

RESEARCH ARTICLE

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Hypoxia-driven variations in iron and manganese shuttling in the Baltic Sea over the past 8 kyr

Conny Lenz^{1,2}, Tom Jilbert^{2,3}, Daniel J. Conley¹, and Caroline P. Slomp²¹Department of Geology, Lund University, Lund, Sweden, ²Faculty of Geosciences, Department of Earth Sciences, Utrecht University, Utrecht, Netherlands, ³Now at Department of Environmental Science, University of Helsinki, Helsinki, Finland

Key Points:

- Baltic Sea hypoxia alters shelf-to-basin transfer of Fe and Mn
- Extended hypoxia leads to more limited Mn sequestration in sediments
- Modern hypoxia is more widespread than earlier in the Holocene

Supporting Information:

- Supporting Information S1
- Data Set S1

Correspondence to:

C. P. Slomp,
C.P.Slomp@uu.nl

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Abstract The Baltic Sea has experienced three major intervals of bottom water hypoxia following the intrusion of seawater circa 8 kyr ago. These intervals occurred during the Holocene Thermal Maximum (HTM), Medieval Climate Anomaly (MCA), and during recent decades. Here we show that sequestration of both Fe and Mn in Baltic Sea sediments generally increases with water depth, and we attribute this to shelf-to-basin transfer (“shuttling”) of Fe and Mn. Burial of Mn in slope and basin sediments was enhanced following the lake-brackish/marine transition at the beginning of the hypoxic interval during the HTM. During hypoxic intervals, shelf-to-basin transfer of Fe was generally enhanced but that of Mn was reduced. However, intensification of hypoxia within hypoxic intervals led to decreased burial of both Mn and Fe in deep basin sediments. This implies a nonlinearity in shelf Fe release upon expanding hypoxia with initial enhanced Fe release relative to oxic conditions followed by increased retention in shelf sediments, likely in the form of iron sulfide minerals. For Mn, extended hypoxia leads to more limited sequestration as Mn carbonate in deep basin sediments, presumably because of more rapid reduction of Mn oxides formed after inflows and subsequent escape of dissolved Mn to the overlying water. Our Fe records suggest that modern Baltic Sea hypoxia is more widespread than in the past. Furthermore, hypoxia-driven variations in shelf-to-basin transfer of Fe may have impacted the dynamics of P and sulfide in the Baltic Sea thus providing potential feedbacks on the further development of hypoxia.

1. Introduction

Bottom water hypoxia (<2 mg/L O₂) is an increasing problem in coastal marine systems worldwide and is linked to human activities and climate-induced global warming [Carstensen *et al.*, 2014; Diaz and Rosenberg, 2008]. The dynamics of iron (Fe) and manganese (Mn) and other metals in marine sediments respond strongly to changes in bottom water redox conditions [Canfield *et al.*, 1996; Lyons and Severmann, 2006; Wijsman *et al.*, 2001]. Changes in Fe and Mn dynamics can impact the sequestration of phosphorus (P) in sediment, thus affecting the availability of phosphorus in the water column, the development of algal blooms, and the further expansion of hypoxia [Conley *et al.*, 2002; Jilbert and Slomp, 2013a; Vahtera *et al.*, 2007]. Iron oxides can also reduce pore water sulfide concentrations and thus modulate the release of poisonous hydrogen sulfide (H₂S) to the water column [Diaz and Rosenberg, 2008].

Typically, a decline in bottom water oxygen initially leads to enhanced release of both dissolved Fe and Mn from sediments to the overlying water column [e.g., Severmann *et al.*, 2010; Slomp *et al.*, 1997]. However, upon bottom water anoxia, the complete and persistent depletion of oxygen, Fe, and Mn release to the water column can decline markedly. This is generally attributed to depletion of the sediment Fe or Mn source, i.e., the lack of reducible Fe or Mn oxides in surface sediments [Wijsman *et al.*, 2001] or enhanced sequestration of the metals in the sediment as Fe sulfides [Raiswell and Canfield, 2012; Scholz *et al.*, 2014], Mn carbonates, which are associated with Ca and other impurities, or Mn sulfides [Huckriede and Meischner, 1996; Lepland and Stevens, 1998].

In anoxic marine basins adjacent to continental shelves, enrichments of Fe in sediments can record past redox-dependent changes in Fe release and lateral transfer (“Fe shuttling”) from those shelves [Canfield *et al.*, 1996; Lyons and Severmann, 2006]. When such basins contain anoxic, sulfidic (“euxinic”) bottom waters, all incoming shelf Fe is thought to be trapped in the form of Fe sulfides. As a consequence, total iron (Fe) contents normalized to aluminum (Al) are typically elevated compared to oxic environments. The

magnitude of the Fe/Al enrichment is thought to be a function of (1) the escape efficiency of the iron from the shelf, (2) the shelf area (source) to basin (sink) ratio [Raiswell and Anderson, 2005], and (3) the rate of sedimentation of siliciclastic material [Lyons and Severmann, 2006]. In the Black Sea, for example, Fe/Al weight ratios for euxinic basin and oxic sediments range from 0.6 to 1.2 and 0.4 to 0.6, respectively [Lyons and Severmann, 2006].

Manganese enrichments in various anoxic and euxinic basins have also been interpreted within the context of the redox shuttle model. Enrichments in total Mn in the Black Sea, for example, are thought to reflect export from suboxic pore waters of the oxic shelf and scavenging and burial in the deep basin as Mn sulfide [Lyons and Severmann, 2006]. In basins that undergo brief periods of reoxygenation, Mn may be sequestered through the formation of Mn carbonates from Mn oxides precipitated directly after a reoxygenation event [Huckriede and Meischner, 1996; Jakobsen and Postma, 1989; Lepland and Stevens, 1998]. Sediments in most euxinic basins are characterized by manganese depletions, however, because the Mn(II) escapes to the water column where it typically accumulates in dissolved form [Brumsack, 2006; Calvert and Pedersen, 1993; Dellwig et al., 2010].

