Establishment of eukinic conditions in the Holocene Black Sea

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ABSTRACT

The paleoenvironmental evolution of the Black Sea is closely linked to the ingestion of Mediterranean seawater over the Bosporus sill after the Last Glacial Maximum. We have reconstructed the temporal and spatial development of the Black Sea suboxic chemocline, which divides oxic surface water from anoxic, sulfidic (eukinic) deep water. By combining high-resolution geochemical records of bulk parameters (carbonate, total organic carbon, sulfur), trace metals (Cu, Mo, V), and an isotopic proxy ($\delta^{56}$Fe) from seven sediment cores in the Black Sea, we generated a single composite geochemical core log that serves as a reference archive for the entire basin. Our proxy records reflect the changing depositional and redox conditions of the Black Sea and permit us to estimate the inflow budget of Mediterranean seawater throughout the Holocene. Our data indicate a gradual rise of the chemocline until ca. 5.3 ka, when suboxic waters flooded the shelf for the first time. Trace metal and isotopic inventories document one major descent of the chemocline since the onset of brackish/marine conditions before the present stable situation was established.

INTRODUCTION

The Black Sea is an enclosed marine basin where the ingestion of Mediterranean seawater over the shallow Bosporus sill is causing stratification of the water column. The stable pycnocline coincides with the chemocline, and stagnant sulfidic deep water favors the deposition of organic-rich sediments (sapropels). There is an ongoing debate whether the seawater ingestion into the basin during the Holocene sea-level rise occurred catastrophically in one single step (the Great Flood; Ryan et al., 1997), or more gradually over a longer time period (Aksu et al., 2002; Degens and Ross, 1974; Yanko-Hombach et al., 2007). The suboxic chemocline, separating oxic surface from sulfidic deep water, is currently at ~150 m water depth (Huang et al., 2000). Its vertical migration ultimately governs the redox development in the Black Sea. Using metal abundances (Fe and Mo) and Fe isotopes ($\delta^{56}$Fe), we unravel the Holocene history of the chemocline and provide evidence for the temporal and spatial development of eukinic conditions in this type location of a restricted basin (Brumsack, 2006; Calvert and Pedersen, 1993).

Sedimentary enrichment of Fe has been observed in sapropels from the Black Sea and other restricted basins (e.g., Anderson and Raiswell, 2004). The most widely accepted explanation for these characteristic enrichments implies the lateral transfer of reactive Fe from suboxic shelf sediments to the sulfidic water column of euxinic basins, where it is sequestered into syngenetic pyrite (Canfield et al., 1996; Wijsman et al., 2001; Wilkin et al., 1997). In this model, microbially induced diagenetic reactions within the suboxic shelf sediments cause mobilization of reactive Fe with a light Fe isotope composition, which is laterally conveyed in the suboxic chemocline. Strong support for this Fe shuttle model comes from the covariation between bulk sedimentary Fe/Al ratios and Fe isotope composition (Severmann et al., 2008). Euxinic sediments with elevated Fe/Al ratios have lower $\delta^{56}$Fe values due to the basinward transport of isotopically light Fe.

Water column studies show elevated concentrations of dissolved and particulate Fe within the chemocline (Lewis and Landing, 1991), corroborating the model of enhanced lateral Fe transfer along this oxygen-depleted interface (Lyons and Severmann, 2006). Consequently, the efficiency of the Fe shuttle is linked to the depth of the chemocline and therefore the surface area of either slope or shelf sediments intercepting with suboxic waters (Anderson and Raiswell, 2004). Changing sea level may exert additional control on the vertical migration of the chemocline (Arthur and Sageman, 2005).

