, sediment-depth profiles of $S_{\text{DGT}}$ and $F_{\text{DGT}}$ concentrations are shown in Fig. 4. $S_{\text{DGT}}$ values equal the average value of every 0.08 mm horizontal section. The variable peaks in the $S_{\text{DGT}}$ profiles of Praslin Bay and Savannes Bay offshore sediments represent sulfide producing microniches and $S_{\text{DGT}}$ concentrations were much higher at site SB4 compared to other sites (Fig. 4). $F_{\text{DGT}}$ concentrations mostly increased with increasing sediment depth though this pattern was not pervasive (Fig. 4).

In sediments supporting sulfate reduction and containing abundant reactive iron oxides and hydroxides, dissolved sulfide is essentially removed from the pore water allowing $\text{Fe}^{2+}$ to

---

**Fig. 5.** Representative $S_{\text{DGT}}$ data from AgI impregnated gels. Z-scale and grayscale bar denotes the concentration of sulfur per unit area.
Fig. 6. Iron and sulfur sediment geochemistry. Leftmost column only shows dithionite-extractable iron (FeD), boiling HCl-extractable iron (FeH), and total iron (FeT) values for sites PB6, PB4, SB4, and SB3. FeD and FeH data are marked by x’s and open diamonds, respectively. All other sites correspond to data markers in the legend and are labeled in the figure. DOP = degree of pyritization and py subscript indicates pyrite.
accumulate. Even when the reactive iron phases have been exhaustedor sulfide begins to accumulate in the pore water, the pore water iron and sulfide concentrations are usually controlled by equilibrium with an iron-sulfide mineral, typically amorphous FeS or mackinawite (FeS) (Canfield and Raiswell, 1991). Using SDGT and FeDGT concentrations, site SB4 was the only site where saturation with mackinawite or amorphous FeS was attained (Fig. 4). In that core, saturation with respect to mackinawite was reached by ~5 cm and higher IAPs were found further down core (Fig. 4). All other sediments were undersaturated with respect to both mackinawite and amorphous FeS; thus iron-monosulfide formation was not likely to occur from direct precipitation in the bulk pore water, but rather by locally generated sulfide reacting with solid-phase iron or Fe^{2+} in microniche. Though a direct two-dimensional comparison of SDGT and FeDGT concentration was not possible, maximum SDGT concentration from all sites was 17–33 μM, similar to the highest horizontally-averaged concentrations in the SB4 core (Fig. 4). Therefore, saturation with respect to either mackinawite and/or amorphous FeS likely existed in many of the high SDGT microniche, as has been observed by other DGT investigations (Motelica-Heino et al., 2003; Naylor et al., 2004).

4.5. Sedimentary iron pools

Representative sediment-depth profiles of FeD, FeH, and FeT concentrations from each depositional environment are shown in Fig. 6 along with FeD/FeT ratios and pyrite sulfur (Spy) concentrations from each site. FeD comprised 19–44% of the total iron and FeD/FeT ratios decreased down core as Spy concentrations increased (Fig. 6). Though FeD and Spy concentrations changed with depth, average FeHR/FeT ratios of the Saint Lucian marine sediment sites were ≥0.41, which was significantly higher than values for global average continental margin and deep-sea sediments reported in Poulton and Raiswell (2002) (Fig. 7). Due to varying carbonate concentrations, Saint Lucian sediments spanned a range of total iron concentrations, but FeHR/FeT ratios were more similar to global riverine sediments than average continental margin or deep-sea sediments (Fig. 7). Globally, the difference in FeHR/FeT between riverine particulates and continental margin and deep-sea sediments is likely due to the preferential removal of FeHR from riverine sources into inner shore reservoirs such as estuaries, floodplains, and salt marshes, though additions of glacial sediments with low FeHR/FeT ratios cannot be completely discounted (Poulton and Raiswell, 2002; Raiswell, 2006; Raiswell et al., 2006). While the Saint Lucia marine sediments had FeHR/FeT ratios (0.41–0.50) within the range (0.26–0.63) of inner shore environments sampled from North America and Europe, higher values might be expected as FeHR/FeT ratios generally reflect weathering intensity with high FeHR/FeT values associated with high runoff or runoff ratio values (Canfield, 1997; Poulton and Raiswell, 2002; Poulton and Raiswell, 2005). The Saint Lucia rocks and soils sampled from the watersheds surrounding Praslin Bay and Savannes Bay

