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Trace element cycling in a subterranean estuary:
Part 1. Geochemistry of the permeable sediments

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Abstract—Subterranean estuaries are characterized by the mixing of terrestrially derived groundwater and seawater in a coastal aquifer. Subterranean estuaries, like their river water-seawater counterparts on the surface of the earth, represent a major, but less visible, hydrological and geochemical interface between the continents and the ocean. This article is the first in a two-part series on the biogeochemistry of the subterranean estuary at the head of Waquoit Bay (Cape Cod, MA, USA). The pore-water distributions of salinity, Fe and Mn establish the salt and redox framework of this subterranean estuary. The biogeochemistry of Fe, Mn, P, Ba, U and Th will be addressed from the perspective of the sediment composition. A second article will focus on the groundwater and pore-water chemistries of Fe, Mn, U and Ba.

Three sediment cores were collected from the head of Waquoit Bay where the coastal aquifer consists of permeable sandy sediment. A selective dissolution method was used to measure the concentrations of P, Ba, U and Th that are associated with "amorphous (hydr)oxides of iron and manganese" and "crystalline Fe and Mn (hydr)oxides." The deeper sections of the cores are characterized by large amounts of iron (hydr)oxides that are precipitated onto organic C-poor quartz sand from high-salinity pore waters rich in dissolved ferrous iron. Unlike Fe (hydr)oxides, which increase with depth, the Mn (hydr)oxides display midcore maxima. This type of vertical stratification is consistent with redox-controlled diagenesis in which Mn (hydr)oxides are formed at shallower depths than iron (hydr)oxides. P and Th are enriched in the deep sections of the cores, consistent with their well-documented affinity for Fe (hydr)oxides. In contrast, the downcore distribution of Ba, especially in core 3, more closely tracks the concentration of Mn (hydr)oxides. Even though Mn (hydr)oxides are 200–300 times less abundant than Fe (hydr)oxides in the cores, Mn (hydr)oxides are known to have an affinity for Ba which is many orders of magnitude greater than iron (hydr)oxides. Hence, the downcore distribution of Ba in Fe (hydr)oxide rich sediments is most probably controlled by the presence of Mn (hydr)oxides. U is enriched in the upper zones of the cores, consistent with the formation of highly reducing near-surface sediments in the intertidal zone at the head of the Bay. Hence, the recirculation of seawater through this type of subterranean estuary, coupled with the abiotic and/or biotic reduction of soluble U(VI) to insoluble U(IV), leads to the sediments acting as a oceanic net sink of U. These results highlight the importance of permeable sediments as hosts to a wide range of biogeochemical reactions, which may be impacting geochemical budgets on scales ranging from coastal aquifers to the continental shelf. *Copyright © 2005 Elsevier Ltd*

1. INTRODUCTION

Geochemical studies of coastal marine sediments have typically focused on fine-grained cohesive deposits. High concentrations of organic matter and clay minerals in these muddy and silty sediments lead to chemical and mineral diagenesis involving the microbial degradation of organic matter and the development of redox gradients (Froelich et al., 1979; Aller, 1980). Permeable sediments, which constitute a large fraction of sediments in coastal aquifers, intertidal zones and continental shelves throughout the world, consist primarily of coarse-grained sands low in organic matter. By their nature, permeable sediments are more open to the advective transport of water, dissolved solutes and fine suspended particles, which results from the action of groundwater transport, waves and tides. Permeable sediments typically undergo suboxic rather than anoxic chemical diagenesis as observed in many cohesive sediment deposits (Slomp et al., 1997; Kristensen et al., 2002, 2003).

Despite the relatively low solute concentrations found in permeable sediments, the solute fluxes to the overlying water column may be large because flow rates may be orders of magnitude greater than from fine-grained sediments. This results in relatively high solute fluxes to the overlying water column (Huettel and Gust, 1992; Huettel et al., 1996, 1998; Huettel and Rusch, 2000; Rusch and Huettel, 2000; Roy et al., 2002; Jahnke et al., 2003; Precht and Huettel, 2003). The field studies and flume experiments of Huettel et al. (1998) revealed that permeable sediments from the North Sea undergo a variety of diagenetic reactions that include the consumption of dissolved oxygen and organic matter and the production of metabolic nutrients. Reimers et al. (2004) demonstrated a positive correlation between flow and oxygen consumption in permeable sediments of the USA Middle Atlantic Bight.

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The permeable sediments that characterize sandy beaches, which are often influenced by groundwater flowing through coastal aquifers toward the sea, have also been overlooked as zones of biogeochemical transformations. This led Moore (1999) to introduce the concept of a “subterranean estuary,” which he defined as the mixing zone between terrestrially derived fresh groundwater and seawater in a coastal aquifer. Subterranean estuaries, like their river water-seawater counterparts on the surface of the earth, represent a major, but less visible, hydrological interface between the continents and the ocean. With respect to “surface estuaries,” the river transport of solutes, colloids and suspended particles and reactions during the mixing of river water and seawater play a major role in the biogeochemical cycles of many inorganic elements in the oceans (e.g., Boyle et al., 1977; Li and Chan, 1979; Edmond et al., 1985; Coffrey et al., 1997). In contrast to the large literature on the hydrology, estuarine chemistry and biogeochemistry of surface estuaries, subterranean estuaries have not been studied in any systematic fashion (Moore and Shaw, 1998; Burnett et al., 2001, 2002). However, recent studies indicate that the oceanic budgets of alkaline earth elements (Ba, Sr and Ra) must be reevaluated from the perspective of submarine groundwater discharge and biogeochemical reactions within subterranean estuaries (Moore, 1996; Shaw et al., 1998; Basu et al., 2001).