While the use of both Fe/Al and Mn as redox proxies for ancient euxinic basins is well established [e.g., Duan et al., 2010; Owens et al., 2012; van Helmond et al., 2014], their role as tracers of redox-driven changes in Fe and Mn dynamics on shelves on time scales of decades to thousands of years has been less well explored. A recent study by Eckert et al. [2013] shows the great potential of this approach for Fe. These authors used long-term changes in Fe/Al in the continuously euxinic deep basin sediments of the Black Sea combined with records of molybdenum (Mo), which is a proxy for the presence of sulfide near the sediment-water interface [Erickson and Helz, 2000], to infer changes in redox conditions on the adjacent shelf over the past 7.6 kyr. In their interpretation, periods of low Fe/Al indicate fully oxic shelves, whereas high Fe/Al indicates the occurrence of low oxygen waters on the shelves and an intense transfer of Fe to the deep basin. Using a similar approach, Scholz et al. [2014] used Fe/Al records to constrain variability in Fe export from Peru margin sediments over the past 140 kyr. Their work demonstrates that release of Fe from Peru continental margin sediments is restricted to a narrow "redox window" between oxic and sulfidic conditions [Scholz et al., 2014]. Finally, depth profiles of Fe isotopes and Fe/Al for Holocene sediments in the Baltic Sea [Fehr et al., 2008, 2010; Scholz et al., 2013] also suggest temporal variations in shelf-to-basin transfer of Fe but a link with variations in shelf hypoxia was not established.

The Baltic Sea is an ideal environment to further assess the role of temporal variations in shelf hypoxia on Fe and Mn dynamics and shuttling on decadal to millennial time scales. Since its formation upon the establishment of a connection with the North Sea and its transition from a fresh water lake to a brackish coastal basin, the Baltic Sea has experienced three distinct intervals of extensive hypoxia. These intervals occurred during the Holocene Thermal Maximum, during the Medieval Climate Anomaly and during recent decades [Zillén et al., 2008], and are henceforth referred to as HI_{HTM} (circa 8000–4000 cal years B.P.), HI_{MCA} (circa 1200–750 cal years B.P.), and $HI_{Mod.}$ (since circa 1960), respectively.

Here we assess the impact of variations in past hypoxia on Fe and Mn shuttling in the Baltic Sea using sediment records of Fe/Al, Fe/Ti, and Mn for four locations along a water depth gradient in the eastern Gotland Basin area that cover the past 8 kyr. All records except one (Fårö Deep) capture the transition from the Ancyclus freshwater lake to the brackish/marine Littorina Sea and the first onset of hypoxia in the Baltic Sea. Profiles of loss-on-ignition (LOI) and total organic carbon (TOC) and the presence of laminations are used to detect hypoxic intervals. Profiles of sediment Mo are used as a proxy for anoxic and sulfidic bottom waters at the time of deposition [Helz et al., 1996; Lyons and Severmann, 2006]. Our results highlight a nonlinear response of shelf-to-basin transfer of Fe and Mn in the Baltic Sea to widespread hypoxia over recent decades, distinct differences between intervals of past and present hypoxia and the potential for feedbacks on the further development of hypoxia.

2. Materials and Methods

A total of six multicores and six long cores (6–12 m) were retrieved from four sites at different water depths in the eastern Gotland Basin area during three research cruises in 2009, 2010, and 2011 (Table 1; Figure 1). All sites are currently situated below the halocline and, apart from periods directly after occasional inflows of oxygenated North Sea water [e.g., Matthäus and Franck, 1992], the sediments are currently overlain by

Table 1. Location of the Stations With Corresponding Water Depth, Length of the Retrieved *Littorina* (Brackish/Marine) Sequence, and Mean Sedimentation Rate

Site Name	Cruise (Ship and Date)	Position	Water Depth (m)	Littorina Sea Sequence Length (m)	Mean Sedimentation Rate (mm/yr)
LF3	R/V Pelagia May 2011	57°59.50N 20°46.00E	95	7.30	~1
LL19A & B	R/V Aranda May/June 2009	58°52.84N 20°18.65E	169	3.70	~0.5
F80A & B	R/V Aranda May/June 2009	58°00.00N 19°53.81E	181	~4.10	~0.5
MSM16/1-073-13	R/V Maria S. Merian Sep 2010	57°58.75N 19°53.33E	193.5	7.85	~1

anoxic and sulfidic bottom waters, i.e., are located below the chemocline [Jilbert *et al.*, 2011]. All sediments are fine grained (based on visual observations). LF3 is situated on the eastern slope of the eastern Gotland Basin at 95 m depth whereas LL19 is located at a depth of 169 m further to the north in a separate subbasin of the eastern Gotland Basin. Site F80 and MSM 16/1-073-13 (further referred to as MSM 16/1) are located on the western side of the basin in the Fårö Deep at depths of 181 and 193.5 m, respectively.

2.1. Sediment Sampling

Two sets of multicore and gravity core were taken at sites LL19 and F80 during a cruise with R/V Aranda in 2009 (Table 1). One multicore from each site was directly transferred into a nitrogen filled glovebox and sampled at a depth resolution of 0.5–2 cm. A gravity core from each site was cut into 1 m sections, stored at 4°C and transported to the laboratory at Utrecht University (LL19-A, F80-A). There, each core was sampled in a glovebox at 1 cm resolution and the samples were freeze dried and ground by hand with an agate mortar and pestle.

The second set of multicores (LL19-B, F80-B), as well as the multicores from sites MSM 16/1 (taken during the 2010 R/V Maria S. Merian) and LF 3 (from the 2011 R/V Pelagia cruise) were sliced directly onboard in