Fig. 7. Highly reactive iron (FeHR)/total iron (FeT) vs. total iron of Saint Lucia marine sediments, rocks, and soils. Only data from the samples collected in 2004 are shown since FeD was not analyzed for samples collected in 2001. Data for global rivers, continental margin sediments, and deep-sea sediments are from Poulton and Raiswell (2002) and references therein. Data points indicate averages and bars show 1σ distributions.
had lower FeHR/FeT ratios (0.11 – 0.15), suggesting that these semi-protected bays may also store high FeHR phases and/or that a significant portion of FeHR phases has already been removed from the soils and bedrock (Fig. 7).

FeHR–FeT–Al relationships provide additional insights to the origin of highly reactive iron phases. There was a strong linear correlation between FeHR and FeT in the Saint Lucia marine sediments, FeHR = 0.41 * FeT + 0.15, r² = 0.94 (Fig. 8A). Compared to the FeHR–FeT correlation of worldwide bulk riverine sediments (FeHR = 0.54 * FeT – 0.58, r = 0.8), the Saint Lucia sediments had a lower slope and a positive FeT intercept (Fig. 8A). For global riverine sediments, the positive intercept on the FeT axis (1.07 wt.%) has been interpreted as silicate-associated iron that is relatively resistant to weathering (Fig. 8A; Poulton and Raiswell, 2002; Poulton and Raiswell, 2005). In the Saint Lucia sediments, the negative FeT intercept is strongly influenced by the relatively low FeHR/FeT ratios of the PB6 deltaic sediments. Removal of this site from the regression results in a correlation of FeHR = 0.54 * FeT – 0.19 (r² = 0.8), which has a positive FeT intercept of 0.35 wt.% FeT (Fig. 8A). This line is marked as the “non-deltaic marine” line in Fig. 8A. The lower FeHR/FeT of site PB6 is likely caused by the preferentially removal of fine-grained, FeHR-rich particles during estuarine mixing as the deltaic sediments were composed of larger grain sizes than the more distal sites. There is no strong linear FeHR–FeT relationship for the Saint Lucia rocks and soils, though any regression would have a significant positive FeT intercept indicating the presence of a relatively large iron pool that is relatively resistant to weathering (Fig. 8A).

FeT and total Al concentrations generally scale linearly in global riverine sediments and in Saint Lucia marine sediments (not shown, r = 0.89), thus FeHR also correlated linearly with aluminum, which demonstrated that FeHR phases are closely associated with iron-bearing aluminosilicate minerals (Fig. 8B; Poulton and Raiswell, 2005). The positive Al-intercepts of 1.97 – 2.78 wt.% imply that not all aluminosilicate surfaces are coupled to FeHR phases (Fig. 8B; Poulton and Raiswell, 2005). The Saint Lucia soils and rocks had much lower FeHR/Al ratios than the marine sediments, but similar FeT/Al ratios. Average FeT/Al ratios were 0.21 for rocks, 0.26 for soils, and 0.22 – 0.29 for all marine sites except PB6, which had a ratio of 0.46 (Fig. 2). Compared to Saint Lucia marine sediments and global riverine sediments, the aluminosilicate phases in Saint Lucia soils and rocks contain much less FeHR (Fig. 8B).

While FeHR/FeT ratios typically increase with smaller grain sizes (Poulton and Raiswell, 2005), this alone cannot account for the relatively high FeHR/FeT ratios of the Saint Lucia sediments because the sediments were muddy silts to silty sands and not completely dominated by fine particles such as clays. The difference in the FeT- and Al-intercepts and FeHR–FeT–Al correlations between the Saint Lucia marine sediments and terrestrial materials in Fig. 8 appear to be caused by the preferential removal and transport of FeHR phases from iron-bearing aluminosilicate source rocks to the nearshore environment. This conclusion should be viewed with caution as the soils and rocks sampled here may not be completely representative of the terrestrial sediments delivered to Praslin Bay and Savannes Bay. Nonetheless, these results suggest that tropical, semi-protected bays may be additional “inner shore” environments that preferentially store FeHR-rich phases. The high concentrations of FeHR or FeD phases in coastal tropical sediments could result in greater pyrite burial than in average marine sediments in cases where pyrite formation is limited by reactive iron concentrations.

