

Oxidative precipitation of groundwater-derived ferrous iron in the subterranean estuary of a coastal bay

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[1] Sediment cores from the intertidal zone of Waquoit Bay (Cape Cod, Massachusetts) yielded iron oxide-coated sands in the subterranean estuary, which underlies the head of the bay. The oxides were dark red, yellow and orange colors and are formed by the oxidation of ferrous iron-rich groundwater near the groundwater-seawater interface. Within these iron oxide-rich sediments, the concentration of the combined amorphous and crystalline forms of iron oxides ranged between 2500 and 4100 ppm of Fe. These concentrations were 4–6 times greater than the surface sands, and 10–15 times more Fe rich than sands collected from an off-site location. The precipitation of iron oxides in subterranean estuaries could act as a geochemical barrier by retaining and accumulating certain dissolved chemical species carried to the coast by groundwater. Indeed, phosphorus concentrations in the iron oxide-rich sands of Waquoit Bay were 5–7 times greater than the overlying surface sands. **INDEX TERMS:** 4875 Oceanography: Biological and Chemical: Trace elements; 1832 Hydrology: Groundwater transport; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4235 Oceanography: General: Estuarine processes

1. Introduction

[2] Recent studies indicate that groundwater may contribute significant fluxes of dissolved chemical species to the oceans [Simmons, 1992; Moore, 1996; Krest *et al.*, 2000; Charette *et al.*, 2001]. The magnitude of such fluxes is influenced by biogeochemical processes occurring in the subterranean estuary, defined as the mixing zone between groundwater and seawater in a coastal aquifer [Moore, 1999]. Here we report the discovery of iron oxide-coated sands in a subterranean estuary on Cape Cod. The responsible process is the precipitation of groundwater-borne dissolved ferrous iron and subsequent accumulation of ferrihydrite, lepidocrocite, and goethite onto subsurface sands at the groundwater-seawater interface. As naturally-occurring iron oxides are strong adsorbers of many dissolved chemical species [e.g., Stumm and Morgan, 1981; Salomons and Forstner, 1984], the occurrence of iron oxide precipitates in subterranean estuaries may have broad implications for transport of natural and anthropogenic materials from aquifers into coastal waters. This point will be illustrated with data on the phosphorous content of iron-rich sands.

2. Study Site and Methodology

[3] Waquoit Bay is an ideal natural laboratory to study the geochemistry of subterranean estuaries. This Bay is a shallow estuary located on the south shoreline of Cape Cod, MA, U.S.A; a map of the bay can be found in Charette *et al.* [2001]. A significant portion of the freshwater input into the bay occurs as submarine discharge of groundwater [Cambareri and Eichner, 1998; Valiela *et al.*, 1990; Charette *et al.*, 2001]. Page meter studies indicate that

groundwater discharge occurs in a narrow (~25 m-wide) band along the head of the bay [Michael *et al.*, 2001]. Hence, the subterranean estuary lies beneath the intertidal zone extending back underneath the beach.

[4] A series of sediment cores were collected at the head of Waquoit Bay using a vibra-coring technique. A significant amount of compaction, ranging from factors of 1.49 to 1.73, occurred during vibra-coring. Of the six recovered cores, analyses from cores 2, 3, and 5 are presented in this paper; they were chosen because they each had a unique color stratigraphy. Cores 2 and 5 were cut open by running a power saw down the length of the tubes. This technique left an intact core for photographing (Figure 1), sectioning, and storing. The sediment in core 3 was removed by extrusion onto a long plastic sheet and collected in 3 to 5 cm sections.

[5] Groundwater was sampled from two land sites at the head of the bay. The samples were collected hermetically and filtered using all-plastic syringes with 0.2 μm Millipore Sterivex filters. One portion of the filtrate was immediately analyzed for dissolved ferrous Fe by the ferrozine colorimetric method. The second portion was acidified to pH 2 and used to measure the concentration of total dissolved iron (Fe (III) plus Fe (II); [Stookey, 1970]).