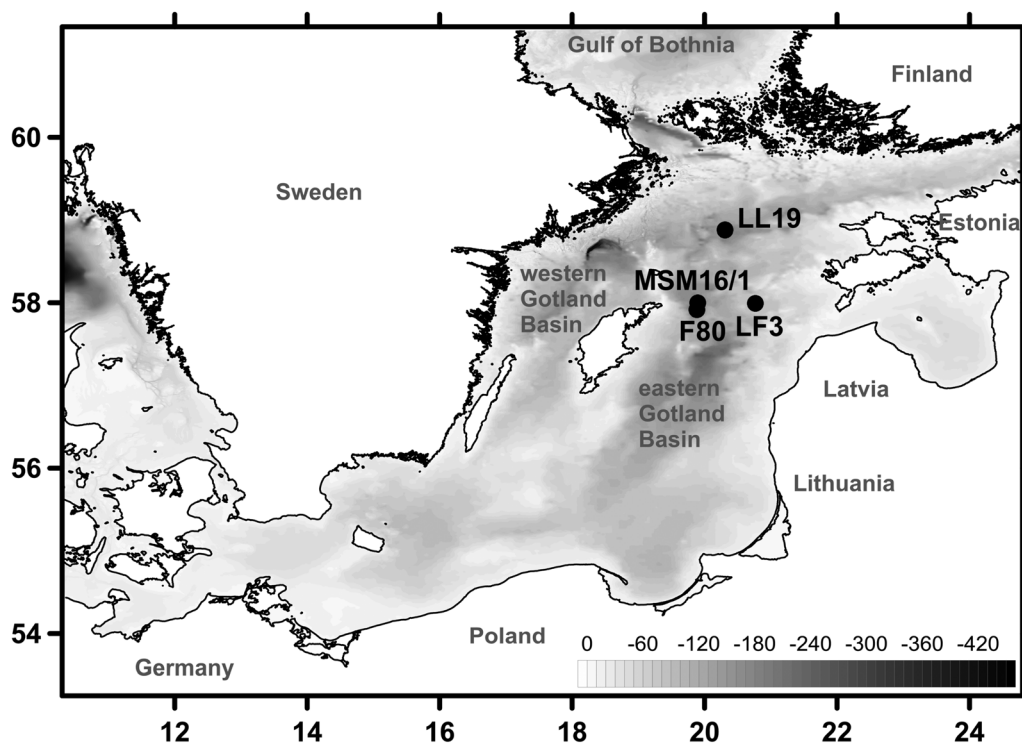


Figure 1. Bathymetric map of the Baltic Sea showing the locations of the four sampling sites.

Table 2. Accuracy of the Measured Elements for the Laboratory and In-House Standards ISE 921

	This Study (n = 9)		Long-Term Average (n = 159)		MM91 This Study (n = 9)	
	Average	SD	Average	SD	Average	SD
	Mn (ppm)	1,143	36	1,126	28	815
Ca (ppm)	43,337	1,691	42,233	1,125	150,233	4,650
Fe (ppm)	31,124	661	30,789	714	26,075	748
S (ppm)	683	31	667	107	6,999	289
Al (ppm)	56,815	1,213	56,147	1,336	41,076	1,282

1 cm slices and transferred to plastic bags. Onboard, the 6–16 m long gravity cores were split into 1 m sections and stored at 4°C until sampling in the laboratory at Lund University. After opening, U-channels were taken along the full length of the core. The U-channels were later used for X-ray fluorescence scanning (XRF). The remaining sediment was sectioned at 1 cm resolution, freeze dried, and ground as described above.

2.2. Sediment Analyses

The discrete samples of cores LL19-A and F80-A were analyzed for total organic carbon (TOC) using a Fisons NA 1500 NCS elemental analyzer at Utrecht University. A relative error of less than 5% for C_{org} was achieved using laboratory reference materials and replicates. Before analysis, 0.3 g of sample was decalcified with 1 M HCl, initially for 12 h and for a further 4 h after addition of new acid [van Santvoort *et al.*, 2002]. The samples were then washed with deionized water, dried in an oven at 60°C, and analyzed. Another 0.1 g of freeze-dried sample was dissolved in a closed Teflon bomb at 90°C using a mixture of 2.5 mL HF (40%) and 2.5 mL HClO₄/HNO₃ for 12 h. After evaporating the acids at 190°C, the resulting gel was dissolved in 1 M HNO₃ and the solutions were analyzed for total Mn, Fe, S, Ca, Mo, and Al by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES; Perkin Elmer Optima 3000). The accuracy and precision of the measurements were established by measuring laboratory reference materials (ISE-921 and the in-house standard MM91) and sample replicates; relative errors were <5% for most reported elements; Table 2.

The loss-on-ignition (LOI) of the sediment, which provides a measure of the organic matter content, was determined for cores F80-B, MSM 16/1, LL19-B, and LF3. The LOI is defined as the weight loss of a sample (0.5 g) after drying at 105°C for 12 h and burning at 450°C for 4 h [Heiri *et al.*, 2001].

Nondestructive X-ray Fluorescence scanning (XRF) was performed on the subsamples taken in U-channels. The measurements were made using a Cox instruments ITRAX core scanner at Stockholm University, equipped with a molybdenum X-ray source and the generator running on 30 kV. The sampling time was set to 60 s. The measurement resolution was between 3 and 0.2 mm and results are given in counts per second. The data are presented at 0.5 cm resolution. All sediment data are included in supporting information.

2.3. Sediment Chronologies

A combination of dating approaches was applied to obtain a sediment chronology for the four sites. The multicore and the upper sediments of the gravity core of site LL19-B were dated with ²¹⁰Pb and pollution lead as described by Zillén *et al.* [2012]. The surface sediment of site F80 was dated by counting annual maxima in high-resolution Mo profiles [Lenz *et al.*, 2015]. The chronology for sites LF3, MSM 16/1, and F80, LL19-A was based on the assumption of synchronous changes in organic matter burial in the Gotland Basin [Jilbert and Slomp, 2013b] and constant rates of sedimentation between tie-points in each core. The age of each tie-point was taken from a reference core from the Gotland Deep dated using a combination of paleomagnetic secular variation (PSV), pollution lead content, and ¹⁴C of benthic foraminifera [Lougheed *et al.*, 2012]. For the sediments below the oldest ages given in Lougheed *et al.* [2012], the major peaks in organic matter were synchronized and a constant sedimentation rate was applied. Given the relatively high uncertainty in the dating before 6.3 kyr B.P., no corresponding age scale is provided in the figures. Note: 0 ka B.P. refers to the year 1950. The dating for core LF3 has a relatively high uncertainty because of the limited number of distinct features that can be used as tie-points. Further details on the age models are provided as supporting information.

3. Results

Two distinct sedimentological units can be distinguished in the sediments at sites LF3, LL19, and MSM 16/1 based on their organic matter contents (LOI, TOC), inorganic geochemistry, and visual observations (Figure 2). The lower unit, which represents sediments from the freshwater Ancylus Lake sequence, consists of very fine-grained light grey clays with generally low contents of organic matter Mn and Fe. The record for LL19 indicates that the lake sediments also contain only minor amounts of Mo and S. The upper unit consists of the brackish/marine Littorina Sea sequence. Here sediments show a gradual increase in organic matter and generally higher contents of Mn and Fe (all sites) and Mo and S (LL19 and F80). There is also a clear change in color in the upper unit where dark grey homogeneous sections are interbedded with dark or light laminated sections. Only the upper unit is present in our core from site F80. The length of the brackish/marine Littorina sequence in the cores ranges from ~ 3.7 to ~ 7.85 m (Table 1). If the freshwater-brackish transition is assumed to have occurred circa 8 kyr B.P. [Zillén *et al.*, 2008], this indicates sedimentation rates in the order of ~ 0.5 to ~ 1 mm/yr.