In the Black Sea sediments, Mo is a tracer for both seawater inflow and water column redox conditions. While Mo is the most abundant trace metal in oxic seawater, it may undergo significant drawdown under euxinic conditions (Bertine, 1972). At dissolved sulfide concentrations >11 µM, Mo is transformed into highly particle-reactive thiomolybdates or Mo-Fe-S nanostructures that are quantitatively scavenged from the water column (Erickson and Helz, 2000; Helz et al., 2011). Low-deep-water Mo concentrations (Neubert et al., 2008) document the almost complete transfer of the water column Mo inventory to the sedimentary pool. Thus, sedimentary Mo records of restricted basins broadly reflect the amount of inflowing seawater and at the same time serve as euxinia proxies under marine conditions, independent from the Mo removal pathway via sulfide or organic matter (Brumsack, 1989; Algeo, 2004; Algeo and Lyons, 2006; Helz et al., 2011).

SAMPLES AND METHODS

Instead of showing individual sediment cores, we combine high-resolution data sets from seven sites throughout the basin (Fig. DR1 in the GSA Data Repository1) in a composite geochemical core log (CGCL) that serves as a reference for the entire Black Sea (Fig. 1; Fig. DR3). This approach is based on the assumption that water column processes in the Black Sea occurred synchronously on a basinwide scale, only influenced by variations in local sedimentation rate. All cores originate from the euxinic part of the water column. GeoB gravity cores follow a transect through the western basin (R/V Meteor expedition M51/4); cores from station 8, 14, and 22 were recovered in the northwestern part of the basin and off the eastern Anatolian coast (R/V Meteor expedition M72/5). A single composite core instead of seven cores illustrates basinwide similarities and highlights ubiquitous environmental changes in the geological record of the Black Sea after seawater ingestion. Unit boundaries are based on lithological and geochemical criteria. Mean ages of the unit boundaries were taken from data in the literature (for details, see the Data Repository). For constructing the CGCL, we further considered distinct geochemical characteristics such as Mo, total organic carbon (TOC), and Fe maxima. Based on these adjustment points, core depths were normalized to a reference depth scale. CGCL depicts the averaged and normalized vertical element distribution in Black Sea sediments.

Major and trace elements were analyzed by X-ray fluorescence and inductively coupled plasma–optical emission spectrometry. TOC and total sulfur (TS) were measured by coulometry and infrared spectrometry. Iron isotope compositions, reported here as $\delta^{56}$Fe/$^{56}$Fe delta notation normalized to average igneous rocks ($\delta^{56}$Fe), were determined by...
into the basin, HS– accumulated in euxinic unit II sediments and started significant postdepositional overprinting. Following the inflow of seawater marine (anoxic and/or euxinic) conditions, increasing productivity, changing TOC and Mo/Al values reflect the transition from limnic (oxic) to (Arthur and Dean, 1998; Degens and Ross, 1974). Synchronously increased Fe enrichments (Fe/Al > 0.55; Wedepohl, 1991) are characterized by light Fe isotope values (Figs. 1 and 2; Fig. DR3). This Fe/Al peak documents the first establishment of a fully expanded euxinic water column in the Black Sea (Fig. 1), where the chemocline impinged on the shelf with its much larger surface area compared to the slope, causing an intensified shuttling of Fe with a low $\delta^{56}$Fe signature (Figs. 1, 2, and 3B). Increasing Mo/Al ratios record the growing Mo reservoir fed by continuing seawater inflow, and an increasing Mo drawdown owing to the expansion of euxinic water masses. The TOC maximum reflects higher surface productivity, but is also affected by improved organic matter preservation in a sulfidic water column (Calvert and Pedersen, 1993).

We estimate the past seawater influx into the Black Sea from the gradual Mo increase between the unit II-III boundary and the Mo peak in unit II (for details, see the Data Repository). Based on today’s deep-water salinity of 22, the Mediterranean seawater inflow increased from 110 km$^3$/a at the onset of Mo enrichment at ca. 8 ka (Piper and Calvert, 110) to 350 km$^3$/a at the Mo maximum in unit II, which is comparable to the present 305 km$^3$/a inflow (Özsoy and Ünlüata, 1997). A simple budget calculation demonstrates that the water column of the Holocene Black Sea was replenished at least twice during deposition of unit II to account for the Mo enrichment in the sapropel. This is in line with a renewal time of ~5.3 ka.

