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

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### SAMPLES AND METHODS

All samples presented in this study were collected during the 1988 Black Sea Oceanographic Expedition conducted on the RV Knorr (Tab le DR1, DR2, Figure S2). Com plete details of sampling procedures and core de scriptions are found in Lyons (1991). Briefly, sediment samples were taken using a 50 cm<sup>3</sup> box corer. The box cores were then sub-sampled with plastic tubes. All sediment samples were eith er oven-dried at 80 °C or freeze-dried. Afte r drying, sam ples were disaggregated with a ceramic mortar and pestle. Because we are using bulk sample analysis, there is no risk of alteration artifacts (e.g., oxidation effects) during sample storage.

Molybdenum (Mo) and other elemental concentrations were measured by ICPMS using either a multi-element external standard solution combined with the use of internal standards to monitor for drift in instrum ent sensitivity or by isotope dilution using a calibrated <sup>97</sup>Mo spike solution. Molybdenum isotope compositions were determined by multiple collector - inductively coup led plasma mass spectrometry (MC-ICPMS, Thermo Neptune <sup>®</sup>) at the W.M. Keck Foundation Laboratory for Environm ental Biogeochemistry at Arizona State University. A detailed description of sample preparation and analysis for Mo isotope composition is available in Gordon et al. (2009). Data are reported using delta no tation, relative to an in-house standard (Johnson Matthey Chemical, Specpure lot#702499I), where,

$$\delta^{98} \text{Mo} = \left( \frac{{}^{98} \text{Mo}_{95} \text{Mo} \text{sample}}{{}^{98} \text{Mo}_{95} \text{Mo} \text{standard}} - 1 \right) \cdot 1000 \text{ \%},$$

with an external precision of  $\pm 0.08$  ‰ (based on >100 m easurements of our in-house rock standard). For comparison to data reported as  $\delta^{97}$ Mo:  $\delta^{97}$ Mo =  $\frac{2}{3} \cdot \delta^{98}$ Mo.

### **CORRECTION FOR LITHOGENIC CONTENT**

Where Mo concentratio ns are low (generally less than 1 0 ppm), we correct for the Mo contribution from lithogenic sources, which could account for 10% or more of the bulk Mo signal (Table S1). For the purposes of this study we use a  $\delta^{98}$ Mo<sub>lithogenic</sub> = -0.07 ± 0.08 ‰ and [Mo]/[A1]<sub>average lithogenic</sub> = 0.075 ± 0.033 (Table DR1). The se are the average values of all oxic sediments in this study, where no authigenic enrichment of Mo has occurred (all samples from stations 16 and 17 and the 2-4 cm interval from stations 3 and 4). The Mo isotope composition of authigenic Mo is calculated as

$$\delta^{98}$$
Mo<sub>auth</sub> = ( $\delta^{98}$ Mo<sub>bulk</sub> -  $\delta^{98}$ Mo<sub>lithogenic</sub> · f<sub>lithogenic</sub>)/(1-f<sub>lithogenic</sub>).

where,

 $\delta^{98}Mo_{bulk} = direct analysis by MC-ICPMS,$ [Mo]<sub>lithogenic</sub> (ppm) = ([Mo]/[Al])<sub>average lithogenic</sub> · [Al]<sub>sample</sub>, f<sub>lithogenic</sub> = [Mo]<sub>lithogenic</sub>/[Mo]<sub>bulk</sub>.

#### CALCULATION OF HISTORICAL SULFIDE CONCENTRATIONS

The linear relationship (Figure 1B) between the concentration of bottom -water  $H_2S_{aq}$  and the authigenic Mo isotope com position of the su rface sediments deposited under th ose waters is defined as

 $\delta^{98}$ Mo<sub>auth</sub> (± 0.08) = 0.1239 (± 0.0214) · [H<sub>2</sub>S<sub>aq</sub>] (± *x*) – 0.1653 (± 0.1515). Rearranging, we can solve for [H<sub>2</sub>S<sub>aq</sub>]:

$$[H_2S_{aq}] (\pm x) = (\delta^{98}Mo_{auth} (\pm 0.08) + 0.1653 (\pm 0.1515)) / 0.1239 (\pm 0.0214).$$

From the calculation of  $\delta^{98}Mo_{auth}$ , (see abo ve) we can calculate the bottom -water  $H_2S_{aq}$  concentration under which that sediment was deposited.

