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Changes in trace metal sedimentation during freshening of a coastal basin

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ABSTRACT

Holocene freshening has turned the Bothnian Bay, northern Baltic Sea into an oligotrophic basin. Sequestering of trace elements has changed significantly during the oligotrophication process. In principle, trace metals have been transferred from permanently buried sulfides to Fe–Mn-oxyhydroxides in the top layers of the sediment. The oxyhydroxide layers restrict the flux of trace metals from the sediment to the oxic bottom water. Hence, Fe–Mn cycling in the suboxic sediment enriches a number of trace metals in the surface sediment. Arsenic, Sn, Ge and Bi show enrichment in the Fe-oxyhydroxide layer, whereas Mo, Cd, Ni, Co, Cu, and Sb are enriched in the uppermost Mn-oxyhydroxide layer. This natural redox cycling in the sediment obscures pollution effects. The oligotrophication process started approximately 3500 years ago, reflected in decreasing deposition of Zn, a proxy for phytoplankton production, and formation of Mn oxyhydroxide layers. Similarly, Ba/Al data indicate a decrease in the pelagic input of plankton. Barium data also suggest that dissolved sulfide in the sediment never reached high concentrations. Germanium is closely related to Ba, suggesting that Ge can be used as a proxy for phytoplankton production. Vanadium, U, Re, and Mo all indicate that the bottom water never has been significantly sulfidic during the last 5500 years. Rhenium data indicate that the organic carbon oxidation rate has decreased during the last 5500 years. Cadmium follows the organic matter distribution, but started to increase 1000 YBP (years before present). The reason for this enhanced input of Cd is unclear.

1. Introduction

Increasing global temperature will change the freshwater input to marginal marine basins. Similarly, transgression and regression changes the salinity in coastal basins. A decrease in salinity from approximately 8 to 3 psu, has already occurred in the Bothnian Bay, northern Baltic Sea, during the Litorina Sea–present-day Baltic Sea transition (L/B transition) (Widerlund and Andersson, 2011), a freshening mainly caused by crustal uplift. The Fennoscandian uplift area has its center located in the Bothnian Bay, showing an uplift-rate around 10 mm per year (Lidberg et al., 2007). This suggests that the sedimentary record of the L/B transition in the Bothnian Bay may be useful to predict future, salinity-related environmental changes in other parts of the Baltic Sea (and other coastal areas), such as bottom-water redox conditions, nutrient regeneration and phytoplankton production. With respect to salinity, the future development of the Baltic Proper, in relation to climate change, may be analogous to the historical development of the Bothnian Bay.

The sediment in the Bothnian Bay has many similarities with sediment in the Arctic Ocean (März et al., 2011), White Sea (Rozanov and Volkov, 2009), and Lake Baikal (Och et al., 2012). They all belong to a family of sediment showing low phytoplankton input, high terrestrial carbon input, low sedimentation rate, oxidized bottom water, low sulfide concentrations, large oxygen penetration depth, pulsed delivery of organic matter, fluctuating redox in upper sediment, and buried Mn–Fe oxyhydroxide layers. Similar to the Bothnian Bay, productivity in the central Arctic Ocean is generally low, and the short vegetation period results in a pulsed annual delivery of organic material to the seafloor. Hence, fluctuating redox is an important characteristic of Arctic Ocean sediments (e.g. Gobeil et al., 2001), similar to the Bothnian Bay (compare Winterhalter and Siivola, 1967; Ingri and Pontér, 1986). Studies of the sediment record in the Bothnian Bay can therefore shed some light on the origin of the Mn bands found in Arctic sediment. An important question is how these sediments respond to climate change.

A current view is that increased freshwater input of nutrients (due to climate change), promotes phytoplankton productivity and therefore eutrophication in the coastal zone (e.g. Finkel et al., 2010). This is also assumed in recent assessments of climate change effects for the Baltic Sea (Neumann, 2010). However, it has been shown that increased freshwater discharge can decrease phytoplankton production, although the river input of nitrogen and phosphorus increases (Wikner and Andersson, 2012, and references therein). The Bothnian Bay today has 3-fold higher freshwater discharge per volume than the Bothnian Sea, but lower phytoplankton carbon production, lower phosphate, and higher nitrate concentrations (Sandberg et al., 2004). We show that

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phytoplankton production has decreased since approximately 3500 years before present. A number of established sediment proxies (Tribovillard et al., 2006), reflecting phytoplankton input and redox, have been evaluated. Marine plankton, and the biogenic particles they produce, influences the biogeochemical cycling and vertical transport also for particle reactive trace elements not actively taken up by plankton for growth (Stewart et al., 2008). We have used Ba, Cd, Ge, Cu, Ni and Zn as proxies for phytoplankton production, Bi, Sb and Sn as proxies for scavenging, and the proxies Mo, U, Re and V to evaluate bottom water and sediment redox. We show that freshening and regression, promote formation of Fe–Mn-oxyhydroxides in the upper part of the sediment. How this barrier influences trace metal cycling and burial in the sediment is specifically addressed, testing the hypothesis "freshening increases the importance of suboxic redox cycling in the sediment".

2. Methods

2.1. Study area

The Gulf of Bothnia is located in the northern part of the Baltic Sea (Fig. 1). The sill at the North Kvark (water depth approximately 25 m, Fig. 1) divides the Gulf of Bothnia into two basins, the Bothnian Sea and the Bothnian Bay. The Bay area is 36,300 km^2 large (average depth of 40 m, maximum depth 148 m) with a catchment area of 269,500 km^2, that includes the northernmost regions of Sweden and Finland. Meta-sediments, granite, granodiorite, gabbro and greenstone of Precambrian age dominate the bedrock, which is covered by glacial deposits from the latest glaciation. During the last glacial period large ice sheets covered the Northern Hemisphere. This additional load depressed the Earth's surface by several hundreds of meters, and the former glaciated land areas are therefore now rising. Considering the crustal uplift, water depth was more or less twice the depth today when the lower part of the core was deposited. Till, the dominating soil type in the Bothnian Bay drainage basin, has a composition close to average upper continental crust (UCC, Öhlander et al., 1991). All the UCC values have been taken from the compilation in Henderson and Henderson (2009).