4.6. Depth profiles of FeD/FeT, S_{ps}, DOP, δ^{34}S_{ps}, and C/S

Upon deposition in the marine environment, ferric FeD phases are involved in redox and dissolution/precipitation reactions to form iron monosulfide phases that continue to react with sulfide to form pyrite (Morse et al., 1987; Schoonen, 2004). This pyritization process continues during burial causing...
Pyrite sulfur concentrations increase until the FeD phases are completely exhausted (Canfield et al., 1993; Wijsman et al., 2001). The parameter DOP quantifies the fraction of total “reactive” iron that has been converted into pyrite. The most common definition of DOP is the amount of pyrite iron divided by the amount of pyrite iron plus HCl soluble iron where pyrite Fe$^{=}\text{Spy}/2$ (Eq. (3); Berner, 1970; Raiswell et al., 1994):

$$\text{DOP} = \frac{\text{pyriteFe}}{\text{pyriteFe} + \text{FeH}}$$

In many cases, FeH overestimates the remaining iron available for sulfidization by extracting iron phases that only react with dissolved sulfide on timescales of $>100$ years (Lyons et al., 2003), but here we define DOP relative to FeH instead of FeD because i) values will be directly comparable to previous studies, ii) FeD was not measured for Saint Lucia sediments collected in 2001, and iii) in some cases, the FeH–FeD fraction can be pyritized on the timescale of hundreds to thousands for years (Ku et al., in preparation). DOP values relative to FeD would be higher than those calculated with FeH, though the FeD fractions of the Saint Lucia sediments were never completely depleted as the lowest FeD/FeT ratio was 0.19 (Fig. 6).

In Saint Lucia sediments, FeD/FeT ratios generally decreased with increasing sediment depth from 0.32–0.44 to 0.19–0.32 as pyrite sulfur and DOP increased to values of 0.4–1.5 wt.% and 0.18–0.56, respectively (Fig. 6). Continuous FeD conversion into pyrite was observed at all sites with three exceptions: 1) in Savannes Bay offshore sediments, FeD/FeT and DOP values reached quasi-steady values of 0.19–0.22 and 0.40–0.56, respectively, 2) in core PB4, the Praslin Bay storm sediments had markedly lower FeD/FeT and higher DOP values than the rest of the core, and 3) the deepest sediment interval (55–60 cm) of core SB4 had lower Spy concentrations and DOP values than the sediments above (Fig. 6). Pyrite sulfur isotope compositions, $\delta^{34}S_{\text{pyr}}$, can help explain the origin of these anomalous features.

