1   Supplementary Information

2   A modern iron isotope perspective on the redox evolution of

3   ancient oceans

4   Silke Severmann, Timothy W. Lyons, Ariel Anbar, James McManus & Gwyneth Gordon

5

6   Materials and methods

7   1) Sample descriptions

8   The samples used in this study were collected during the 1988 *R/V Knorr* Black

9   Sea cruise. The exact locations, sedimentology and geochemistry are described in detail

10   elsewhere (Lyons, 1991; Lyons and Berner, 1992; Lyons et al., 1993; Anderson et al.,

11   1994; Canfield et al., 1996; Lyons, 1997; Hurtgen et al., 1999). Cores from the central

12   euxinic basin (stations 9 and 14, >2000 m) consist entirely of microlaminated, coccolith-

13   rich *Unit 1* mud [using the nomenclature of Ross et al. (1970)]. Organic carbon and

14   calcium carbonate concentrations in these euxinic sediment average 5.3±1.0 and

15   52.5±11.3 (±1s) wt.%, respectively. Pyrites in this unit are present dominantly as fine-

16   grained framboidal aggregates, which is indicates that they formed syngenetically in the

17   water column (Wilkin and Arthur, 2001).

18   Stations 3, 4, 16, and 17 were on the shallow oxic shelf, where sediments are

19   characterized by high degrees of bioturbation. Below the surface interval, organic carbon

20   and calcium carbonate concentrations at the four shallow stations collectively average

21   1.3±0.4 and 20.1±5.3 wt.%, respectively. The shallower Black Sea sediments contain an

22   increasing proportion of fine-grained euhedral pyrite, which is more typical of diagenetic

23   pyrite formation within the sediments (Wilkin and Arthur, 2001). Sedimentation rates for

24   Unit 1 sediments have been estimated as roughly 15 to 20 cm/kyr (Calvert and Karlin,

25   1991; Crusius and Anderson, 1992; Arthur et al., 1994; Jones and Gagnon, 1994). Rates

26   at stations 3, 16 and 17 range between 60 and 90 cm/kyr (Anderson et al., 1994; data are

27   unavailable for Station 4).

28

29   *2) Sample preparation and analysis*

30   For analysis of total iron isotope compositions, ~0.1g of dried sediment was fully

31   dissolved using a mixture of HNO_3, $HClO_3$ and HF. For determination of pyrite isotope

32   composition we used a chemical leaching procedure modified after Huerta-Diaz and

33   Morse (1992). Briefly, ~0.5 g of dry sediment was extracted in concentrated boiling HCl

34   for 1 min. The residue was treated with two sequential HF extractions (30 ml 10M HF for

35   1 hr, then 30 ml 10M HF for 16 hrs) to dissolve any remaining silicate phases. The only

36   significant iron phase remaining after this treatment is pyrite, which was extracted in 10

37   ml of concentrated HNO_3 for 2 hrs. All extractions were performed at room temperature

38   under constant shaking. Chemically extracted pyrite-Fe was dried down repeatedly in

39   concentrated HNO_3 and H_2O_2 to break down any residual organic carbon. Dry residue

40   was dissolved in 7M HCl, and ~100 µg of iron was purified on Bio-Rad AG1X8 anion

41   resin (~250µl volume) following the procedure of Beard et al. (2003). Column yields

42   were carefully monitored by *Ferrozine* analysis of each sample before and after chemical

43   processing, and only samples that had ≥95% recovery were used for iron isotope analysis.

44   Iron isotope analysis was performed on a ThermoFinnigan *Neptune* multi-

45   collector inductively coupled plasma mass-spectrometer (MC-ICP-MS) at Arizona State

46   University, following the method of Arnold et al. (2004). Samples were introduced as 2

47   ppm or 3 ppm solutions through a desolvating nebulizer. The analysis was performed in

48   medium mass resolution mode (mass resolving power of 8000-9000). Mass bias during

49   the analysis was corrected by using a Cu elemental spike, which was added to the

50   purified samples to a concentration matching that of the Fe concentration. In addition,

51   sample isotope ratios were normalized to the average of two bracketing standards as an

52   additional correction for instrumental mass discrimination. ^{53}Cr, ^{54}Fe, ^{56}Fe, ^{57}Fe, ^{58}Fe,

53   ^{60}Ni, ^{63}Cu and ^{65}Cu were measured in dynamic mode, where masses 53 to 60 were

54   measured during the first integration and the two Cu isotopes were measured during the

55   second integration.