Paleomagnetic data show no major breaks in the sedimentation, and no turbidity currents effects are seen in the core (Suteerasak et al., submitted for publication). Typical for deep-water sediments in the Bothnian Bay is the lack of bioturbation. Deep-water sediments in the Bothnian Bay generally show distinct layering (Ingri and Pontér, 1986), indicating little disturbance of organisms.

2.2. Sampling

Three 6 m long sediment core were collected in the Bothnian Bay (Fig. 1) from S/V Ocean Surveyor of the Swedish Geological Survey (SGU) in September 2009, using a Benthos gravity-corer with a diameter of 6.6 cm. The core analyzed in this study was collected at a depth of 89 m (latitude 65° 11.46 and longitude 23° 23.80) penetrating approximately 5500 years back in time. Seismic data show a flat bottom with an undisturbed sediment pile. The southernmost core shows a higher sedimentation rate but element concentrations are similar, suggesting that the analyzed core is representative for deep-water bottoms in the Bay. In all 93 sediment layers have been analyzed in the core.

2.3. Dating of sediment

Dating of the sediment is based on paleomagnetic measurements (Suteerasak et al., submitted for publication) and a short summary is given here. For paleomagnetic dating of sediments the direction of remanent magnetization and the reconstructed secular variations of the Earth magnetic field are compared with master curves. Snowball and Sandgren (2002) presented a master curve, FENNOSTACK, based on varve chronologies from seven lake sediment sequences in Sweden and Finland, supported by radiocarbon dating and tephra chronology. The master curve presents smoothed inclination and declination patterns of paleomagnetic data back to ca. 10,000 years before present. Dating is based on visual inspection where maxima and minima of the relative declination and inclination, are matched with corresponding peaks in the master curves. The 6 m long sediment core reached down to approximately 5500 years before present (YBP). The sedimentation rate varied from 0.5 mm/year up to 2.0 mm/year, with the highest rate between ca. 2300 and 1800 YBP, and low sedimentation between 3300 and 2300 YBP.

Sedimentation was around 1 mm/year below 3300 and above 1800 YBP (Fig. 2).

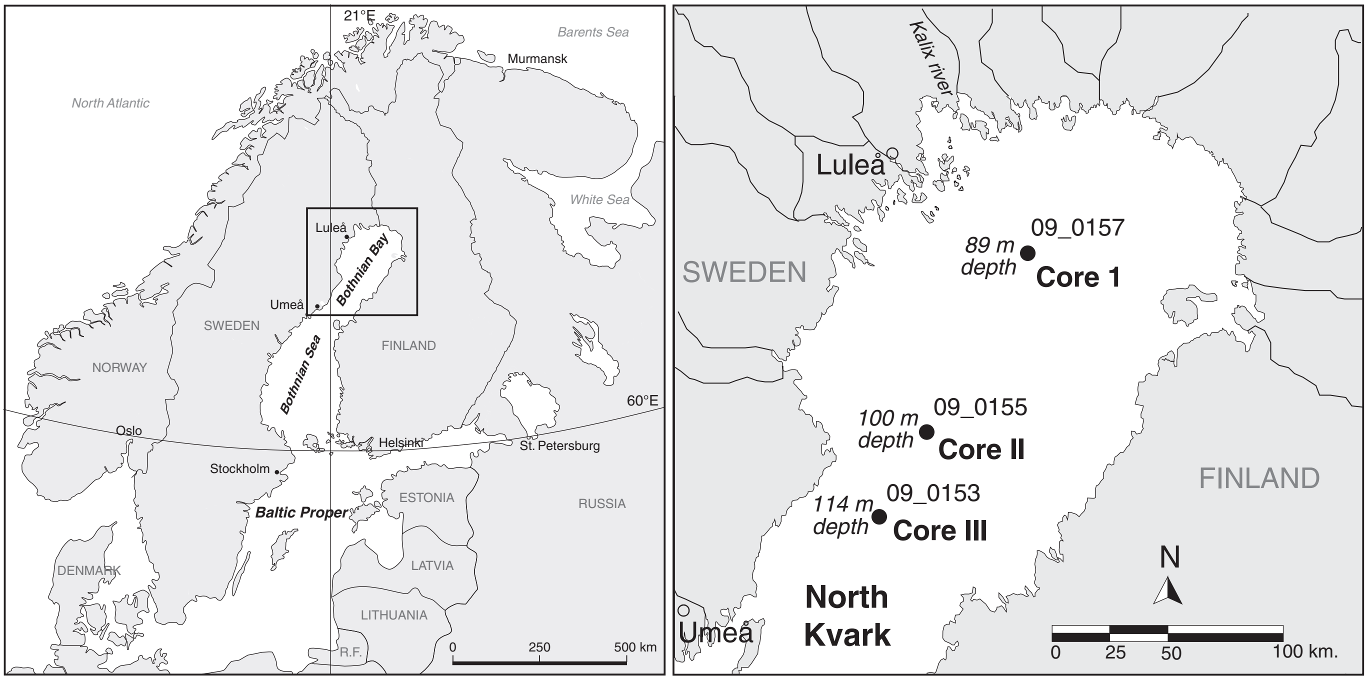

Fig. 1. Sampling locations for 6 m sediment cores. Data from the northernmost core (core I) is presented in this study. Water depth was 89 m.