Pyrite sulfur isotope compositions reflect the overall $\delta^{34}S$ value of bacterially-produced sulfide as there is only a minor isotope fractionation associated with pyrite formation from dissolved H$_2$S (Price and Shieh, 1979). $\delta^{34}S_{\text{pyr}}$ values decrease slightly downcore or remain nearly constant at values from $-22$ to $-34\%o$, except for the Praslin Bay offshore storm sediments and the 55–60 cm interval of site SB4, which had more positive values between $-20.4$ and $-7.8\%o$ (Fig. 6). Decreasing or constant $\delta^{34}S_{\text{pyr}}$ values of $-22$ to $-34\%o$ associated with increasing pyrite sulfur concentrations are typical of aerobic or bioturbated near-surface sediments where sulfate supply is not limited, thus $\delta^{34}S_{\text{pyr}}$ values track the instantaneous $\Delta^{34}S_{\text{(SO}_4^{2-}/\text{H}_2\text{S})}$ fractionation (Fig. 6; Jørgensen, 1979; Goldhaber, 2004). Assuming the standard seawater $\delta^{34}S_{\text{SO}_4}$ value of $+21\%o$, $\delta^{34}S_{\text{pyr}}$ values less than $-25\%o$ exceed $\Delta^{34}S_{\text{(SO}_4^{2-}/\text{H}_2\text{S})}$ fractionations of $>46\%o$, which indicates either the presence of sulfur disproportionation reactions or the recycling of sulfide because pure cultures of sulfate-reducing bacteria cannot achieve $\Delta^{34}S_{\text{(SO}_4^{2-}/\text{H}_2\text{S})}$ fractionations $>46\%o$ (Rees, 1973; Longinelli, 1989; Canfield and Thamdrup, 1994; Habicht and Canfield, 2001). Although the 46\%o isotopic fractionation limit was recently challenged by Brunner and Bernasconi (2005), increasing pyrite concentrations associated with $\delta^{34}S_{\text{pyr}}$ values between $-22$ and $-34\%o$ is normal as pyritization proceeds during burial (Fig. 6). The more positive $\delta^{34}S_{\text{pyr}}$ values in the Praslin Bay storm deposits and lowermost SBS sediments represented sulfidization in a relatively closed system where pore water sulfate was not replenished rapidly enough to maintain near seawater concentrations (Fig. 6; Jørgensen, 1979; Goldhaber, 2004). Thus, pyritization occurred very quickly in the PB4 storm sediments resulting in lower FeD/FeT, higher DOP values, and more a positive $\delta^{34}S_{\text{pyr}}$ value. The high $\delta^{34}S_{\text{pyr}}$ value in the SB4 55–60 cm interval was likely caused by a singular event, possibly the introduction of organic matter at depth, but these conditions were not representative of rest of the sediments (Fig. 6).

The organic carbon/pyrite sulfur (C/S) weight ratio in normal marine siliciclastic sediments is 2.8±0.8 and is controlled by (i) the fraction of the total organic carbon deposited that is metabolized, (ii) the fraction of metabolized organic carbon that is metabolized by sulfate reducing bacteria, and (iii) the fraction of total sulfide produced by sulfate reducing bacteria that is buried as pyrite (Morse and Berner, 1995). During the early stages of diagenesis, C/S ratios are often higher than 2.8 and decrease during continued burial until a value of 2.8±0.8 is attained, which has been interpreted as the completion of early diagenesis (Schimmelmann and Kastner, 1993; Böttcher et al., 2000; Otero et al., 2003). The general trend in the Saint Lucia sediments is decreasing C/S ratios with increasing depth with values of 2.8±0.8 observed by a depth of 20–70 cm (Fig. 6). There was some variability, especially in the Praslin Bay deltaic sediments, which contained dominantly terrestrial organic matter, but the lower C/S ratios in the PB4 storm deposits and the lowermost SB4 sediments can be explained by rapid pyritization (Fig. 6).

4.7. Early diagenetic rates of Fe–S–C sediment properties

In Fig. 9, FeD/FeT, DOP, and C/S values are plotted against $^{210}$Pb-derived deposition ages for the six sites sampled in 2005. Pyritization during early diagenesis changes these sediment properties and the net rates at which this process occurred were determined after considering the following two assumptions. Core PB4 storm sediments (20–25 cm) and the SB4 55–60 cm interval were excluded because pyrite formation did not proceed under the same conditions as in the other sediments of these cores. Secondly, the lower two data points from the Savannes Bay offshore storm sediments (SB3 and SB5) were excluded since there was little change with depth, which may mark the extent of early diagenetic reactions in these sediments (Fig. 9). After excluding these data, FeD/FeT, pyrite Fe/FeT, ln (FeD/FeT), Spy, and C/S values were plotted against burial time and fit with linear regressions (Table 3; Fig. 10). Trends were strongly linear and all but one regression had an $r$-value better than 0.84 (Table 3). Taken together, some important rate determinations can be
drawn from this analysis, keeping in mind the relatively loose
$^{210}$Pb-age control for site PB6.