This article is the first of a two-part series on the biogeochemistry of the Waquoit Bay coastal aquifer/subterranean estuary. This first article will use the pore-water distributions of salinity, Fe and Mn to establish the salinity and redox framework of the subterranean estuary. It will then address the biogeochemistry of Fe, Mn, P, Ba, U, and Th from the perspective of the sediments. By focusing on this group of elements, four important classes of reactions (and reactants) are studied. These include [1] redox-controlled solubility (Fe, Mn and U), [2] adsorption (P, Th, Ba, Ra) onto the oxides of Fe and Mn, [3] release (P, Ba, Ra) from oxides undergoing reductive dissolution, and [4] desorption (Ba, Ra) from sediments via ion-exchange reactions.

The second article will use groundwater, pore-water and Bay surface water data to establish a more detailed view into the estuarine chemistry and the chemical diagenesis of Fe, Mn, U and Ba in the coastal aquifer. By focusing on a small and well-defined subterranean estuary (Waquoit Bay, MA, USA), these two articles will provide an in-depth study of the major biogeochemical reactions operating on the permeable sediments of a coastal aquifer with active Fe and Mn redox cycles and well-defined salinity gradients.

2. STUDY AREA

Waquoit Bay is a shallow semi-enclosed estuary located on the south shoreline of Cape Cod (MA, USA; Fig. 1). The bay is tidally flushed with Vineyard Sound through a narrow inlet to the south. The sedimentary deposits of the study area generally consist of outwash gravel, sand and silt with occasional lacustrine deposits of silts and clays (Oldale, 1976). Several characteristics make this bay an ideal natural laboratory to study the biogeochemistry of subterranean estuaries and their impact on the coastal ocean.

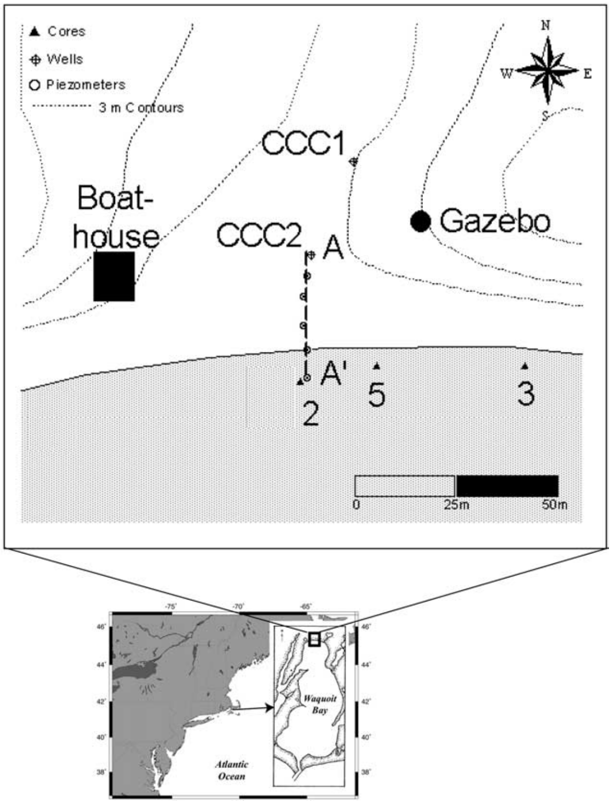

Fig. 1. Location within Waquoit Bay of the vibracores discussed in this article. Also included is the location of the July 2002 piezometer transect (A to A′) used to collect pore-water profiles and the locations of the two multilevel monitoring wells (CCC1 and CCC2).

First, because the soil on Cape Cod is primarily composed of coarse-grained sand, precipitation tends to infiltrate the sediments rather than become surface runoff. Thus, groundwater is the major source of freshwater to the bay and to the two rivers that drain into it (Cambareri and Eichner, 1998; Valiela et al., 1990; Charette et al., 2001; U.S. Geological Survey, 2003). Second, along the shoreline of Waquoit Bay, the upper ~10 m of the Cape Cod aquifer consists of a relatively homogeneous distribution of highly permeable sediment (Cambareri and Eichner, 1998) which results in a well-confined subterranean estuary (Testa et al., 2002; Talbot et al., 2003). This sediment forms the end moraine deposit from the late Wisconsinan deglaciation of ~12,000 to 15,000 yr ago (Oldale, 1981).

Waquoit Bay, due to its status as a National Estuarine Research Reserve, has been the focus of many prior studies documenting the importance of submarine groundwater discharge (SGD) on nutrient budgets and water balances (e.g., Valiela et al., 1990; Charette et al., 2001; Abraham et al., 2003; Michael et al., 2003). For example, seepage meter studies indicate that submarine groundwater discharge occurs in a narrow (~25 m wide) band along the head of the bay (Michael et al., 2003; Sholkovitz et al., 2003). Surface water samples collected by Charette et al. (2001) show that the head of the Bay is less saline and have higher activities of Ra isotopes than the ocean end of Bay. Their Ra isotope based estimate of SGD confirms that the input of fresh and brackish groundwater is an important process at the head of the Bay.