56   Several standard reference materials of known isotope composition, including

57   IRMM-014, were measured routinely for each sample batch. In addition, we measured

58   gravimetric standards, which were prepared by adding a known amount of enriched ^{54}Fe

59   tracer (97.7% purity, Oak Ridge National Lab) to IRMM-014 standard. Of the 64 samples

60   analyzed in this study, 15 were processed through duplicate chemical treatment, including

61   sample dissolution or pyrite-Fe extraction and chromatographic extraction. Data are

62   reported in per mil (‰) δ notation using the $^{56}Fe/^{54}Fe$ sample ratio relative to the average

63   of igneous rocks ($\delta^{56}Fe$), which have a $\delta^{56}Fe$ of 0.00 ±0.05 ‰ (Beard et al., 2003). On

64   this scale, the IRMM-014 standard has $\delta^{56}Fe$ = –0.09 ‰. Replicate analyses were made

65   on different days, and errors for samples with $\geq$ 2 repeat analyses are reported as two

66   standard deviations (2-SD). The average external 2-SD reproducibility, as determined by

67   duplicate analysis via re-processing of several powdered samples through chemistry, is

68   ±0.06 ‰ for $\delta^{56}Fe$ and ±0.07 ‰ for $\delta^{57}Fe$.

69   The iron isotope fractionation between coexisting phases A and B is described by

70    $\Delta^{56}Fe_{A-B} = \delta^{56}Fe_A - \delta^{56}Fe_B \approx 10^3 \ln \alpha_{A-B},$ (E1)

71   where α_{A-B} is the isotope fractionation factor in terms of $^{56}Fe/^{54}Fe$ ratios.

72   The isotope composition of the benthic export flux $\delta^{56}Fe_{Ex}$ may be calculated

73   using the iron isotope composition of either Fe_T or Fe_{Py}:

74    $\delta^{56}Fe_{Ex} = (\delta^{56}Fe_T * [Fe_T])/[Fe_{Ex}]$ (E2)

75   or

76    $\delta^{56}Fe_{Ex} = (\delta^{56}Fe_{Py} * [Fe_{Py}])/[Fe_{Ex}],$ (E3)

77   where $[Fe_{Ex}]$ denote concentrations of the individual iron pools. Benthic export iron flux

78   is assumed to be quantitatively converted to pyrite, and concentrations of the exported

79   iron component in the sediments are calculated as

80    $[Fe_{Ex}] = [Fe_T]-[Al]*0.6,$ (E4)

81   where 0.6 is the Fe_T/Al ratio for the lithogenic baseline. This ratio represents the highest

82   ratio measured for sediments from the oxic shelf (Station 17, mean Fe_T/Al=0.60, see

83   Table S1) and is higher than the commonly used Fe_T/Al ratio for average shale of 0.5

84   (Taylor and McLennan, 1985). Shuttling of reactive Fe from the shelf sediments to the

85   deep basin causes a decrease of the Fe_T/Al ratio, suggesting that our elevated ratios are

86   not due to post-depositional modification of the detrital material, but rather that they

87   reflect a local lithogenic Fe_T/Al baseline for the Black Sea that deviates from the

88   generally accepted global average (Lyons and Severmann, 2006). Probably the best

89   approach to derive an estimate of the Fe_T/Al baseline would be to measure the

90   composition of particles from the zone of estuarine mixing, since riverine particles

91   undergo some modification during passage through the estuary (Poulton and Raiswell,

92   2005). In the absence of a direct measure of the Fe_T/Al ratio for the local terrestrial

93   particulate input, we assume that our highest measured sediment Fe_T/Al ratios best

94   represent a lithogenic baseline value for the Black Sea, although we recognize that this is

95   not ideal. We note, however, that the choice of the Fe_T/Al baseline as well as its isotope

96   composition does not affect our principal observation, which is the systematic decrease in

97   iron isotope compositions from the shelf sediments to the deep basin sediments and their

98   inverse relationship with Fe_T/Al ratios (Fig. 3).

Table S1: Iron and aluminum concentrations, and iron isotope compositions of Black Sea sediments.