We can further estim ate the historical total sulfide concentrations, following Almgren et al., (1976) and Millero et al., (1988), where  $[H_2S]$  of Almgren et al. (1976) and Millero et al., (1988) corresponds to  $[H_2S_{aq}]$  of Neubert et al. (2008) and

$$K_1^* = [H^+] \cdot [HS^-] / [H_2S_{aq}],$$
 (1)

with total sulfide  $[TS] = [HS^-] + [H_2S_{aq}].$  (2)

Substituting equation 2 into equation 1 and rearranging yields

$$[TS] = [H_2S_{aq}] \cdot (1 + K_1 * / [H^+]), \qquad (3)$$

where  $K_1^* = 1.110E-07 \pm 1.338E-08$  (for temperature = 5° C and salinity = 20‰).

 $[H^+] = 1.889E-08 \pm 2.575E-09$  (Goyet et al., 1991; pH data from Station 6, average 95 to 500 m).



Figure S1. Isorenieratene (after Repeta, 1993, box core 3), Mo isotope compositions (this study),  $Mn_T/Al$  ratios (Lyons and Severmann, 2006), total chromium reducible sulfur (S<sub>T</sub>), and total organic carbon (TOC) (Lyons et al., 1993) versus ag e for sediments at stations 3 and 4. Due t o their low Mo concentrations, the Mo isotope co mpositions for samples with ages >100 ybp we re corrected for the lithogenic Mo contribution (Tab le DR1). Diamonds and squares = stations 3 and 4, respectively. Error bars for  $\delta^{98}$ Mo do not exceed the size of the sym bol (± 0.08 1SD). The dashed line represents the average value for all oxic samples (Mn<sub>T</sub>/Al) or for seawater ( $\delta^{98}$ Mo); the shaded area indicates the range of Mn<sub>T</sub>/Al values present in recent deep-basin sediment samples (data from Lyons and Severmann, 2006). Sediment ages for stations 3 and 4 were determined from an average sedimentation rate of 0.059 cm yr<sup>-1</sup> based on an extrapolation of <sup>210</sup>Pb relationships (Lyons et al., 1993).

Sample	Depositional	[Mo] <sub>bulk</sub>	[AI]	Mo/Al	δ <sup>98</sup> Mo <sub>bulk</sub>	normalized for lithogenic content				
-	redox condition	ppm	wt %	ppm/wt%	‰	[Mo] (lithogenic)	f (lithogenic)	[Mo] (authigenic)	f (authigenic)	δ <sup>98</sup> Mo <sub>auth</sub> ‰
<sup>a</sup> Station 3,	41 30.37 N, 28 5	51.66' E, 85	m							
2-4 cm	Oxic	0.8	17.7	0.05	-0.04	lithogenic Mo content only -0				
8-10 cm	Euxinic	1.9	2.1	0.91	0.56	0.16	0.08	1.75	0.92	0.62
12-14 cm	Euxinic	4.6	6.5	0.70	1.00	0.49	0.11	4.06	0.89	1.13
16-18 cm	Euxinic	8.8	7.0	1.25	2.00	0.52	0.06	8.26	0.94	2.13
<sup>a</sup> Station 4,	41 37.37' N, 28	52.55' E, 1 <sup>.</sup>	15 m							
2-4 cm	Oxic	0.8	8.0	0.10	0.05	lithogenic Mo content only				0.05
8-10 cm	Euxinic	8.1	10.1	0.81	1.37	0.75	0.09	7.40	0.91	1.51
16-18 cm	Euxinic	6.5	7.9	0.82	1.86	0.59	0.09	5.87	0.91	2.05
Oxic Static	ons - lithogenic	end-memb	er							
<sup>a</sup> Station 17	', 41 46.80' N, 35	36.50' E,	97 m				average δ	<sup>98</sup> Mo <sub>lithogenic</sub> :		
0-2 cm	Oxic	0.7	7.2	0.10	0.04	-	-0.07 ± 0.08 ‰ (1SD)			
2-4 cm	Oxic	0.6	11.6	0.06	-0.12					
6-8 cm	Oxic	0.7	6.7	0.10	-0.17	average lithogenic Mo/AI (ppm/wt%):				
<sup>a</sup> Station 16	, 41 50.10' N, 35	38.40' E,	129 m			_	0.075 ± 0.	033		
0-2 cm	Oxic	0.8	6.2	0.12	-0.04	_				
6-8 cm	Oxic	0.6	11.5	0.05	-0.16					
10-12 cm	Oxic	0.5	13.6	0.04	-0.04					
14-16 cm	Oxic	0.5	11.0	0.05	-0.10					

## Table DR1. Elemental and isotopic data for Black Sea sediments.

<sup>a</sup>samples from Lyons et al., 1993.