For sites LF3, LL19, F80, and MSM 16/1, three intervals with enrichments in TOC and/or high values of LOI can be identified within the upper brackish/marine unit. These are related to the three major hypoxic intervals (HI_{HTM} , HI_{MCA} , and $HI_{Mod.}$) occurring over the past 8 kyr (Figures 2 and 3). Organic matter contents increase with water depth. Molybdenum (Mo) contents, where available, generally follow trends in TOC and LOI (Figure 2).

Manganese profiles as measured with XRF for sites LL19 and F80 (Figure 2) confirm the trends in Mn as determined using total dissolution of discrete sediment samples and highlight the high temporal variability. Manganese contents at all sites increase around the start of the HI_{HTM} . Trends in Mn are then variable, with Mn contents generally increasing with water depth. At the shallowest site, the Mn content is mostly below detection. Mn contents at the northern Gotland Basin site (LL19) are generally low with the exception of a maximum at 5.6 kyr B.P. during the HI_{HTM} , a series of maxima directly following the HI_{MCA} and a maximum in the initial phase of the modern interval (Figures 2 and 3). At site F80, Mn contents are higher in oxic periods than during intervals of hypoxia (Figures 2 and 3). At site MSM 16/1, Mn enrichments are present throughout the sediment record with the exception of the material deposited during the later part of the HI_{MCA} and during the modern hypoxic interval. At sites LL19, F80, and MSM 16/1, strong enrichments in sediment Mn and Ca (or Ca/Ti) generally coincide (supporting information).

Sediment contents of Fe, normalized to either Ti (XRF) or Al (discrete samples), generally increase with water depth, with lowest values at the shallowest site (LF3) and highest values at the two deepest sites (F80 and MSM 16/1). Apart from an increase in Fe contents at the start of the HI_{HTM} , there is no clear contrast between hypoxic and oxic periods at site LF3. At all other sites, Fe is enriched in the sediment during the HI_{HTM} and HI_{MCA} . While at LL19, Mo and Fe profiles show similar trends with depth during the past intervals of hypoxia, this does not hold for site F80. Here Fe contents show a decline when Mo is at a maximum. This decline is even more pronounced during the $HI_{Mod.}$ where TOC and Mo contents increase and Fe decreases (Figure 3).

4. Discussion

4.1. Variations of Fe and Mn Sequestration With Water Depth

Sequestration of both Fe and Mn in Baltic Sea sediments generally increases with water depth (Figures 2 and 3) which is in line with the transfer of Mn and Fe from the shelves to deep basins through the shuttle mechanism [Canfield *et al.*, 1996; Lyons and Severmann, 2006]. Scholz *et al.* [2013] obtained evidence for Fe shuttling in the modern Baltic Sea previously from sediment Fe and Mn data for sites along a water depth gradient in the Gotland Deep. Similarly, variations in shelf-to-basin transfer of Fe over the Holocene were assessed using relatively low depth resolution Fe isotope and total Fe records for Gotland Deep sediments [Fehr *et al.*, 2008, 2010].

At the shallowest station, LF3 (at 95 m), little Fe and Mn was sequestered in the sediment after the initial phase of the HI_{HTM} indicating that this site has not acted as a significant sink of Fe and Mn over the past 8 kyr, despite its current position below the chemocline (Figures 2 and 3). At the deeper sites, the trends in Fe and Mn are decoupled and differ from site to site. This is likely related to differences in the controls on formation of Fe sulfides and Mn carbonates and the lateral and vertical input of Mn and Fe. Because of the efficient trapping of Fe by sulfides in the euxinic water column, the trends in Fe may be assumed to directly