Figure 1. Composite geochemical core logs of Fe/Al, Mo/Al, and total organic carbon (TOC), comprising data of seven cores (see text and Samples and Methods discussion); colored areas reflect standard deviation; vertical dashed lines are average shale values (Wedepohl, 1991); horizontal dashed line displays first ingression of Mediterranean seawater (ca. 9.0 ka; Soulet et al., 2011); horizontal gray bars depict unit boundaries; beige bar depicts first establishment of shelf suboxia (ca. 5.3 ka).

multicollector–inductively coupled plasma–mass spectrometry (Thermo Scientific NEPTUNE). For further details on samples and methodology, see the Data Repository.

RESULTS AND DISCUSSION

Common features observed in all Black Sea sediment cores are distinct Fe enrichments (Fe/Al > 0.55; Wedepohl, 1991) in the Holocene section. According to the Fe shuttle hypothesis, these enrichments may be explained by the impingement of suboxic chemocline waters on the broad Black Sea shelf. Suboxia on the shelf caused diagenetic mobilization of Fe with low $\delta^{56}$Fe values and its trapping in euxinic basin sediments (Lyons and Severmann, 2006; Severmann et al., 2008). In turn, during chemocline descent, Fe/Al ratios should be significantly lower (and $\delta^{56}$Fe values higher) in basin sediments (Figs. 2 and 3).

An initial Fe enrichment coinciding with the unit II-III boundary (ca. 7.6 ka) is characterized by light Fe isotope values (Figs. 1 and 2). This boundary documents the onset of anoxia in Black Sea bottom waters, followed by a chemocline rise and the expansion of euxinic conditions (Arthur and Dean, 1998; Degens and Ross, 1974). Synchronously increasing TOC and Mo/Al values reflect the transition from limnic (oxic) to marine (anoxic and/or euxinic) conditions, increasing productivity, changing redox conditions, and a growing Mo inventory as seawater entered the Black Sea basin.

The onset of marine conditions at the unit II-III boundary led to significant postdepositional overprinting. Following the inflow of seawater into the basin, HS– accumulated in euxinic unit II sediments and started migrating downward into limnic unit III sediments. Here it reacted with oxide-bound Fe, creating opposing gradients of Fe$^{2+}$ and HS–. The sulfidization front, currently located well below the sapropel, is marked by a distinct band of diagenetic FeS precipitates (Neretin et al., 2004). Continuous supply of sulfide from bacterial sulfate reduction in the sapropel forms an effective barrier to upward-migrating Fe$^{2+}$. Mass balance calculations confirm the downward movement of the reaction front (Jørgensen et al., 2004). Consequently, a diagenetic origin of the Fe enrichment observed in unit II can be excluded.

Further upcore, a prominent Fe enrichment at ca. 5.3 ka is observed in the central part of unit II, coinciding with maxima in TOC, Mo/Al, and light Fe isotopes (Figs. 1 and 2; Fig. DR3). This Fe/Al peak documents the first establishment of a fully expanded euxinic water column in the Black Sea (Fig. 1), where the chemocline impinged on the shelf with its much larger surface area compared to the slope, causing an intensified shuttling of Fe with a low $\delta^{56}$Fe signature (Figs. 1, 2, and 3B). Increasing Mo/Al ratios record the growing Mo reservoir fed by continuing seawater inflow, and an increasing Mo drawdown owing to the expansion of euxinic water masses. The TOC maximum reflects higher surface productivity, but is also affected by improved organic matter preservation in a sulfidic water column (Calvert and Pedersen, 1993).

Figure 2. Depth profiles of Fe/Al (black dots—measured data; solid lines—two-point average smoothing; gray areas—standard deviation of the measurement) and $\delta^{56}$Fe (large dark gray dots; note inverted scale) for gravity cores GeoB 7604, GeoB 7608, and 22-GC-7. Vertical dashed lines show average shale Fe/Al ratio of 0.55 (Wedepohl, 1991); error bars represent 2σ standard deviation; gray horizontal bars are unit boundaries; mbsl—meters below sea level.