During pyritization, the FeD fraction of the total iron should
decrease as pyrite iron/total iron increases (Wijsman et al.,
2001; Krom et al., 2002). This general relationship occurred in
all six cores and the fastest pyritization occurred at site SB4,
which had the greatest DGT-S fluxes and a distinct lowering of
pore water SO$_4$/Cl ratios (Table 3; Figs. 4 and 10AB). Zero time
intercepts of pyrite Fe/FeT were near zero and FeD/FeT
intercepts represented the initial FeD/FeT ratios prior to
sulfidization, which were similar for all Praslin Bay sediments,
0.43–0.45, but lower for the Savannes Bay offshore, 0.39–0.40,
and nearshore sediments, 0.31 (Table 3; Fig. 10AB). These
initial FeD/FeT ratios were much higher than average values for
Saint Lucia soils (0.15) and rocks (0.11) and provided further
evidence that FeD or Fe$_{IR}$ phases were preferentially removed
from their source materials. The rate of pyrite iron increase was
1.3–3.0 times that of FeD decrease in all sites except the Praslin
Bay deltaic site PB6 where it was half that of the FeD decrease
(Table 3). The differences between the two rates can be
explained by the addition of FeD from upward diffusing Fe$^{2+}$
that was oxidized near the sediment–water interface, by
pyritization of non-FeD phases, or, for site PB6, by the
reduction of ferric iron that was not quantitatively retained as
pyrite.

The graphical approach of Raiswell and Canfield (1996) was
used to estimate the first-order half-lives of FeD sulfidation: In
(FeD/FeT)$_{t=0}$− In (FeD/FeT)$_{t=r} = -kt$ where $k = (ln 2)/T_{1/2}$
(Table 3; Fig. 10C). Linear trends, $r = −0.84$ to $−0.99$, were
found in all cores and calculated half-lives of FeD sulfidation
were 71–159 years with core SB4 having the shortest half-life
(Table 3). These field rates were much slower than laboratory
determined rates of sulfidation of iron oxides and hydroxides,
which ranged from minutes to days, and highlight the difference
between laboratory and field determined rates with the latter
greatly influenced by H$_2$S exposure, pH, repeated iron redox.

<table>
<thead>
<tr>
<th>Site ID</th>
<th>(FeD/FeT) vs. time</th>
<th>(Pyrite Fe/FeT) vs. time</th>
<th>R(Pyrite Fe/FeT)/R(FeD/FeT) vs. time</th>
<th>LN (FeD/FeT) vs. time</th>
<th>T$_{1/2}$ FeD vs. time</th>
<th>C/S vs. time</th>
<th>Time until C/S = 2.8</th>
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<td>PB4</td>
<td>$y = −2.40(10^{-3})T^2 + 0.43$</td>
<td>$y = 3.37(10^{-3})T + 0.01$</td>
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<td>$y = 6.32(10^{-3})T^2 + 0.05$</td>
<td>110</td>
<td>$y = 1.46(10^{-3})T^2 + 0.01$</td>
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<td>[r = −0.99]</td>
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<td>PB5</td>
<td>$y = −1.71(10^{-3})T^2 + 0.45$</td>
<td>$y = 2.21(10^{-3})T + 0.02$</td>
<td>1.3</td>
<td>$y = 4.37(10^{-3})T^2 − 0.78$</td>
<td>159</td>
<td>$y = 0.59(10^{-3})T^2 + 0.14$</td>
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<td>$y = 6.60(10^{-3})T^2 − 0.78$</td>
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<td>$y = −1.80(10^{-3})T^2 + 0.39$</td>
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<td>$y = 6.94(10^{-3})T^2 − 0.90$</td>
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<td>$y = 1.48(10^{-3})T^2 − 0.02$</td>
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<tr>
<td>SB4</td>
<td>$y = −2.75(10^{-3})T^2 + 0.31$</td>
<td>$y = 8.35(10^{-3})T + 0.06$</td>
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<td>$y = 7.94(10^{-3})T^2 − 1.16$</td>
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<tr>
<td>SB5</td>
<td>$y = −2.33(10^{-3})T^2 + 0.40$</td>
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<td>$y = 7.52(10^{-3})T^2 − 0.90$</td>
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</table>

$T$ = Time in years.
Linear regressions plotted from data in Fig. 10 (see text).
cycles, competitive absorption of other solutes, surface areas, secondary mineral precipitation, and mineral impurities (Canfield and Berner, 1987; Canfield et al., 1992; Poulton et al., 2004).