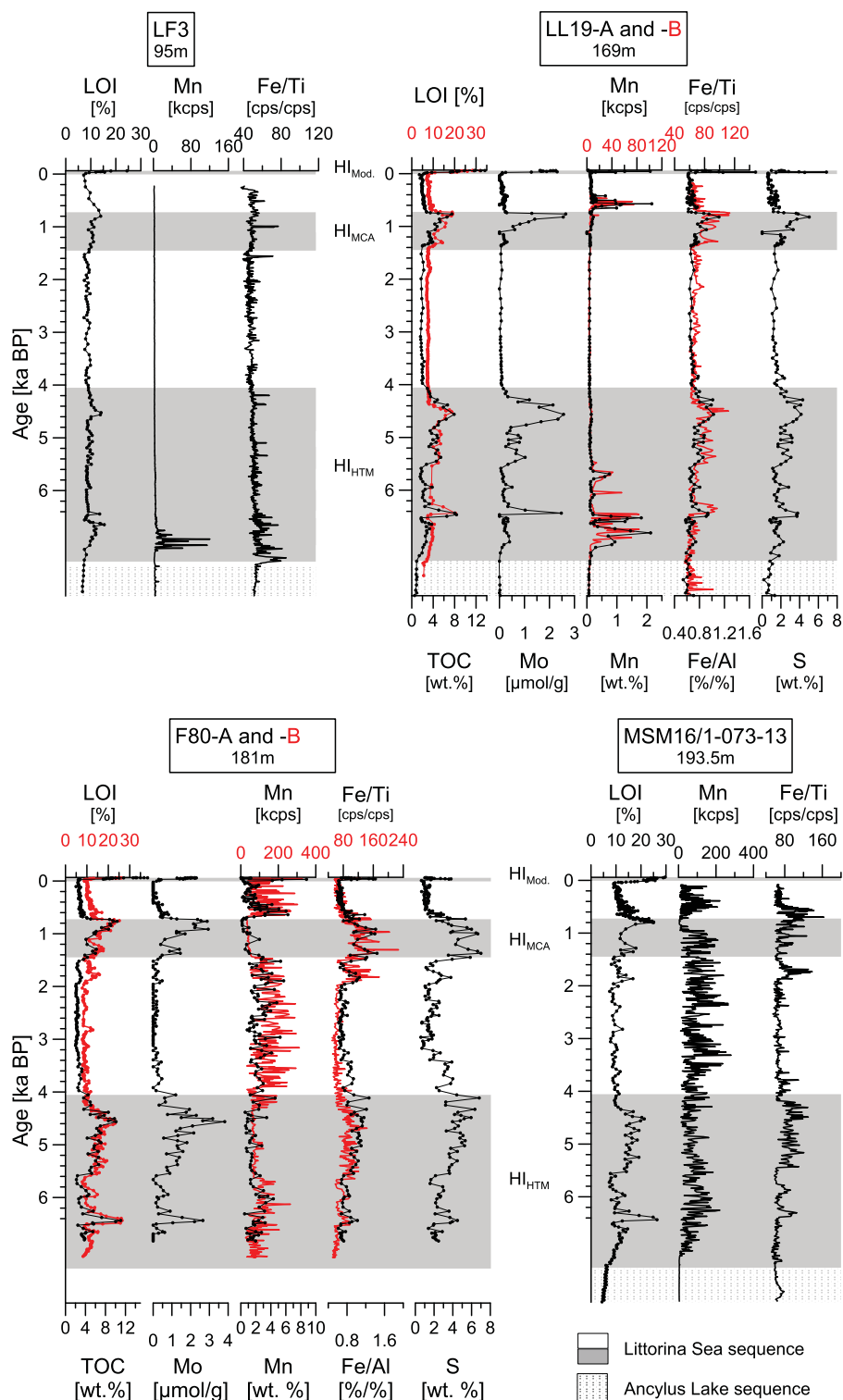


Figure 2. Sediment profiles of selected elements for sites LF3, LL19-A and LL19-B, F80-A and F80-B, and MSM16/1-073-13. Abbreviations: loss-on-ignition (LOI, in wt %), total organic carbon (TOC, in wt %), molybdenum (Mo in $\mu\text{mol/g}$), manganese (Mn, in intensities in kilo-counts per second, kcps or wt %), iron/titanium (Fe/Ti, cps/cps) and iron/aluminum (Fe/Al in wt %/wt %), and sulfur (S, in wt %). The dotted area at the bottom for cores LF3, LL19, and MSM 16/1 indicates the Ancylus Lake sediments. Above follows the Littorina sequence. The horizontal grey bars indicate hypoxic intervals as defined by *Jilbert and Slomp [2013b]* corresponding to maxima and minima in Mo/Al ratios.

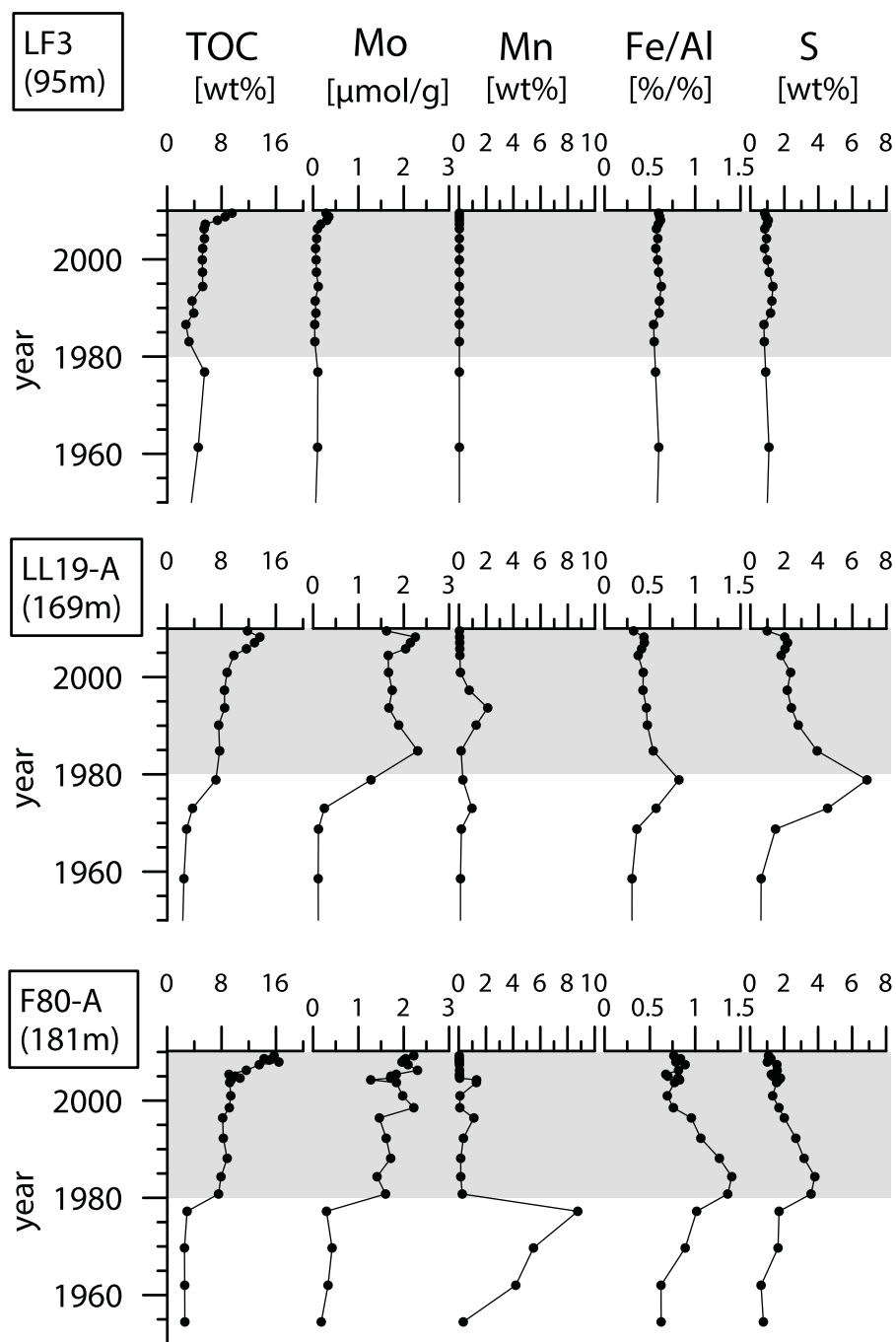


Figure 3. Sediment profiles of total organic carbon (TOC in wt %), molybdenum (Mo in $\mu\text{mol/g}$), manganese (Mn, in wt %), iron/aluminum (Fe/Al, in wt %/wt %), and sulfur (S, in wt %) for multicores from sites LF3, LL19-A, and F80-A.

reflect inputs from lateral Fe shuttling from the shelf, potentially modulated by oxidation and precipitation of Fe from the water column following North Sea inflows [Scholz *et al.*, 2013]. Mn enrichments, in contrast, may be formed through various mechanisms including precipitation of Mn carbonates following reoxygenation of the deep euxinic basins linked to North Sea inflows [e.g., Huckriede and Meischner, 1996] or in deep bathymetric depressions with strong focusing of particulate Mn [Slomp *et al.*, 1997].