The return to very low Fe/Al and relatively heavy Fe isotope values in the upper unit II (Figs. 1 and 2) documents the descent of the chemocline. Slope sediments previously sulfidized by direct contact with euxinic waters could not serve as a source for dissolved Fe, so the Fe shuttle was
shut off (Fig. 3A). At the same time, Mo/Al ratios gradually decrease from maximum values in unit II to lower values at the base of unit I (Fig. 1), either due to stronger hydrographic restriction or increased river input and freshening of the Black Sea basin (Repeta, 1993; van der Meer et al., 2008). While our geochemical data do not allow us to distinguish between these two processes, decreased seawater input due to a shoaling of the Bosporus sill by tectonic activity or a local sea-level regression seems very plausible (Brückner et al., 2010). Despite diminished seawater input, euxinic conditions still persisted in the deeper water column, as documented by the decreasing but still relatively high TOC and Mo/Al values (Fig. 1). Mo removal from the euxinic water column outbalanced its replenishment by deep-water renewal.

Elevated Fe/Al ratios with light $^{56}$Fe values in unit I, similar to the peak seen in unit II (Figs. 1 and 2), indicate the recurring rise of the chemocline to its present location on the shelf break (Fig. 3B). Surface productivity, organic matter preservation (TOC profiles in Fig. 1), and chemocline depth (as documented by relatively invariant Fe/Al and $^{56}$Fe; Fig. 2) are fairly stable throughout unit I with some minor fluctuations ~200–300 a ago (Lyons et al., 1993; Repeta, 1993). Unit I represents the stable marine stage of the Black Sea basin, with a rather constant and balanced inflow and outflow of marine and brackish waters.

Our data strongly suggest a variable efficiency of the Fe shuttle mechanism. In unit I sediments, an excess Fe fraction of 22% explains the Fe/Al CGCL. A simple inventory calculation demonstrates that the Fe shuttle mechanism does not significantly deplete the Fe pool in Black Sea shelf sediments (see the Data Repository). Based on our average unit I $^{56}$Fe value of $-0.25\%$, isotope mass balance calculations suggest an Fe shuttle contribution of $\sim36\%$. This value is in broad agreement with the previous value.

The Black Sea chemocline oscillation reported here agrees with earlier studies on syngenetically formed pyrite framboids (Wilkin and Arthur, 2001) and biomarkers, which suggest that the chemocline was located below the photic zone during deposition of unit III, upper unit II, and unit I, but intersected with the photic zone during deposition of lower unit II (Repeta, 1993; Huang et al., 2000). Our results confirm these studies, as we find low Fe/Al ratios in units III and upper unit II, but higher Fe/Al ratios in lower units II and unit I (Fig. 1).

**CONCLUSION**

Our high-resolution composite geochemical core log and Fe isotope data demonstrate that the establishment of the chemocline and euxinic conditions in the Black Sea water column did not occur in one single step. High-resolution Fe/Al records show that within unit II, ca. 5.3 ka, suboxic waters spread over large areas of the shelf for the first time, initiating the transfer of Fe from the shelf toward the basin by the Fe shuttle mechanism. In parallel, the gradual sedimentary Mo increase documents that Mediterranean seawater inflow was comparable to today. After this first fully euxinic stage, a prominent chemocline drop and concomitant decrease in Fe/Al ratios and Mo inventory is observed, due either to hydrographic
reduction or increased fluvial input. With the onset of unit I ca. 2.7 ka, the Fe shuttle was re-established, and the chemocline reached its present position. We show that sedimentary archives in anoxic systems like the Black Sea precisely record basinwide changes in water column processes. Similar budget calculations may be important for the interpretation of trace metal records in ancient anoxic settings.