### Table DR2. Elemental and isotopic data for Black Sea deep sea sediments.

Sample	Depositional redox condition	[Mo] ppm	[AI] wt %	Mo/Al ppm/wt%	δ <sup>98</sup> Mo <sub>bulk</sub> ‰	
Deep Basin Stat	ions (Unit I sedime	nts) - eux	inic end-m	ember		
<sup>a,b</sup> Station 9, 42 5	4.51' N, 31 21.93' E,	2094 m				
0-2 cm	Euxinic	19	na	na	2.31	
16-18 cm	Euxinic	25	1.2	20.4	2.39	
<sup>a</sup> Station 14, 43 04	4.26' N, 33 58.71' E,	2218 m				
8-10 cm	Euxinic	17	1.3	13.2	2.50	
20-22 cm	Euxinic	39	1.9	20.5	2.30	
<sup>a</sup> Station 18A, 42	28.15' N, 37 35.30'	E, 2149 m	<u> </u>			
18-20 cm	Euxinic	23	1.9	12.2	2.22	
<sup>b</sup> BC 10-1, 41 57.7	71' N, 29 05.24' E, 1	503 m				average $\delta^{98}Mo_{euxinic}$ :
10-15 cm	Euxinic	35	3.5	10.0	2.46	<b>2.36 ± 0.09 ‰</b> (1SD)
<sup>b</sup> BC 21-1, 43 05.5	52' N, 32 01.56' E, 2	092 m				
0-6 cm	Euxinic	45	1.7	26.5	2.29	
10-14 cm	Euxinic	48	1.8	26.7	2.27	
<sup>b</sup> BC 25-1, 42 44.9	91' N, 37 34.80' E, 2	164 m				
13-17 cm	Euxinic	34	3.4	10.0	2.46	
<sup>b</sup> BC 43-1, BC 43-	2, 41 49.38' N, 40 1	2.82' E, 1	861 m			
10-17 cm (43-1)	Euxinic	27	5.2	5.2	2.39	
20-26 cm (43-2)	Euxinic	35	4.7	7.4	2.29	
<sup>b</sup> BC 55-4, 42 44.9	91' N, 37 34.80 <u>'</u> E, 2	164 m				
8-12 cm	Euxinic	33	2.6	12.7	2.43	

<sup>a</sup>samples from Lyons et al., 1993. <sup>b</sup>samples from Ravizza et al., 1991.

Sample	average age	TOC	$S_{T}^{a,b} \\$	Mn <sub>T</sub> /Al <sup>c</sup>					
<sup>b</sup> Sedimentation rate = 0.059 cm yr <sup>-1</sup>	ybp	wt %	wt %	ppm/wt%					
Station 3, 41 30.37 N, 28 51.66' E, 85 m									
0-2 cm	17	2.2	0.07	0.008					
2-4 cm	51	1.5	0.15	0.006					
4-6 cm	85	1.4	1.32	0.006					
6-8 cm	119	1.3	3.19	-					
8-10 cm	153	1.4	3.23	0.025					
10 -12 cm	186	1.4	2.41	0.021					
12-14 cm	220	1.4	1.19	-					
14-16 cm	254	1.5	2.06	0.016					
16-18 cm	288	1.7	1.86	-					
18-20 cm ( <i>end of core</i> )	322	1.7	1.52	0.016					
Station 4, 41 37.37' N, 28 52.55' E, 11	5 m								
0-2 cm	17	1.5	0.09	-					
2-4 cm	51	1.3	0.09	-					
4-6 cm	85	1.3	0.81	-					
6-8 cm	119	1.4	1.79	-					
8-10 cm	153	1.9	2.28	-					
10-12 cm	186	2.1	2.40	-					
12-14 cm	220	1.7	1.50	-					
14-16 cm	254	1.8	1.39	-					
16-18 cm (end of core)	288	1.9	1.15	-					

#### Table DR3. Geochemical data for stations 3 & 4.

-, not reported.  ${}^{a}S_{T}$  = total chromium reducible sulfur.

<sup>b</sup>data from Lyons et al., 1993. <sup>c</sup>data from Lyons and Severmann, 2006.



Figure S2. Google<sup>®</sup> map of sample locations used in this study

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