4.2. Widespread Mn Burial After Lake-Brackish/Marine Transition and First Onset of Hypoxia

The distinct rise in TOC and the color changes of sediment at depth indicate that, except for F80, all our cores capture the transition from the organic-poor sediments of the freshwater Ancylus Lake to the more

organic-rich, brackish/marine Littorina Sea [e.g., *Ignatius et al.*, 1981; *Sohlenius et al.*, 2001]. During the lake phase, productivity was low [*Andrén et al.*, 2000] and oxygen penetration into the sediments was therefore likely high. The rise in primary productivity during the lake-brackish marine transition [*Andren et al.*, 2000; *Willumsen et al.*, 2013], in combination with the increased stratification, likely led to a gradual decline in oxygen concentrations in the bottom waters in the Gotland Basin. As a consequence, laminated sediments enriched in Mo were deposited (Figure 2) [*Jilbert and Slomp*, 2013b].

A strong enrichment in sediment Mn is observed at the beginning of the HI_{HTM} at all sites (Figure 2). This enrichment has also been described previously for sediments in the Bornholm Basin [*Sohlenius et al.*, 2001]. Such widespread deposition of Mn is unique in the Littorina sediment sequence and requires a significant external or internal source of Mn to the Baltic Sea at this time. The retreat of the Scandinavian Ice Sheet during the late Pleistocene and early Holocene may have increased erosion and transport of Mn-bearing particulates from land to the Baltic Sea in meltwater streams and rivers, providing an external Mn source. However, the underlying lake sediments may also have acted as an internal source of Mn to the young Baltic Sea [*Sohlenius et al.*, 2001]. Surface sediments in the presently well-oxygenated and low-salinity Bothnian Sea contain abundant Mn oxides [e.g., *Ingri and Pontér*, 1986; *Slomp et al.*, 2013], offering a possible analogue for conditions throughout the Baltic Sea at the onset of salinization. A widespread surface-sediment Mn pool would likely have been mobilized during the expansion of hypoxic conditions, and recaptured into the sediments during short-lived reoxygenation events in the early HI_{HTM} , to be buried permanently as carbonates [*Huckriede and Meischner*, 1996; *Neumann et al.*, 1997; *Sohlenius et al.*, 1996; *Sternbeck and Sohlenius*, 1997]. The observed coincidence of Mn enrichments during the early HI_{HTM} with enrichments of Ca, at the three deepest sites (supporting information) suggests widespread sequestration of Mn in the carbonate phase.

4.3. Response of Shelf-to-Basin Transfer of Mn to Hypoxia

The three distinct intervals of hypoxia during the Littorina brackish/marine water phase (HI_{HTM} , HI_{MCA} , and HI_{Mod}) can be clearly identified using the depth profiles of organic matter (LOI and TOC) and, where available, Mo, for Gotland Basin sites [*Jilbert and Slomp*, 2013b; *Zillén et al.*, 2008] (Figures 2 and 3). The distinct increase in organic matter content with water depth in the Gotland Basin is consistent with enhanced preservation of organic matter linked to reduced ventilation at greater water depth, as suggested for the Baltic Sea based on modern sediments [*Jilbert et al.*, 2011]. Such a relationship of bottom water redox conditions with water depth has also been observed in other anoxic marine basins, such as the eastern Mediterranean Sea during sapropel formation [*De Lange et al.*, 2008].

During all three intervals of hypoxia, Mn burial at our sites in the Gotland Basin area shows a similar water-depth variation, which is likely the combined result of changes in redox conditions, lateral and vertical inputs of Mn oxides, and sources of Mn(II), and alkalinity in the sediment pore water (Figure 4) [*Lenz et al.*, 2015]. During oxic intervals, Mn is only sequestered at the deepest sites, F80 and MSM 16-1 (Figures 2, 3, and 4a). After the initial phase of the HI_{HTM} with widespread sequestration of Mn in the sediment, presumably linked to frequent oxygenation events (Figure 4c), Mn burial declined at three out of four of our sites and the Mn likely accumulated as Mn(II) in the water column. This trend toward low Mn burial during hypoxic events has been interpreted to reflect high sulfide concentrations in the pore water and bottom water [*Lenz et al.*, 2014, 2015]. Under such conditions, Mn oxides formed after inflows can no longer persist in the sediment for long enough to allow their conversion to Mn carbonates and the Mn is released back to the water column (Figure 4e). The ongoing but moderate burial of Mn at MSM 16/1 suggests that in the deepest parts of the basin, Mn carbonate could still form during the late HI_{HTM} despite the likely euxinic bottom water conditions (based on the Mo records for the adjacent F80 site), presumably because of strong focusing of particulate Mn into bathymetric depressions, and highly alkaline pore waters [*Lenz et al.*, 2015].

Similarly to the HI_{HTM} , Mn burial during the HI_{MCA} and HI_{Mod} was nearly absent at most sites. During these two intervals, the rise in TOC and Mo at the Fårö Deep (F80) site coincides with a severe decline in Mn. Even at the deepest site (MSM 16/1), a rise in organic matter (LOI) and a decline in Mn during the HI_{MCA} can be observed. This suggests that sulfide concentrations in the pore water of the surface sediments and in the bottom waters of the deep basins were higher in the final phase of the HI_{MCA} and during the HI_{Mod} than during the HI_{HTM} . For reference, we note that during our sampling at site F80, sulfide concentrations in the bottom water and pore water of the surface sediments were ~ 45 and $\sim 1000 \mu M$, respectively [*Lenz et al.*, 2015].