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Reconstructing the history of euxinia in a coastal sea

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Areas of the coastal ocean where oxygen is low or absent in bottom waters, so-called dead zones, are expanding worldwide (Diaz and Rosenberg, 2008). Increased inputs of nutrients from land are enhancing algal blooms, and the sinking of this organic matter to the seafloor and subsequent decay leads to a high oxygen demand in bottom waters. Depending on the physical characteristics of the coastal system, this may initiate periodic or permanent water column anoxia and euxinia, with the latter term implying the presence of free sulfide (Kemp et al., 2009). Global warming is expected to exacerbate the situation, through its effects on oxygen solubility and water column stratification. In many modern coastal systems, anthropogenic changes are superimposed on natural variation and lack of knowledge of such variation makes the prediction of future changes in water column oxygen challenging (e.g., Grantham et al., 2004). That natural drivers alone can be the cause of widespread coastal anoxia is evident from studies of greenhouse periods in Earth’s past, including the oceanic anoxic events of the Cretaceous and Toarcian (Jenkyns, 2010).

Sediment proxy records are essential to any reconstruction of variations in anoxia and euxinia on time scales beyond several decades to a century. A variety of biological and geochemical indicators can be used for this purpose, such as the presence of the remains of benthic and pelagic organisms, laminations, biomarkers for eukaryotes or prokaryotes, and inorganic geochemical and mineralogical signatures in the sediment, and ideally, these methods are combined. Sediments that are deposited below a euxinic water column are, for example, typically enriched in organic carbon, sulfur, iron, and trace metals such as rhenium and molybdenum (Gooday et al., 2009). Recent additions to this paleo-redox toolbox are the isotope systems of Fe and Mo (Lyons et al., 2009). Reconstruction of the temporal changes in the oxic-anoxic interface (chemocline) in the water column forms a key step in the identification of the external drivers and internal feedbacks that contribute to anoxia and euxinia in a given system. In their study of sediments from the Black Sea, Eckert et al. (2013, p. 431 in this issue of Geology), make this step by providing, for the first time, a basin-wide reconstruction of the evolution of the chemocline in this silled coastal basin over the Holocene.

Silled basins in humid areas such as Kau Bay (Indonesia), the Baltic Sea, and the Black Sea, are particularly sensitive to low oxygen conditions because of salinity stratification and associated reduced vertical mixing (Kemp et al., 2009). All these inland seas have an intriguing history and were originally coastal lakes that were transformed to marine basins due to postglacial sea-level rise. Kau Bay is only semi-euxinic, and is subject to incursions of low-oxygen non-sulfidic bottom waters that alternate with periods of anoxic, sulfidic bottom waters (Middelburg et al., 1991). The Baltic Sea also alternates between redox states: it experienced various periods of low oxygen over the Holocene, but is currently subject to a human-induced period of anoxia, with its bottom waters largely oxic around 1900 CE (Conley et al., 2009). The Black Sea is the largest euxinic basin in the world and differs in being permanently euxinic. This is the result of the strong stratification that developed after its fore-runner fresh water lake became connected to the Mediterranean Sea through the narrow, shallow Straits of the Bosporus at ca. 9 kyr B.P. Water column anoxia developed across the deep basin from ca. 7.5 kyr B.P. onward (Degens and Ross, 1974), and the chemocline is presently located at ~100 m depth.

Strong variations in the geochemical and paleo-ecological composition and genetic signature of the sediments in the Black Sea provide testimony that the conditions in the water column have been far from constant over the past ~7.5 kyr. Two phases of deposition are generally distinguished based on visual characteristics of the sediments. Following the onset of anoxia, a finely laminated, dark, organic-rich sediment layer formed first (Unit II), followed by deposition of alternating microlaminae of calcareous (white) and organic- and clay-rich material (black) from ca. 2.6 kyr B.P. to the present (Unit I). The shift from Unit II to Unit I was originally attributed to the invasion of the coccolithophore Emiliania huxleyi when salinity rose above 11 (Arthur and Dean, 1998). However, genetic analyses show that this calcifying haptophyte colonized the photic zone of the Black Sea shortly after the connection to the Bosporus, and the Unit I–II transition marks the moment that coccoliths began to be preserved in the sediments (Coolen et al., 2009).

