

# Extreme change in sulfide concentrations in the Black Sea during the Little Ice Age reconstructed using molybdenum isotopes

G.L. Arnold<sup>1\*</sup>, T.W. Lyons<sup>2</sup>, G.W. Gordon<sup>3</sup>, and A.D. Anbar<sup>3,4</sup>

<sup>1</sup>Max Planck Institute for Marine Microbiology, 28359 Bremen, Germany

<sup>2</sup>Department of Earth Sciences, University of California, Riverside, California 92521-0423, USA

<sup>3</sup>School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404, USA

<sup>4</sup>Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1404, USA

## ABSTRACT

The Black Sea is the largest and most studied anoxic basin in the modern world. Much of this research has focused on the redox structure of the water column, specifically on the driving forces behind variations in the position, stability, and structure of the oxic-anoxic interface (chemocline). However, none of these studies has been able to quantify the historical sulfide concentrations associated with the changes in chemocline depth. Using the isotopic composition of molybdenum in sediments as a proxy, we show for the first time that varying concentrations of dissolved sulfide can be fingerprinted in historical systems. Our molybdenum isotope data indicate that in the region of the Bosphorus inlet, the chemocline rose more than 65 m, reaching concentrations over 100  $\mu\text{M}$  sulfide in the bottom water ca. 300 yr B.P. This historical shoaling of the chemocline and extreme change in bottom-water sulfide concentration exceeds the modern changes that have been observed directly and attributed to anthropogenic influences on the Black Sea chemistry/hydrology. The first cold interval of the Little Ice Age, when temperature and circulation changes occurred in the Black Sea basins, may have provided the natural trigger for this extreme rise in bottom-water sulfide concentrations.

## INTRODUCTION

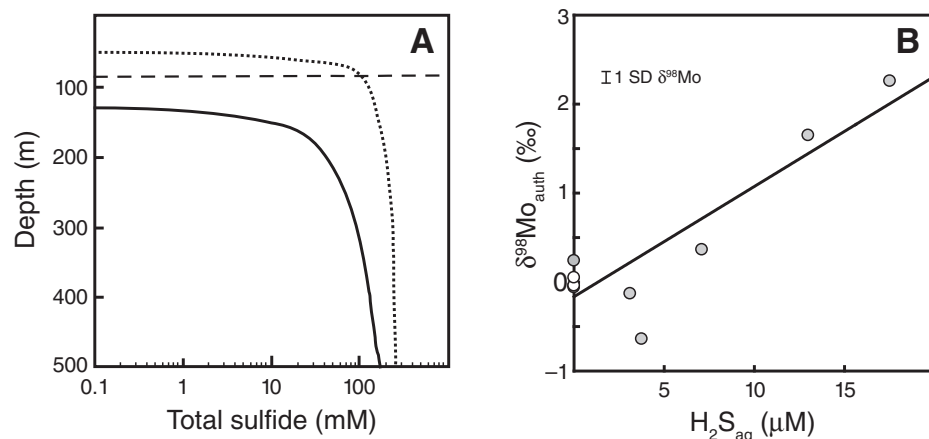
The sulfide interface in the modern Black Sea is located at a depth of  $\sim 80$  m in the central western basin, and deepens to 130 m along the basin margin in the area of the Bosphorus inlet (Lyons et al., 1993; Repeta, 1993; Manske et al., 2005). Several lines of geochemical evidence, including sedimentary sulfur, iron, and manganese concentrations, as well as organic biomarkers, suggest that the depth of the sulfide interface in the Black Sea has varied in the past and that sediments deposited on the presently oxic shelf in the area of the Bosphorus inlet were covered by sulfidic bottom waters for a period of time during the past 300 yr (Lyons et al., 1993; Repeta, 1993; Damsté et al., 1993; Lyons and Severmann, 2006; Severmann et al., 2008). Although these geochemical proxies yield information about the presence or absence of sulfidic bottom waters in the past, they are unable to quantify the concentration of sulfide at any point in time. Such quantification is essential to characterizing the magnitude of natural perturbations as a baseline against which potential anthropogenic impact can be assessed.