[6] The amount of iron oxides in the sediment cores was measured using the selective dissolution protocol of Hall *et al.* [1996]. We used their "L3" solution to dissolve amorphous oxides of iron and manganese, followed by their "L4" solution that dissolves crystalline Fe and Mn oxides. Each leach is performed twice on ~0.4 g of sample. The L3 leach solution consists of 10 mL of 0.25 M hydroxylamine hydrochloride in 0.05 M HCl; sample plus leach is heated for two hours at 60°C. The L4 solution consists of 25 mL of 1 M hydroxylamine hydrochloride in 25% glacial acid and is heated at 90°C for 3 hrs. The results in Figure 2 report the sum total of the L3 plus L4 leaches. Inorganic phosphorous was determined on subsamples of the L3 and L4 leaches using the ammonium molybdate method on a Lachat QuickChem 8000 flow injection analyzer.

3. Results and Discussion

[7] Groundwater, entering the head of the bay, contained high (40–50 $\mu\text{mol l}^{-1}$) concentrations of dissolved Fe. A major fraction (~95%) of the total dissolved Fe existed in the reduced state as ferrous (Fe (II)) iron. No precipitation or coagulation of dissolved Fe occurred when seawater was added to groundwater under oxygen-free conditions. Hence, the dissolved Fe in our groundwater was not colloidal as normally observed in rivers [Sholkovitz, 1976]. Conversely, stirring air into a filtered sample of this groundwater resulted in the complete oxidation of dissolved Fe (II) to a yellow-brown ferric iron precipitate over a period of 2–3 hrs. This observation led us to hypothesize that iron oxides would precipitate in the subterranean estuary beneath the Bay.

[8] Recovered sediment cores revealed the occurrence of iron oxides within the bay's subterranean estuary in the form of subsurface sands having dark red, yellow and orange colors (Figure 1). The color changes occurred over a transition zone of

many tens of centimeters. Core 2 changed from grey to dark red at a depth of about 85 cm; approximately half of this core was dark red in color. Core 3 changed from grey to red to orange; the grey section was restricted to the top 30 cm of this 112 cm-long core. Core 5 changed from grey to yellow, with the transition to yellow occurring 15 cm below the top of the core.

[9] Different pieces of evidence all lead to the conclusion that the dark red, yellow and orange colors of the sands under Waquoit Bay were caused by the precipitation of iron oxides during submarine groundwater discharge of ferrous-Fe rich ground waters.

When viewed under a microscope, the quartz grains had a colored veneer. Mild shaking in water removed a large portion of the colored material from the sands. Leaching in a strong (1.4 M) solution of hydroxylamine hydrochloride in 6M HCl, a well known reductant of amorphous and/or crystalline iron (III) oxides, stripped the quartz-rich sands of their unique color and left a tan colored beach-like sand. The above observations indicate that the iron oxide precipitates were loosely bound to sand grains.

[10] Extended X-Ray Absorption Fine Structure Spectroscopy (EXAFS) at the Stanford University Synchrotron Radiation Laboratory confirmed that the iron oxide composition differed greatly amongst the three cores. The red coating of core 2 consisted predominantly of ferrihydrite (80%) with 10% each of goethite and lepidocrocite. The yellow coating of core 5 contained only goethite and ferrihydrite at 61 and 39% respectively. The orange coating of core 3 consisted of all three forms of oxides at significant levels. It has the largest amount of lepidocrocite (19%), and goethite and ferrihydrite represent 31 and 50% respectively.

[11] To investigate the down-core magnitude of the iron oxide content, we chemically leached sands from (a) selected core samples, (b) samples from the beach at the head of Waquoit Bay and (c) three samples from an off-site beach located 10 km from the bay. The leached-Fe concentrations of the off-site beach sands ranged from 230 to 300 ppm, suggesting that no Fe-rich groundwater was present at this location. Waquoit Bay beach sands were slightly higher, ranging from 350 to 560 ppm. The leached-Fe concentration of the surface layers of the three cores was between 500 and 700 ppm, and increased with depth to reach maximum values of 3040, 4060 and 2540 ppm in cores 2, 3 and 5 respectively (Figure 2). Cores 2 and 3 displayed the smoothest down-core profiles of leached-Fe and exhibited the best correlation between color and iron oxide content. Their transition zones from grey to red and from grey to orange coincided with a marked increase in the concentration of leached-Fe. The down-core profile of leached-Fe in core 5 (yellow sands) was less smooth. The above observations demonstrate that the colored sands in the three cores were significantly enriched (4–6 fold) in amorphous and/or crystalline iron oxides relative to their surface sands.