The delayed appearance of Unit II on the slopes of the basin has been taken as an indicator of a slow rise of the chemocline following the onset of anoxia (Degens and Ross, 1974). The rise was fast enough, however, for the chemocline to reach the photic zone by the time of deposition of the lower part of Unit II, as indicated by the presence of biomarkers for photosynthetic green sulfur bacteria (Sinnighe Damsté et al., 1993; Repeta, 1993). Results of similar analyses for the upper part of Unit II suggested a subsequent descent of the chemocline followed by re-establishment in the photic zone during deposition of Unit I. At the time, controversy remained about the temporal and spatial variability in the position of the chemocline, and the extent to which the water column and photic zone remained euxinic throughout deposition of Units I and II. This debate was partially resolved when Wilkin et al. (1997) showed that the size of the pyrite frambooids in Units I and II were in line with a continuously euxinic water column. Using a composite record of sediment Fe, Mo, and Fe-isotopes derived from data for nine sites throughout the basin, Eckert et al. (2013) now confirm the evolution of Black Sea euxinia, as suggested in these earlier studies, and provide a more consistent and basin-wide timing for the series of events.

The variation in strength of the ‘Fe shuttle’ forms the heart of their reconstruction. This term is used to describe the lateral transfer of Fe released from suboxic shelf sediments to the deep basin. The authors use their Fe/Al record as a direct indicator of the position of the chemocline, where low Fe/Al indicates a weak shuttle with a chemocline impinging on the slope. A high Fe/Al, in contrast, indicates a chemocline allowing suboxic water to spread over part of the shelf and supporting an intense Fe shuttle. The authors also make use of the fact that Mo data can be used to reconstruct the hydrography of a basin, which for the Black Sea allows an estimate of the infl ow of Mediterranean seawater. Fe isotope analyses bolster the argument for the shelf-source of Fe. The emerging timeline is as follows (Unit II): (1) a gradual rise of the chemocline over a period of ~2 kyr following the onset of anoxia at ca. 7.6 kyr B.P., (2) fully developed euxinic conditions with an ascent of the chemocline onto the shelf at ca. 5.3 kyr B.P., (3) a subsequent descent of the chemocline, and (Unit I) (4) establishment of the chemocline in its present-day position at the shelf break from 2.7 kyr B.P. onward.

But this is not the full story. Besides a good timeline for euxinia in the Black Sea, we need to understand the hydrographic and biogeochemical processes that drove these changes in redox conditions, and there much
work still needs to be done. The evolution of the salinity in the basin, for example, is not well constrained. Recent qualitative reconstructions of salinity based on various proxies suggest that values of surface water salinity in the Black Sea rose until ca. 3 kyr B.P., followed by a gradual freshening to present-day values (van der Meer et al., 2008; Coolen, 2011). Possible causes for the freshening include an increase in fluvial discharge and decreased evaporation (Giosan et al., 2012). An associated increase in stratification may have contributed to the shallowing of the chemocline at the onset of the deposition of Unit I. Also, the processes leading to the increased total organic carbon (TOC) in Unit II as compared to the overlying and underlying units are not well understood. The high TOC is frequently interpreted as an indicator of enhanced nutrient availability and productivity following the infl ow of Mediterranean seawater, and transition of limnic (oxic) to marine (anoxic and euxinic) conditions (also see Eckert et al., 2013). However, the sources of the nutrients fuelling this productivity have not been identified and whether, for example, phosphorus release from sediments or river water is more important is still an open question. Finally, the cause of the descent of the chemocline after ca. 5.3 kyr B.P. remains unknown. While Eckert et al. (2013) propose a decreased seawater input or increased river input as potential causes, van der Meer et al. (2008), in contrast, suggest that the absence of a shallow chemocline can be best explained by the high sea-surface salinity at the time.

Despite the open questions, the Eckert et al. (2013) study is important because it provides a more solid timeline and integrated view of the evolution of euxinia in the Black Sea, which is highly useful for assessments of climatic and other drivers of temporal change. The tools used can also be applied to better interpret sediment records from other marine systems, both modern and ancient, and can thereby aid in the assessment of the time scales of a possible decline into, and recovery from, wide-scale anoxia and euxinia. Such knowledge is important in a warming world where water column deoxygenation in the coastal zone is becoming more and more common.

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