The molybdenum (Mo) isotope system can provide quantitative information on historical trends in bottom-water sulfide concentrations. Molybdenum isotope data ( $\delta^{98}\text{Mo}$ ; see the GSA Data Repository<sup>1</sup>) have previously been used

as a proxy for the global distribution of anoxic conditions in ancient oceans (e.g., Barling et al., 2001; Siebert et al., 2003; Arnold et al., 2004; Wille et al., 2007; Pearce et al., 2008) but are sensitive to local redox conditions, requiring high and persistent sulfide concentrations in bottom waters for effective use of the global proxy (Gordon et al., 2009; Dahl et al., 2010). Due to this sensitivity, the  $\delta^{98}\text{Mo}$  of sediments may reflect not only the presence/absence of sulfide but also its concentration. This relationship between the  $\delta^{98}\text{Mo}$  of modern sediments and bottom-water concentrations of dissolved sul-

fide in the Black Sea was explored by Neubert et al. (2008), who surveyed surface sediments deposited under bottom-water sulfide concentrations less than, approaching, and greater than the geochemical switch point (aqueous hydrogen sulfide concentration,  $[\text{H}_2\text{S}_{\text{aq}}]$ ,  $\sim 11 \mu\text{M}$ ) described by Erickson and Helz (2000). Neubert et al. (2008) found that sediments on the Black Sea margin show a linear increase in the authigenic Mo isotope composition ( $\delta^{98}\text{Mo}_{\text{auth}}$ ; see the Data Repository) with increasing bottom-water  $[\text{H}_2\text{S}_{\text{aq}}]$  up to  $\sim 20 \mu\text{M}$  (Fig. 1B). The linear relationship between these parameters is attributed to fractionations among the oxythiomolybdate intermediate species ( $\text{MoO}_{4-x}\text{S}_x^{2-}$ ) that form at the onset of sulfidic conditions during the transformation from molybdate ( $\text{MoO}_4^{2-}$ ) to tetrathiomolybdate ( $\text{MoS}_4^{2-}$ ) (Tossell, 2005). For  $[\text{H}_2\text{S}_{\text{aq}}]$  greater than  $\sim 20 \mu\text{M}$ , the  $\delta^{98}\text{Mo}_{\text{auth}}$  of the sediments remains generally constant despite the continuing increase in sulfide concentration with increasing depth (Neubert et al., 2008; Nögler et al., 2011), presumably reflecting complete conversion to tetrathiomolybdate.

These findings suggest that the  $\delta^{98}\text{Mo}$  preserved in sediments deposited under euxinic water conditions is, within a certain range, related to bottom-water sulfide concentrations. Because the  $\delta^{98}\text{Mo}$  of modern sediment



**Figure 1. A:** Total sulfide concentration with depth in the water column of the Black Sea (after Neretin et al., 2001). Solid and dotted lines represent the sulfide concentration profile today and at ca. 300 yr B.P., respectively. **B:**  $\delta^{98}\text{Mo}_{\text{auth}}$  in surface sediments versus concentration of  $\text{H}_2\text{S}_{\text{aq}}$  in overlying bottom waters. Open circles ( $\delta^{98}\text{Mo}$  for oxic sites, this study) and filled circles (data from Neubert et al., 2008) establish a linear relationship:  $\delta^{98}\text{Mo}_{\text{auth}} \pm 0.08 = (0.1239 \pm 0.0214)[\text{H}_2\text{S}_{\text{aq}}] - (0.1653 \pm 0.1515)$ ,  $R^2 = 0.79$ ; all errors are one standard deviation (1 SD).

\*E-mail: gail.l.arnold@gmail.com.

<sup>1</sup>GSA Data Repository item 2012179, description of methods, historical sulfide calculations, supporting figures, and data table, is available online at [www.geosociety.org/pubs/ft2012.htm](http://www.geosociety.org/pubs/ft2012.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

records the bottom-water sulfide concentration at the time of deposition, a  $\delta^{98}\text{Mo}$  profile for a sediment column can reveal historical variation in bottom-water sulfide concentrations for that site. If the relationship of Neubert et al. (2008) is representative of conditions expressed more broadly in the Black Sea over both space and time, sedimentary  $\delta^{98}\text{Mo}$  can be used to track the historical changes in bottom-water sulfide concentration, something that has so far escaped quantification.

