

Reconstruction of the geochemical history of the Anholt Basin, Southern Kattegat, Baltic Sea

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Introduction

During the Integrated Ocean Drilling Program (IODP) Expedition 347 in 2013, sedimentary records were recovered in the Baltic Sea that cover the Eemian interglacial and Weichselian glacial periods. This non-steady state depositional system was characterized by shifts from limnic to brackish/marine phases over the glacial-interglacial cycle which has subjected the sample location in the Anholt Basin to profound changes in depositional and diagenetic conditions.

Here, comprehensive pore-water and solid-phase data of sediments are presented and used to (1) geochemically characterize the different depositional environments, (2) identify key biogeochemical processes and (3) reveal the influence of the abundance and reactivity of metal oxide phases on the cycling of iron, manganese and sulfur and the formation of authigenic iron sulfides across depositional boundaries.

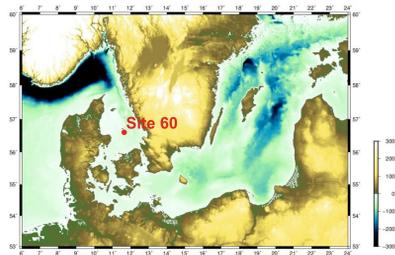


Figure 1: Overview of the Baltic Sea with the location of Drilling Site 60.

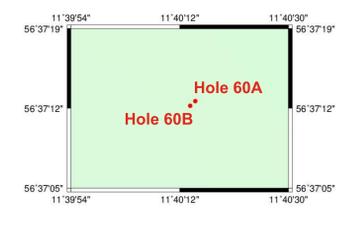


Figure 2: Core locations of Hole 60A and Hole 60B retrieved at Site 60.

Methods

- Onboard sampling of pore water (Hole 60A+B) and sediment immediately after core recovery (Hole 60B) and during the OSP (Hole 60A) in 2014
- Storage of sediment under anoxic conditions at -20°C
- Storage of pore water at 4°C until analyses were performed during the Onshore Science Party (Andrén *et al.*, 2015)

institute	samples	analyses	procedure/quantification
UCR	Hole 60B	sequential sulfur extraction: S ⁰ , AVS, CRS	S ⁰ : Zopfi <i>et al.</i> (2004) Canfield <i>et al.</i> (1986) ZnAc, Cline (1969)
		sequential iron extraction: Fe _{Asc} , Fe _{Dith} , Fe _{Oxal}	Poulton and Canfield (2005) ICP-MS
		separate iron extraction: Fe _{Acet}	Reyes and Torrent (1997)
AWI	Hole 60A + 60B	total acid digestions	e.g., Nöthen and Kasten (2011)
	Hole 60A	sequential sulfur extractions: AVS, CRS	Canfield <i>et al.</i> (1986) AgNO ₃ , gravimetrically
		sequential iron extraction: Fe _{Asc} , Fe _{Dith} , Fe _{Oxal}	Poulton and Canfield (2005) ICP-OES
	Hole 60B	DIC, δ ¹³ C-CH ₄	Hall and Aller (1992) GC-MS

Results and Discussion

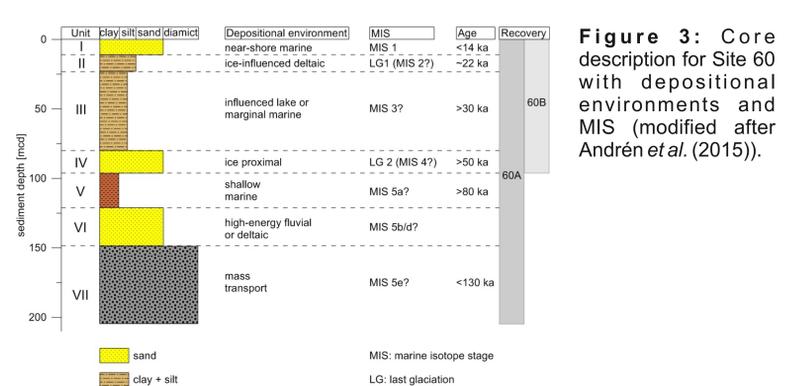


Figure 3: Core description for Site 60 with depositional environments and MIS (modified after Andrén *et al.* (2015)).