Pyrite sulfur concentrations increased steadily at rates of 0.59–1.80 wt.%/100 years with the fastest rate measured at site SB4 (Table 3; Fig. 10D). A comparison with the DGT-Fe fluxes showed that iron was cycled only 0.8–1.9 times before being incorporated into pyrite (Table 2). Other studies of iron cycling in marine sediments have found that iron was recycled ≤8 to 300 times before final burial (Canfield et al., 1993; Krom et al., 2002), thus the Saint Lucia results were somewhat surprising considering the high concentrations of reactive iron and the apparent dominance of iron production over sulfide production in the upper 10 cm of sediment (Table 2). The DGT-Fe fluxes were at the low end of reported DGT-Fe fluxes in marine sediments and may not accurately quantify the net production of Fe$^{2+}$ (Krom et al., 2002; Fones et al., 2004; Naylor et al., 2004), but these results suggest a relatively low rate of iron recycling in these tropical nearshore sediments.

Increases in pyrite sulfur also caused C/S ratios to decrease with progressive burial time. Plots of C/S vs. burial time indicated that core SB4 had an initial C/S ratio of 30.8 while all other sites had initial values between 5.7 and 13.1 (Table 3; Fig. 10E). Using these initial C/S values and the slope from Fig. 10E, the time required to reach the normal marine sediment value of 2.8 was 22–79 years (Table 3; Fig. 10E). Thus, “final” C/S values were attained fairly rapidly in coastal tropical sediments and early Fe–S–C diagenesis was usually complete in tens of years in sediments accumulating at rates of 0.11–1.71 g/cm$^2$/yr.

4.8. Influence of organic carbon on pyrite formation

Among the $^{210}$Pb-dated sediments, Savannes Bay nearshore site SB4 had the highest average pyrite formation rate associated with a decrease in pore water SO$_4$/Cl at ∼5 cm depth and the highest DGT-sulfide production rate (Tables 2 and 3; Fig. 2). Pyritization also occurred rapidly in the organic-rich PB4 storm sediments as FeD/FeT and C/S values were much lower and DOP values much higher than underlying and overlying sediments in that core (Figs. 6 and 9). In contrast, the Savannes Bay offshore sediments required the longest times to reach C/S values of 2.8, despite having the highest average organic carbon concentrations (Tables 1 and 3). From these observations, it was clear that the rate of organic carbon deposition influenced the rates of sulfate reduction and pyrite formation. To evaluate these relationships, average accumulation rates of bulk sediment, calcium carbonate, organic carbon, and total iron were calculated for the six sites sampled in 2005 (Table 4). Since pyritization progressed during burial, $S_{py}$ accumulation rates were determined from maximum non-storm $S_{py}$ concentrations and the bulk sedimentation rates and represented the rate of $S_{py}$ burial after early diagenesis (Table 4). Site SB4 had the highest accumulation rates of bulk sediment, organic carbon, and $S_{py}$ burial and had total iron sedimentation rates similar to the other sites (Table 4). For all iron recycling between the pore water and sediment (Krom et al., 2002). Since DGT-Fe rates only covered the upper 12–15 cm of sediment, we assumed that the rate of pyrite iron determined from the entire core was valid for this upper interval and used an average bulk density (g dry sed/cm$^3$ wet sed) to determine an integrated rate of pyrite iron addition for the upper 10 cm (Table 2). A comparison with the DGT-Fe fluxes showed that iron was cycled only 0.8–1.9 times before being incorporated into pyrite (Table 2). Other studies of iron cycling in marine sediments have found that iron was recycled ≤8 to 300 times before final burial (Canfield et al., 1993; Krom et al., 2002), thus the Saint Lucia results were somewhat surprising considering the high concentrations of reactive iron and the apparent dominance of iron production over sulfide production in the upper 10 cm of sediment (Table 2; Fig. 4). The DGT-Fe fluxes were at the low end of reported DGT-Fe fluxes in marine sediments and may not accurately quantify the net production of Fe$^{2+}$ (Krom et al., 2002; Fones et al., 2004; Naylor et al., 2004), but these results suggest a relatively low rate of iron recycling in these tropical nearshore sediments.