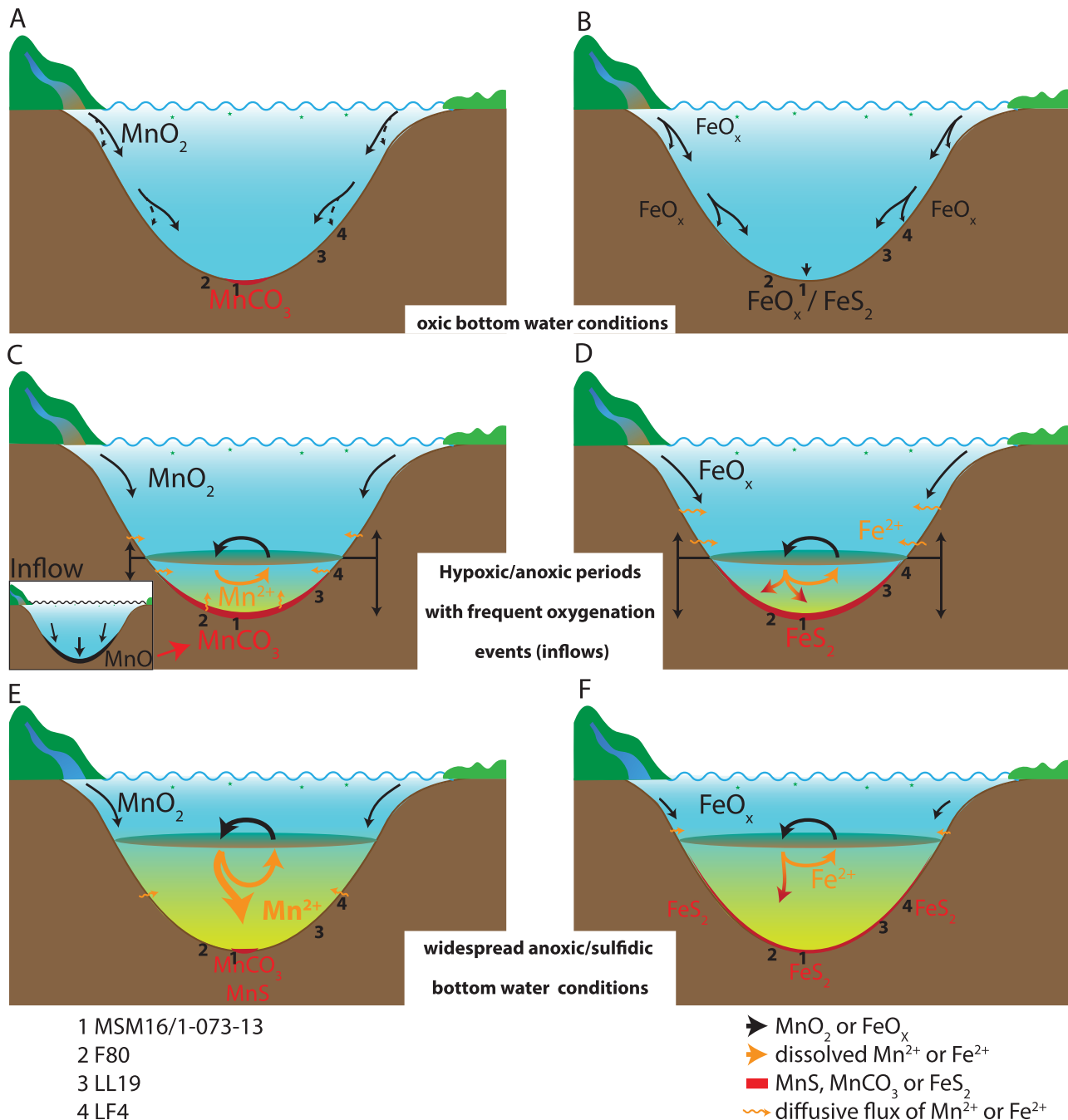


Figure 4. Schematic of the shelf-to-basin transfer of (a, c, and e) manganese and (b, d, and f) iron in relation to the expansion of hypoxic conditions in the water column. Figures 4a and 4b are representative for long lasting oxygenation of the water column during the Littorina phase. Figures 4c and 4d show the Baltic Sea during intervals of hypoxia where frequent inflows contribute to formation of Mn carbonates from Mn oxides (e.g., Hl_{HTM} and early Hl_{MCA}) and where Fe shuttling from shelves contributes to burial of FeS_2 in the deep basins. Figures 4e and 4f reflect the situation during intervals of widespread anoxia and sulfidic bottom water as observed during the late Hl_{MCA} and the Hl_{Mod} , where burial of Mn and Fe in the sediments of the deep basins is more limited.

4.4. Response of Shelf-to-Basin Transfer of Fe to Hypoxia

At all sites except LF3, Fe/Al, and/or Fe/Ti, profiles for the past intervals of hypoxia are more similar to those of TOC and/or LOI than to those of Mn, indicating that to a first approximation, hypoxic intervals were characterized by enhanced remobilization of Fe from shelf sediments relative to oxic conditions and subsequent burial of the Fe in the deep basins, presumably in the form of iron sulfide minerals (Figure 4d). The continued release of Fe from shelf sediments throughout the Hl_{HTM} and most of the Hl_{MCA} suggests that shelf

bottom waters were neither oxic nor sulfidic at this time, thus providing a window of opportunity for Fe escape throughout the hypoxic interval.

Closer observation of the individual sites shows variation from this basic pattern with water depth. Thus, for example, trends in TOC, Mo/Al, and Fe/Al at site F80 (at 181 m) and LOI and Fe/Ti at site MSM 16/1 (at 193.5 m) are less clearly linked than those of TOC, Mo/Al, and Fe/Al at site LL19 (at 169 m). At F80 and MSM16/1, burial of Fe associated with the HI_{MCA} occurs for a more extended period before and after the boundaries of the event and peaks before the timing of maximum euxinia, as deduced from the Mo/Al record for F80.

A yet more pronounced deviation in the Fe/Al profile from that of Mo/Al is observed during the HI_{Mod} , at both F80 and LL19 (Figure 3). Here an increase in Fe sequestration began before the onset of euxinia in the deep basins and peaked around 1980, when the Mo/Al profiles indicate that euxinia first appeared. Present-day Fe/Al values are equal to or only slightly higher than those observed before 1960, when the basin was still largely oxygenated [Carstensen *et al.*, 2014]. The decoupling of the trends in Mo and Fe suggests that the modern hypoxic interval is different from the earlier intervals of hypoxia in that the shallower shelf sediments today no longer act as a major source of reactive Fe. Similarly, the HI_{MCA} apparently experienced maximum shelf-to-basin transfer of Fe before the timing of maximum deep basin euxinia. There are three likely explanations for these observations. First, there has been an extremely rapid expansion of areas with hypoxic and with sulfidic bottom waters over the past decades [Carstensen *et al.*, 2014]. As a consequence, the shelf (source) to basin (sink) ratio for Fe in the Baltic Sea has decreased. Whereas Raiswell and Anderson [2005] assumed a shelf-to-basin ratio of 99 for the Baltic Sea in their comparison of various modern basins, the ratio now likely lies at least an order of magnitude lower and could be closer to a value of 11 (given the area of the Baltic Sea of 390,000 km² and an estimated maximum area with sulfidic bottom waters of ~34,000 km² [Carstensen *et al.*, 2014]). Second, the escape efficiency of Fe from the remaining shelf source areas has likely decreased because sediments below hypoxic bottom waters may retain more Fe in the form of Fe sulfides thus allowing less Fe to escape to the deep basins (Figure 4f). Both these effects may have also operated (to a lesser degree) in the HI_{MCA} . A third factor influencing Fe dynamics during the modern event is that the retention of Fe in coastal areas, i.e., in estuaries, bays, and nearshore areas including the Archipelago seas, may also have increased linked to expanding hypoxia in the coastal zone [Conley *et al.*, 2011] and the associated increase in sulfide concentrations in pore waters in the coastal zone. Increased trapping of Fe as Fe-sulfide in the sediment in nearshore areas may have compensated for the increased input of Fe that has been reported for rivers along the Swedish coastline [Kritzberg and Ekström, 2012].