[12] Phosphate, a critical nutrient in coastal waters, is known to strongly adsorb onto naturally occurring Fe oxides [Borggaard, 1983; Parfitt, 1989; Torrent *et al.*, 1992; Griffieon, 1994; Van Raaphorst and Kloosterhuis, 1994; Cornell and Schwertmann, 1996]. Indeed, this was the case for the iron oxide-rich sands of Waquoit Bay. The leached-P concentrations of the off-site beach sands ranged from 10 to 12 ppm, similar to Waquoit Bay beach sand. The leached-P concentrations of the grey surface layers of the three cores ranged from 20 to 30 ppm and increased with depth to reach maximum values of 155, 184 and 51 ppm in cores 2, 3 and 5 respectively (Figure 2). Hence, Fe-oxide rich sands of cores 2 and 3 contained up to 5–7 times more leached-P than their grey surface sands. The maximum enrichment for the yellow sands of core 5 was much less (1.5 to 2.5). The concentrations of leached-P



Figure 1. (opposite) Images of Waquoit Bay sediment cores depicting the 'Iron Curtain'. The black scale bar at the base of each core is 10 cm. The sediments were sectioned using two methods. For cores 2 and 5, the Al core barrels (7.6 cm diameter) were split length-wise, photographed and sectioned into 5-cm increments. For core 3, the sediment was extruded onto clean plastic sheeting and sectioned into 3 or 5-cm increments; the stratigraphy of this core was simulated (to scale) in the lab with dried sediment. The vibra-coring technique used to obtain these sediments resulted in compaction of the sediment column. Compression factors were 1.5 for core 2, 1.7 for core 3, and 1.5 for core 5. The recovered length of cores 2, 3, and 5 was 175 cm, 112 cm, and 169 cm, respectively. Due to the angle of the core 3 photograph, the scale bar is not as accurate as with cores 2 and 5.