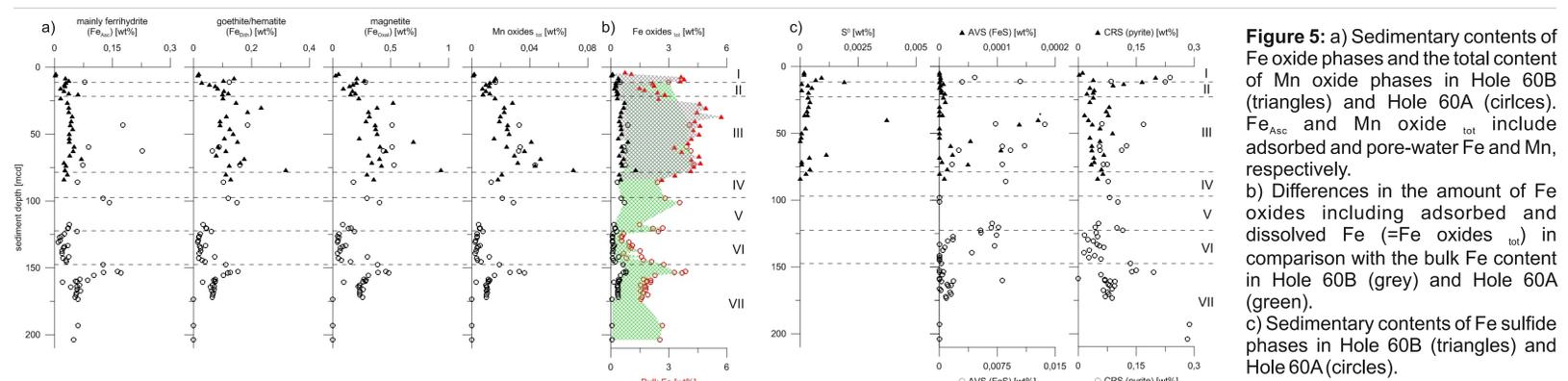
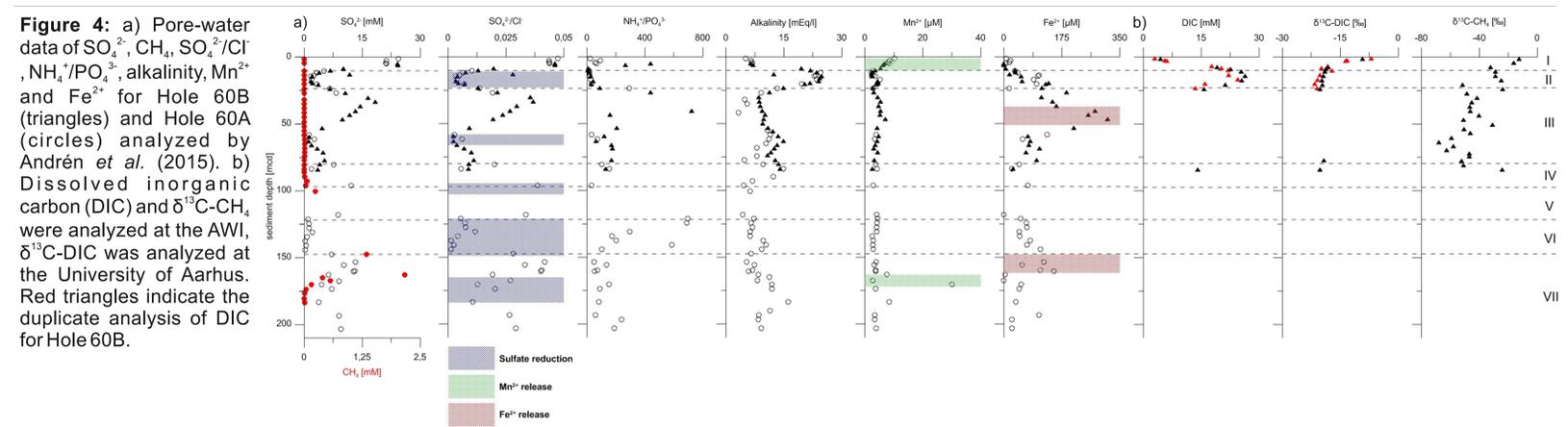


Figure 5: a) Sedimentary contents of Fe oxide phases and the total content of Mn oxide phases in Hole 60B (triangles) and Hole 60A (circles). Fe_{Asc} and Mn oxide_{tot} include adsorbed and pore-water Fe and Mn, respectively. b) Differences in the amount of Fe oxides including adsorbed and dissolved Fe (=Fe oxides_{tot}) in comparison with the bulk Fe content in Hole 60B (grey) and Hole 60A (green). c) Sedimentary contents of Fe sulfide phases in Hole 60B (triangles) and Hole 60A (circles).

- sulfate reduction in Unit II and III indicated by low SO₄²⁻/Cl⁻, NH₄⁺/PO₄³⁻ of ~16, high alkalinity and high DIC (Fig. 4a)
- Mn²⁺ release in Unit I due to the dissimilatory reduction of Mn oxides (cf. Fig. 5a)
- Fe²⁺ liberation in Unit II caused by the reductive dissolution of clay minerals (cf. 5b)
- Mn²⁺ and Fe²⁺ potentially released by metal-mediated AOM in Unit VII, simultaneous AOM-driven sulfate reduction (Fig. 4a)

- highest contents of Fe oxide phases are reached in Unit III and VII
- magnetite is the predominant Fe oxide phase (Fig. 5a)
- the bulk Fe content is on average 7-fold higher compared to Fe oxides_{tot} indicating that a large fraction of Fe is incorporated in clay minerals (Fig. 5b)
- focused formation of Fe sulfides at the Unit II-I, VI-V and VII-VI boundaries (Fig. 5c)
- pyrite is the predominant Fe sulfide phase, note the insignificant amount of AVS in the microbiology Hole 60B
- As S⁰ contents are very low in Hole 60B, oxidation of sulfide is insignificant

Conclusions

In the upper Anholt Basin sediments the dissimilatory sulfate reduction is proposed to be the main microbial process whereas below 93 mcd, methane might be oxidized by sulfate, iron and manganese oxides. Magnetite is the predominant Fe oxide phase. Sedimentary boundaries from limnic to marine conditions are subjected to the focused enrichment of authigenic iron sulfides with the highest degree of diagenetic overprint indicated by significant contents of pyrite. Iron sulfides at the Unit VI-V boundary may be relicts of a former depth position of the SMT.

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Acknowledgments

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