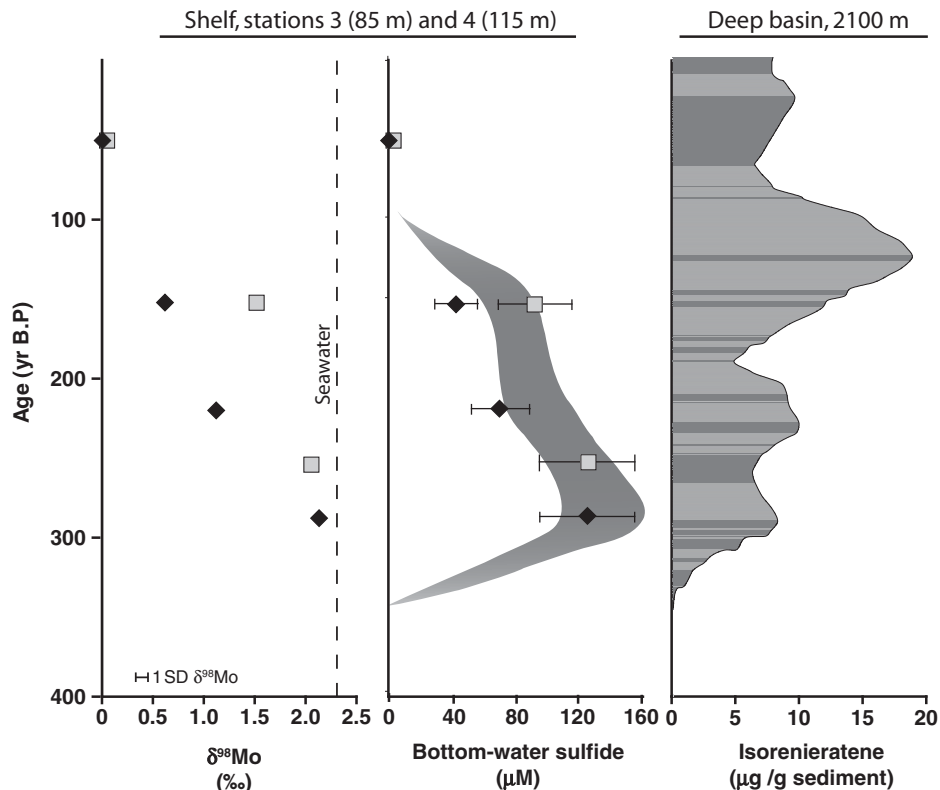
## SAMPLES AND METHODS

We analyzed the Mo isotope composition ( $\delta^{98}\text{Mo}$ ) of sediments from multiple stations in the Black Sea. Stations 3 and 4 (Lyons et al., 1993) are located on the presently oxic western shelf near the inlet of the Bosphorus at water depths of 85 and 115 m, respectively. Stations 16 and 17 are located in the oxic region of the Bay of Sinop. We measured the  $\delta^{98}\text{Mo}$  at various depths in the surface sediment at all four stations. Stations 3 and 4 are of particular interest because both have been identified by other geochemical proxies to record past periods of euxinic bottom waters (Lyons et al., 1993; Lyons and Severmann, 2006; Severmann et al., 2008). The water column at these stations is presently oxic, with undetectable sulfide in the sediment pore water. Cesium isotope and  $^{210}\text{Pb}$  data from station 3 indicate that these sediments have experienced only minimal homogenization that perhaps broadened but did not obliterate the high-resolution chemostratigraphy (Lyons, 1991; Lyons et al., 1993). We specifically generated  $\delta^{98}\text{Mo}$  profiles from these stations over the upper ~18 cm with the goal of reconstructing past chemocline properties and variability over the past ~300 yr (Fig. 2; Table DR1 in the Data Repository). Stations 16 and 17 were used to establish a lithogenic baseline for Mo concentration and  $\delta^{98}\text{Mo}$  representative of persistently oxic shelf sediments.

Molybdenum and other elemental concentrations were measured by inductively coupled plasma–mass spectrometry (ICP-MS), either using a multielement external standard solution combined with internal standards to monitor drift in instrument sensitivity or using isotope dilution with a calibrated  $^{97}\text{Mo}$  spike solution. Molybdenum isotope compositions were determined by multiple-collector ICP-MS (Thermo Neptune<sup>®</sup>) following the analytical procedure outlined by Gordon et al. (2009) (see the Data Repository).