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six sites, $S_{py}$ burial rates scaled linearly with organic carbon accumulation rates ($r^2 = 0.81$) and this relationship improved ($r^2 = 0.99$) if site PB6, the core with the worst age control, was removed (Fig. 11). A minimum estimate of the storm organic carbon and $S_{py}$ burial rate was calculated from the bulk sedimentation rate in the upper 30 cm of sediment and the organic carbon and $S_{py}$ concentrations in the PB4 20–25 cm sediment interval. This estimated rate plotted along the same linear trend between organic carbon deposition and pyrite burial found among the other Saint Lucia sediments (Fig. 11).

The directly proportional rates of organic carbon and pyrite burial have been noted in many other marine sediments and demonstrate that organic carbon deposition is the primary control on pyrite formation (Lin and Morse, 1991; Lin et al., 2000; Lin et al., 2002). Thus, ancient pyrite burial rates can be calculated from the abundance of organic carbon in sedimentary rocks after appropriate corrections for thermal maturation (Berner, 1982; Raiswell and Berner, 1987; Berner and Canfield, 1989). Saint Lucia results were in the upper range of modern global pyrite burial rates and showed that organic carbon and pyrite sulfur formation remained tightly coupled in adjacent depositional environments with varying sedimentation rates (0.1–1.7 mg/cm$^2$-yr). Faster deposition of labile organic carbon increased the sulfate reduction rate and the proportion of organic carbon oxidized by sulfate reduction, which resulted in higher rates of pyrite burial (Lin et al., 2000; Goldhaber, 2004). In Saint Lucia sediments, pyrite formation was not limited by sulfate because pore water sulfate concentrations were not significantly lower than the overlying seawater and most of the $\delta^{34}S_{py}$ values reflected conditions of sulfate reduction utilizing sulfate from an unlimited pool of seawater sulfate (Figs. 4 and 6). Iron was not the limiting component because Fe/D/FeT and DOP values showed an abundance of non-sulfidized reactive iron; therefore, pyrite formation was primarily controlled by the rate of organic carbon deposition (Table 4; Figs. 4, 6, and 11).

Recent studies of large tropical deltaic systems that support high sediment mixing rates, such as the Amazon River delta and the Gulf of Papua, have shown that organic matter was primarily decomposed by suboxic, non-sulfidic processes that resulted in sediments characterized by high total reactive iron, a low proportion of diagenetically reduced iron as pyrite, low DOP values ($\sim 0.1$), and high C/S ratios ($\sim 4–8$) (Aller, 1998; Aller et al., 2004a,b). In comparison, the Saint Lucia sediments had much lower sedimentation rates and similar reactive iron concentrations, but much higher DOP values (0.2–0.55) and normal marine C/S ratios were attained within several tens of years (Table 1 and 4; Figs. 6, 9). It appears that high reactive

---

**Table 4**

<table>
<thead>
<tr>
<th>Site ID</th>
<th>$\text{Bulk sediment MAR (g/cm}^2\text{-yr)}$</th>
<th>$\text{CaCO}_3$ MAR (mg/cm$^2$- yr)</th>
<th>$\text{Organic C MAR (mg/cm}^2\text{-yr)}$</th>
<th>$\text{FeT MAR (mg/cm}^2\text{-yr)}$</th>
<th>$\text{$S_{py}$ MAR (mg/cm}^2\text{-yr)}$</th>
</tr>
</thead>
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<tr>
<td>PB4</td>
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<td>436</td>
<td>20.6</td>
<td>51.4</td>
<td>8.9</td>
</tr>
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<td>10.4</td>
<td>38.2</td>
<td>4.8</td>
</tr>
<tr>
<td>PB6$^c$</td>
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<td>75.9</td>
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</tr>
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<td>38</td>
<td>2.4</td>
<td>3.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>

$^a$ Averaged over entire core.

$^b$ Maximum non-storm rate (see text).

$^c$ See assumptions in text.

---

**Fig. 11.** Pyrite sulfur MAR vs. organic carbon MAR of the Saint Lucia sediment sites. Solid regression line includes all six locations sampled in 2004. Dashed regression line excludes site PB6. Storm data estimated from site PB4 using the bulk sediment MAR for the upper 30 cm and the organic carbon and pyrite sulfur concentrations from the 20–25 cm interval, and is not included in either regression calculation.
iron concentrations and massive sediment reworking are necessary to sustain non-sulfidic diagenesis. In fact, the combination of high concentrations of reactive iron due to intense weathering and rapid sedimentation surrounding high-standing tropical islands (Milliman and Syvitski, 1992) should create an environment that buries substantial quantities of pyrite if the necessary organic carbon is deposited simultaneously.