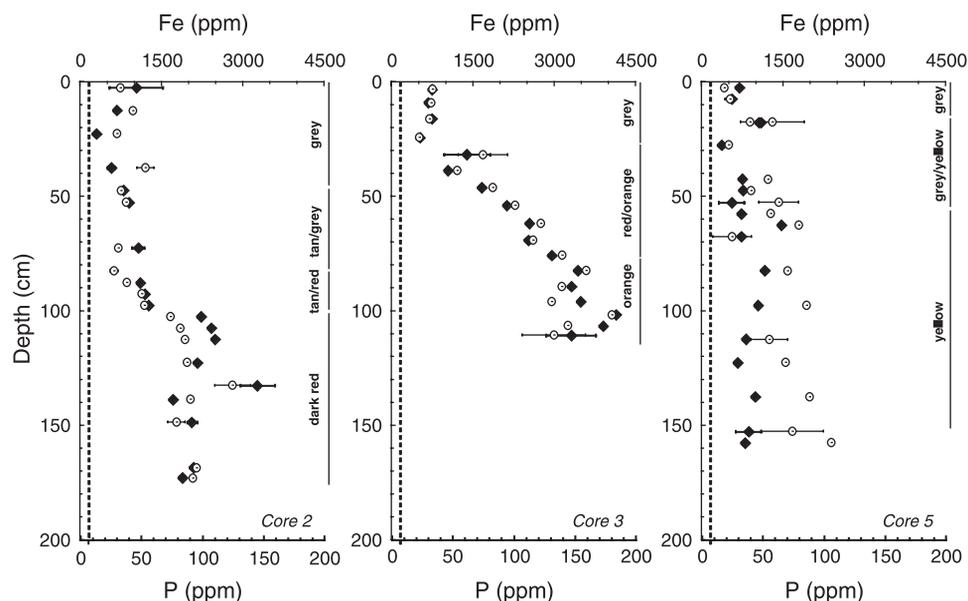


Figure 2. Changes in iron and phosphate concentration with depth in the three sediment cores shown in Figure 1. The open circles indicate Fe concentration (ppm; $\mu\text{g Fe/g}$ dry sediment) while the solid diamonds represent P (ppm; $\mu\text{g P/g}$ dry sediment). Error bars indicate the standard deviation for triplicate leaches performed on a selected number of samples. The dashed lines represent the concentration of Fe and P in 'off-site' quartz sand. Also shown is the approximate color stratigraphy for each core. Sediment core depths are not corrected for compression during sampling. The R^2 value for Fe vs. P in cores 2, 3, and 5 is 0.80, 0.91, and 0.16, respectively.

and leached-Fe were highly correlated in cores 2 and 3 but poorly correlated in Core 5 (Figure 2).

[13] The atomic P/Fe ratios of the hydroxylamine HCl leach averaged over all the depths of cores 2 and 3 were similar (0.08–0.09). In marked contrast, the oxides of core 5 had a two-fold lower ratio (0.05). These data suggest that either the iron oxides in the yellow sands had less affinity for P or that the P had been preferentially removed upstream from the sediment core or by an in situ diagenetic process. The ratios of cores 2 and 3 are in remarkable agreement with the ratio of (Fe-bound P)/(Fe oxide) in other coastal sediments [Slomp *et al.*, 1996 and references there in] even though different methods were employed. Slomp *et al.* [1996] concluded that a ratio of Fe-bound P in poorly crystalline Fe oxides of 0.10 is common for marine sediments. They also argued that the more crystalline form of iron oxide (e.g. goethite) had less affinity for P, leading to lower P/Fe ratios in goethite-bearing sediments. This explanation would fit our Waquoit Bay results in that the goethite-rich (61%) core 5 had a two-fold lower P/Fe ratio than cores 2 and 3. However, we cannot rule out that differences in the source and the form of soluble P to the three coring sites may also be a contributing factor.

4. Conclusions and Implications

[14] An observation unique to this study is the presence of iron oxides coated sands at the groundwater/seawater boundary. Large amounts of ferrihydrite, lepidocrocite and goethite are being precipitated beneath the head of Waquoit Bay. The oxidation of ferrous-iron rich ground water in the bay's subterranean estuary is the responsible mechanism. These iron oxide rich sands could act as a geochemical barrier by retaining and accumulating certain dissolved chemical species carried to the subterranean estuary by groundwater and/or coastal seawater. Significant accumulation of phosphorus in the iron oxide zones of the Waquoit cores exemplifies this process.

[15] Since the vibra-coring technique limited our core penetration to ~ 3 m, we do not know the full vertical extent of the iron-rich sands. Likewise, their aerial extent within the bay has not been

determined. An intriguing and important geochemical observation of the Waquoit Bay subterranean estuary is the along-shore variability in the type of iron oxides formed in cores only separated by 50 to 200 m. Differences in age, extent of diagenesis and aquatic chemistry could be responsible for variations in the types of iron oxides. With respect to the latter, differences in salinity, pH, and concentrations of ferrous Fe, silica and sulfate can lead to different amorphous and crystalline forms of iron oxides [e.g., Mayer and Jarrell, 1996; Cornell and Schwertmann, 1996].

[16] The formation of iron oxide rich sands requires an aquifer with dissolved Fe(II) that outcrops into oxygenated coastal sediments. This condition may not be uncommon in coastal regions. Iron oxide formation has been described for a sandy beach in the German North Sea [Huettel *et al.*, 1998] and for coastal New York, USA [Montlucon and Sanudo-Wilhelmy, 2001]. The geochemistry of subterranean estuaries is at present relatively understudied; future observations will likely reveal more "Iron Curtain" type conditions.

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