## FIDELITY OF THE MO ISOTOPE PROXY

The use of the Mo isotope signature of sediments as a paleoproxy for bottom-water chemistry is not always straightforward. Debate exists, for example, as to whether the Mo isotope signature might reflect pore-water chemistry



**Figure 2.** Mo isotope compositions of sediments and calculated bottom-water sulfide concentrations (station 3, filled diamonds; station 4, filled squares) and isorenieratene (after Repeta, 1993, his box core 3). Due to low Mo concentrations, the Mo isotope composition for samples older than 100 yr B.P. was corrected for the detrital Mo contribution (Table DR1 [see footnote 1]). Sediment ages for stations 3 and 4 were determined from an average sedimentation rate of  $0.059\text{ cm yr}^{-1}$  based on an extrapolation of  $^{210}\text{Pb}$  relationships (Lyons et al., 1993). The start and end of sulfidic bottom waters at station 3 is constrained by the appearance of isorenieratene in the deep basin and the return to oxic sedimentary  $\text{Mn}_T/\text{Al}$  values at station 3, respectively (Fig. DR1; Table DR3; Lyons and Severmann, 2006). The shaded area in the central plot illustrates the rapid rise, followed by gradual retreat, of the sulfide interface.

instead. Although there have been no studies directly addressing this question, the combined sulfide and Mo data available from a site on the Romanian shelf break in the Black Sea may provide insight. During a cruise of the R/V *Petr Kottso* in September 1997, an ~5 m long core was retrieved from a site on the Romanian shelf break (station 6; Nägler et al., 2005; Jørgensen et al., 2004). At the time of core retrieval, the concentration of total dissolved sulfide in the bottom water was  $75\text{ }\mu\text{M}$ , and an increase from a value of  $110\text{ }\mu\text{M}$  ( $\sim 24\text{ }\mu\text{M H}_2\text{S}_{\text{aq}}$ ) just below the sediment-water interface to nearly  $400\text{ }\mu\text{M}$  ( $\sim 89\text{ }\mu\text{M H}_2\text{S}_{\text{aq}}$ ) was observed through the Unit I sediments (Jørgensen et al., 2004). Nägler et al. (2005) measured the Mo isotope composition of the sediment at nine depths over ~5 m of core. Unfortunately, in the study of Nägler et al. (2005), no samples were analyzed in the time windows 500–350 yr B.P. or 350–250 yr B.P., where we would expect to observe the maximum regression and shoaling of the chemocline, respectively. Therefore, we cannot validate a shoaling of the chemocline in the study area of Nägler et al. (2005) contemporaneous with what

we describe from the area of the Bosphorus inlet. However, and importantly, in view of the sulfide switch point required to preserve the heaviest Mo isotope composition ( $\sim 11\text{ }\mu\text{M H}_2\text{S}_{\text{aq}}$ ; Erickson and Helz, 2000), the pore-water sulfide concentrations were well above that critical value. Hence, the sediments were also exposed to pore-water sulfide concentrations well above the proposed switch point.

If Mo enrichment and the isotopic composition are dominated by pore-water chemistry, the sediments analyzed by Nägler et al. (2005) should reflect heavy Mo isotope compositions, as observed in the surface sediments in the deep basin today—i.e.,  $\delta^{98}\text{Mo} = +2.36\text{‰} \pm 0.09\text{‰}$  (one standard deviation [1 SD]) (Table DR2)—where bottom-water sulfide concentrations are similar. Instead, the Mo isotope composition of the Unit I sediments reported by Nägler et al. (2005) is in all cases lighter than this by  $0.5\text{‰}–0.8\text{‰}$  ( $\delta^{98}\text{Mo}$ ), suggesting that bottom-water chemistry and Mo enrichment at or above the sediment-water interface at the time of deposition are the primary controls. By analogy, we can regard  $\delta^{98}\text{Mo}$  in our sediments as

representative of bottom-water conditions at the time of deposition.

## RESULTS AND DISCUSSION

For the sediments of the persistently oxic shelf, the average concentration of sedimentary molybdenum, [Mo], is ~0.7 ppm, with a  $\delta^{98}\text{Mo}$  of  $-0.07\text{‰} \pm 0.08\text{‰}$  (1 SD) (Table DR1). These values fall exactly within expectations for sediments with little to no authigenic Mo enrichment—i.e., average crust—indicating that the Mo in these sediments derives entirely from lithogenic sources.

At stations 3 and 4, we observe a decrease in  $\delta^{98}\text{Mo}_{\text{auth}}$  with shallowing sediment depth from  $+2.1\text{‰}$  to  $-0.04\text{‰}$  and  $+2.1\text{‰}$  to  $+0.05\text{‰}$ , respectively (Fig. 2; Table DR1; Fig. DR1). We infer that the up-core shifts in  $\delta^{98}\text{Mo}$  reflect the progression from higher bottom-water sulfide concentrations in the past to the present-day oxic conditions at these sites. Cesium isotope and  $^{210}\text{Pb}$  chronometers constrain this transition to the past 300 yr (Lyons et al., 1993).