Notably, the ratios of Fe/Al in surface sediments in the euxinic basins of the Baltic Sea studied here range from 0.3 to 0.8 (Figure 3), which is lower than the range of 0.6–1.2 reported for Holocene Black Sea sediments [Lyons and Severmann, 2006]. Two key differences between the Baltic Sea and Black Sea are the shelf-to-basin ratios (~11 for the Baltic Sea as estimated above versus 0.4 for the Black Sea) [Raiswell and Anderson, 2005] and the sediment accumulation rates. The latter are approximately tenfold higher in the Baltic Sea when compared to the Black Sea, assuming that the brackish/marine deposit formed over the past 8 kyr has a thickness of ~400 and ~40 cm in each system, respectively (Table 1) [Eckert *et al.* 2013]. The ~28-fold higher reactive Fe supply in the Baltic is therefore expected to undergo approximately tenfold more siliciclastic dilution leading to roughly threefold higher Fe/Al ratios in the Baltic Sea, all other factors being equal. We interpret the lower Fe/Al ratios observed in the Baltic Sea as evidence that the escape of Fe from shelf sediments in the modern Baltic Sea is less efficient than in the Black Sea.

4.5. Potential Feedbacks on Hypoxia

Iron(II)-phosphates and Mn-Ca-carbonates may constitute significant burial phases for phosphorus in the euxinic basins of the present-day Baltic Sea [Jilbert and Slomp, 2013a]. A reduction in the supply of Fe oxides to and sequestration of Mn in the sediments of these deep basins may have reduced the sediment burial of inorganic P in recent decades. As a consequence, recycling of P relative to carbon may have been enhanced further [e.g., Algeo and Ingall, 2007; Jilbert *et al.*, 2011], thus contributing to a positive feedback on primary productivity [Vahtera *et al.*, 2007].

Variations in input of Fe oxides from the shelves may also impact the dynamics of hydrogen sulfide in the water column of anoxic basins, through the formation of iron-monosulfides and pyrite in the water column and sediment [Middelburg and Levin, 2009]. Using the age model of Lenz *et al.* [2015] and corresponding sediment accumulation rates at F80 (0.04 g cm⁻² yr⁻¹), a Fe flux to the sediment for the modern peak at

the start of the HI_{Mod} . of $\sim 0.5 \text{ mol m}^{-2} \text{ yr}^{-1}$ can be calculated. Because 1 mol of Fe will react with 2 mol of H_2S to form FeS_2 , this Fe flux could remove $\sim 1 \text{ mol m}^{-2} \text{ yr}^{-1}$ of H_2S . Assuming a water column of $\sim 100 \text{ m}$ below the redoxcline at this site, this input of Fe oxide could thus remove on average $\sim 10 \mu\text{M}$ of H_2S per year. This removal of H_2S is of the same order of magnitude as the rate of increase of H_2S in the water column at the onset of the modern hypoxic interval [Jilbert and Slomp, 2013b; Lenz et al., 2015]. The enhanced Fe shuttling, which reached its maximum at the start of the HI_{Mod} , began at least a decade earlier and may have initially buffered sulfide concentrations in the water column, delaying the development of water column euxinia. The sediment record for F80 suggests that the Fe shuttle is more muted since approximately the year 2000. As a consequence, hydrogen sulfide-rich waters may more readily develop following an inflow than at the start of the modern hypoxic event.

Interestingly, the general trend in Fe/Al at site F80 (and LL19) for the HI_{MCA} differs from that for the modern interval. Instead of a rapid increase in Fe/Al and then a decline, the Fe/Al ratio remains elevated (above the background characteristic for oxic periods) throughout the HI_{MCA} . This suggests that the shelf regions surrounding the deep basins continued to shuttle Fe to the deep basins throughout most of the HI_{MCA} , implying that the shelf regions were not as low in oxygen during the HI_{MCA} than they are at present. Furthermore, it suggests that sulfide concentrations in the sediments and water column were buffered by incoming Fe oxides throughout the HI_{MCA} . The stronger changes in shelf-to-basin transfer of Fe suggest that modern hypoxia is more intense and is geographically more widespread than hypoxia during medieval times.

5. Conclusions

In this study, the influence of variations in hypoxia on shelf-to-basin transfer of Fe and Mn in the Baltic Sea over the Holocene was assessed using sediment cores from the Gotland Basin area. The sediment records confirm that the deeper basins are characterized by generally more intense accumulation of Fe and Mn. We show that directly after the transition from the freshwater (Ancyclus) lake to a brackish/marine basin (Littorina Sea), Mn burial greatly increased at all sites. Possible sources of Mn include a remobilization of Mn from the lake sediments where Mn may have been present as oxides in the surface sediments and enhanced input of Mn eroded from land. Generally, sediment Fe was enriched relative to Al during the three major intervals of hypoxia observed in the Gotland Basin, i.e., the HI_{HTM} , HI_{MCA} , and HI_{Mod} . Manganese enrichments increased with water depth but sequestration was reduced upon the development of persistent euxinia, such as observed at the end of the HI_{MCA} and during the HI_{Mod} . The variations in Fe and Mn shuttling from shelves during the Holocene in the Gotland Basin area may have impacted the availability of phosphorus and sulfide in the water column and thus may have modulated the development of euxinia in the deep basins, especially during the initial stages of the modern hypoxic interval and during the HI_{MCA} . The present-day reduction in shelf-to-basin transfer of Fe in the Gotland Basin area is thus not only the result of hypoxia but may also have contributed to the recent intensification of hypoxia [Carstensen et al., 2014].

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