5. Conclusions

Coastal depositional environments in Saint Lucia’s Praslin Bay and Savannes Bay ranged from deltaic sediments containing mostly terrestrial organic carbon to relatively rapidly accumulating (0.9–1.7 g/cm²/yr) mixed carbonate-siliciclastic sediments (∼28–44% CaCO₃) containing a mixture of terrestrial and marine organic carbon to slower depositing (0.1 g/cm²/yr) sediments with dominantly marine organic matter. Continuous sedimentation occurred without significant sediment mixing at all sites except in Praslin Bay deltaic sediments, which had irregular excess ²¹⁰Pb profiles, and in Praslin Bay offshore sediments where organic-rich storm layers were deposited. Compared to average continental margin sediments and local bedrock and soils, the Saint Lucia marine sediments had higher Fe₄HR/FeT ratios which, together with FeT–Al–Fe₄HR relationships, suggest that Fe₄HR phases were derived from iron-bearing aluminosilicate terrestrial materials and were preferentially transported to the coastal marine environment. These tropical semi-protected bays appeared to store high Fe₄HR/FeT phases and should be considered in global budgets of highly reactive iron (Poulton and Raiswell, 2002; Raiswell et al., 2006).

Upon deposition in the marine environment, FeD phases were converted into pyrite causing increasing S_py concentrations and DOP values and decreasing FeD/FeT and C/S ratios with continued burial. Field estimates of FeD sulfidation half-lives were 71–159 years, which were much greater than lab determined rates of minutes to 182 days (Canfield et al., 1992; Poulton et al., 2004). The difference in rates was expected and demonstrated the importance of site-specific conditions such as H₂S concentrations, pH values, available surface areas, and past diagenetic histories. Normal marine C/S ratios of 2.8 were attained within 22–79 years after burial and indicated that pyritization occurred very rapidly in these coastal environments. Overall, the burial rate of pyrite was directly proportional to the organic carbon burial rate and provided further evidence that pyrite formation was controlled by the deposition of organic carbon.

In general, rapid pyritization occurred in sediments that showed variable or little change in bulk pore water SO₄/Cl ratios, though distinctly lower SO₄/Cl ratios and elevated alkalinity concentrations were observed in some deltaic and nearshore sediments. Compared to overlying seawaters, lower pore water SO₄/Cl ratios obtained by DET or centrifugation was only observed in Savannes Bay nearshore sediments that had the fastest rates of pyritization. In most Saint Lucia sediments, pore water SO₄/Cl ratios did not reflect the extent of sulfur cycling due to rapid solute transport and/or chemical cycling. In the upper 12–15 cm of most sediments, DGT-iron and -sulfide fluxes showed that iron production exceeded sulfide production and that most sulfate reduction and iron-sulfide precipitation likely occurred in microneich environments, presumably associated with organic-rich particles. DGT-iron and -sulfide production rates were similar in Savannes Bay nearshore sediments, which had the highest organic carbon burial rates, and demonstrated that iron and sulfate reduction may have occurred simultaneously within this zone or that iron was primarily released by chemical reaction with H₂S. A comparison of net rates of pyritization with DGT-iron fluxes showed that iron was recycled ≤1.9 times before burial as pyrite. This results was somewhat surprising and further work is required to determine if this rate is representative of tropical, iron-rich depositional environments.

In the Fe₄HR-rich, coastal Saint Lucia sediments, reactive FeD phases were rapidly sulfidized. This suggests that high reactive iron concentrations without significant sediment reworking cannot sustain dominantly non-sulfidic diagenesis as observed in mobile, suboxic fluidized bed reactors associated with large deltaic complexes (Aller, 1998). Future diagenetic studies should focus on depositional settings receiving massive quantities of iron-rich sediments from high-standing tropical islands (Milliman and Syvitski, 1992), because these sediments could store large quantities of pyrite and organic carbon, which would greatly influence the biogeochemical cycles of iron, sulfur, carbon, and oxygen.

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