Applying the linear relationship presented by Neubert et al. (2008) to our data, the bottom-water  $[\text{H}_2\text{S}_{\text{aq}}]$  was ~18  $\mu\text{M}$  ( $[\Sigma\text{H}_2\text{S}] \approx 126 \mu\text{M}$ ) between 250 and 300 yr B.P. at shelf depths in the area of the Bosphorus inlet (Table 1; Fig. 2). A steady up-core decrease from the deep heavy  $\delta^{98}\text{Mo}$  toward values typical of detrital sediment lacking Mo enrichment implies that the chemocline returned slowly and continuously over an ~200 yr period to a deeper position, consistent with a progressive decrease in sulfide concentration. Biomarker data from a deepwater site indicate that the chemocline did not retreat entirely. It remains within the euphotic zone in the central basin today (Repeta, 1993). However, due to the convex nature of the chemocline, its retreat on the basin margin extended to greater depths, leading ultimately back to the oxic conditions now seen at stations 3 and 4 (Table 1; Figs. 1A and 3).

Unfortunately, the paucity of older sediment samples from our sites prevents us from fully reconstructing fluctuations in bottom-water sul-

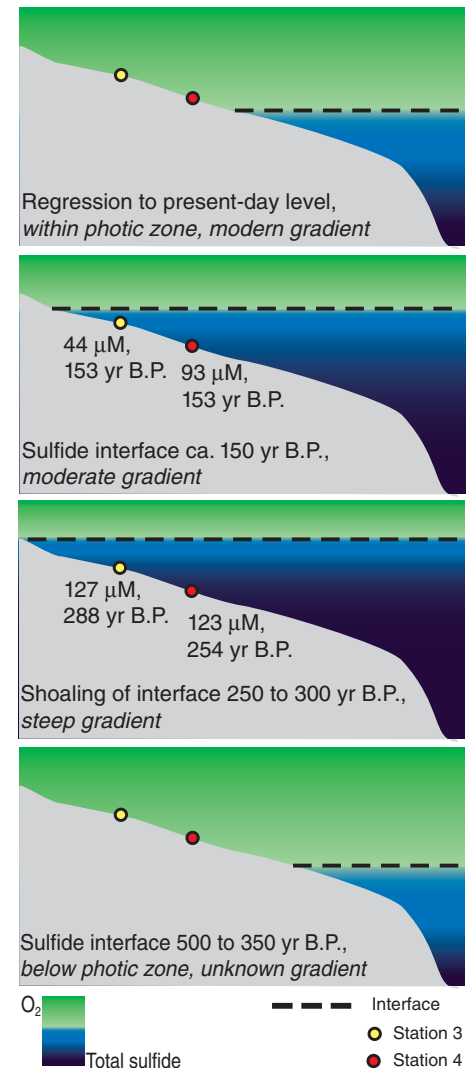
fide concentrations on the shelf prior to 300 yr B.P. However, complementary information can be gained from sediments at a deepwater site ~120 km to the northeast in the central western basin where isorenieratene, an organic biomarker indicative of  $\text{H}_2\text{S}$  in the photic zone, is absent between 500 and 350 yr B.P. (Repeta, 1993) (Fig. 2). From the biomarker data of Repeta (1993), we infer that from 500 to 350 yr B.P., the sulfide interface in the central western basin was below the photic zone (~100 m; Manske et al., 2005), which would place the chemocline almost 20 m below its current depth at ~80 m at this location. Similarly, the chemocline along the basin margin would have been deeper than the modern depth (~130 m; Lyons et al., 1993), yielding a minimum depth of ~150 m in the area of stations 3 and 4, prior to 350 yr B.P. (Fig. 3). The close association between biomarker evidence for sulfide in the photic zone, indicating a shoaling in the chemocline starting ca. 350 yr B.P. (Repeta, 1993), and our heavy  $\delta^{98}\text{Mo}_{\text{auth}}$  ca. 300 yr B.P. indicates that not only did the chemocline rise and bottom-water sulfide appear at stations 3 and 4 during this time, but this excursion happened quickly. Specifically, the chemocline rose more than 65 m in less than 50 yr, thus capturing the heaviest Mo isotope composition—consistent with the high sulfide concentrations seen in deep waters today (Fig. 2). This >65 m change in the depth of the chemocline exceeds the up to 30 m of change that has been observed directly during the last 30 to 40 yr and attributed to anthropogenic influences on Black Sea chemistry/hydrology (Murray et al., 1989, 1995; Kononov et al., 2001; Kononov and Murray, 2001).

The shoaling of the chemocline is not recorded in the margin sediments at stations 16 and 17 in the eastern basin (Table DR1). An explanation for this difference could be that the chemocline in this region today is at a depth of ~175 m, deeper than what is observed in the area of the Bosphorus inlet. If the shoaling event in this region behaved as it did in the Bosphorus,

then a 45 m rise in the chemocline above the modern level (65 m above the inferred ancient level) would barely bring the sulfide interface to the depth of station 16 (129 m) and would not reach station 17 at 97 m. Regional variations in chemocline structure and behavior make it likely that the rise and fall of the chemocline starting ca. 350 yr B.P. would not have been recorded in the sediments at stations 16 and 17.

## IMPLICATIONS

The rapid shoaling of the chemocline in the Black Sea between 350 and 300 yr B.P.



Sketch, not to scale.

**Figure 3. Hypothesized changes in the position of the chemocline from >350 yr B.P. to present. We illustrate that not only has the sulfide interface changed in absolute depth, but the sulfide gradient also steepened. Change in color saturation is representative of the concentration gradients; i.e., darker blue indicates higher total sulfide concentrations (note that the convex structure of the chemocline is neglected because we are depicting the fluctuations as recorded on the basin margin).**

TABLE 1. CALCULATION OF HISTORICAL BOTTOM-WATER SULFIDE CONCENTRATIONS

	Age (yr B.P.)	$\delta^{98}\text{Mo}_{\text{auth}}$ (‰)	1 SD (‰)	$[\text{H}_2\text{S}_{\text{aq}}]$ ( $\mu\text{M}$ ) <sup>a</sup>	1 SD ( $\mu\text{M}$ )	Total sulfide ( $\mu\text{M}$ ) <sup>b</sup>	1 SD ( $\mu\text{M}$ )	
<b>Station 3 (85 m)</b>								
	8–10 cm	153	0.62	0.08	6	2	44	14
	12–14 cm	220	1.13	0.08	10	3	72	19
	16–18 cm	288	2.13	0.08	19	3	127	31
<b>Station 4 (115 m)</b>								
	8–10 cm	153	1.51	0.08	14	3	93	24
	14–16 cm	254	2.05	0.08	18	3	123	30

<sup>a</sup>Using our data for  $\delta^{98}\text{Mo}_{\text{auth}}$  and the equation for the linear relationship defined in Figure 1, we calculate the historical  $[\text{H}_2\text{S}_{\text{aq}}]$  for each time point at stations 3 and 4.

<sup>b</sup>In order to estimate total sulfide, we use pH values representative of the potential span of conditions that stations 3 and 4 may have experienced (pH data from Goyet et al., 1991). We can then estimate the historical total sulfide concentrations, following Almgren et al. (1976) and Millero et al. (1988). See the Data Repository (see text footnote 1) for details of historical  $[\text{H}_2\text{S}_{\text{aq}}]$  and total sulfide calculations.

SD—standard deviation.

corresponds with the end of the “Peak Bloom Period” of *Emiliana huxleyi* (Hay et al., 1991), coincident with the first cold interval of the Little Ice Age. Hay et al. (1991) suggested that cold temperatures were responsible for the bloom in *E. huxleyi*, as potentially facilitated by winter storms that mixed the surface water column and brought nutrient-rich deep water to the surface. The subsequently increased export of organic matter into anaerobic waters may have triggered increased production of hydrogen sulfide by bacterial sulfate reduction. Furthermore, shoaling and steepening/compression of the chemocline may have resulted in a positive feedback, because a smaller portion of the water column was available for aerobic degradation of organic matter, resulting in higher rates of sulfate reduction. This scenario may explain the rapid shift to a shallow chemocline, followed by a more gradual return to deeper chemocline levels in this area.

Here, for the first time, we use the Mo isotope paleoredox proxy in a new way to quantify historical trends in bottom-water sulfide concentrations and the specifics of chemocline dynamics, paving the way for a more detailed basin-wide reconstruction of chemocline fluctuations. Such quantifications and reconstructions have otherwise been elusive. This new application, which exploits the known sensitivity of the Mo isotope system to sulfide concentration, has the potential to yield new insight into the geochemical evolution of the Black Sea and other modern euxinic basins, and may also prove useful in the interpretation of the paleosulfide evolution of ancient anoxic basins throughout Earth history.

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