Depth (cm)	Depositional setting	Fe_T (wt. %)	Al (wt. %)	Fe/Al	Fe_{Py} (wt. %)	$\delta^{56}Fe_T$ (ä)	2-SD	$\delta^{57}Fe_T$ (ä)	2-SD	n[1]	$\delta^{56}Fe_{Py}$ (ä)	2-SD	$\delta^{57}Fe_{Py}$ (ä)	2-SD	n[1]	$\delta^{56}Fe_{Ex}$ (from Fe_{Py})	$\delta^{56}Fe_{Ex}$ (from Fe_T)
Station 16 (129m)																	
0-2	oxic	2.76	5.07	0.54	0.01	0.08	±0.12	0.11	±0.14	2	-0.54	±0.04	-0.71	±0.28	2+2		
4-6	oxic	2.61	5.07	0.51	0.03	0.15	±0.06	0.20	±0.02	2	-1.07	±0.02	-1.56	±0.10	3		
6-8	oxic	3.15	5.79	0.54	0.08	0.08	±0.06	0.10	±0.06	3+2	-1.17		-1.76		1		
8-10	oxic	2.90	5.62	0.52	0.10	0.12	±0.07	0.22	±0.02	2	-1.13	±0.09	-1.66	±0.01	3		
10-12	oxic	3.12	5.80	0.54	0.08	0.03	±0.07	0.04	±0.10	2+2	-1.00		-1.51		1		
12-14	oxic	2.89	5.68	0.51	0.10	0.12	±0.10	0.20	±0.03	3	-0.99	±0.08	-1.43	±0.07	2		
14-16	oxic	3.11	5.79	0.54	0.09	0.06	±0.02	0.08	±0.08	2+2	-0.93		-1.40		1		
16-18	oxic	3.20	5.78	0.55	0.11	0.09	±0.01	0.13	±0.01	2+2	-1.02		-1.56		1		
Station 17 (97m)																	
0-2	oxic	3.77	6.13	0.62	0.01	0.04	±0.05	0.08	±0.08	2	-0.41	±0.06	-0.52	±0.06	2		
2-4	oxic	4.00	6.30	0.63	0.01	0.01	±0.09	0.02	±0.11	2+2	-0.54		-0.71		1		
4-6	oxic	3.79	6.37	0.59	0.01	0.05	±0.04	0.05	±0.01	2					1		
6-8	oxic	3.68	6.16	0.60	0.02	0.05	±0.07	0.06	±0.13	2	-0.87		-1.26		1		
8-10	oxic	3.49	6.03	0.58	0.03	0.03	±0.02	0.06	±0.03	2	-0.94		-1.37		1		
10-12	oxic	3.44	5.98	0.58	0.08	0.05	±0.02	0.07	±0.04	2	-1.28		-1.87		1		
12-14	oxic	3.80	6.31	0.60	0.16	0.01	±0.00	0.02	±0.02	2	-1.19	±0.14	-1.89	±0.60	1		
14-16	oxic	3.56	5.73	0.62	0.21	0.10	±0.13	0.12	±0.04	2+1	-1.16	±0.10	-1.71	±0.05	2		
Station 3 (85m)																	
0-2	oxic	3.08	6.08	0.51	0.06	0.04	±0.01	0.05	±0.02	2							
2-4	oxic	3.27	6.64	0.49	0.13	0.08	±0.05	0.13	±0.03	2							
6-8	paleo-chemocline	4.75	5.95	0.80	2.79	-0.37	±0.09	-0.53	±0.11	2+1							-1.38
8-10	paleo-chemocline	5.08	6.52	0.78	2.83	-0.21	±0.03	-0.31	±0.01	2							-0.88
Station 4 (115m)																	
0-2	oxic	3.04	6.49	0.47	0.08	0.07	±0.01	0.08	±0.08	2							
2-4	oxic	2.93	6.33	0.46	0.08	0.08	±0.01	0.11	±0.02	2							
8-10	paleo-chemocline	4.15	5.65	0.73	2.00	-0.22	±0.01	-0.35	±0.03	2							-1.15
10-12	paleo-chemocline	4.12	5.49	0.75	2.10	-0.13	±0.01	-0.23	±0.03	2							-0.58
Station 9 (2094m)																	
4-6	euxinic	2.19	2.64	0.83	1.24	-0.34	±0.13	-0.44	±0.12	2	-0.74	±0.16	-1.10	±0.11	5	-1.48	-1.18
8-10	euxinic	2.41	2.66	0.91	1.43	-0.06	±0.08	-0.06	±0.15	3	-0.76	±0.01	-1.14	±0.02	2	-1.31	-0.16
14-16	euxinic	0.95	0.94	1.01	0.61	-0.34	±0.09	-0.45	±0.14	4	-0.80	±0.11	-1.23	±0.07	3+2	-1.25	-0.80
16-18	euxinic	2.01	1.96	1.02	1.31	-0.34	±0.07	-0.49	±0.05	3	-0.82	±0.04	-1.22	±0.05	2+1	-1.28	-0.80
24-26	euxinic	1.45	1.39	1.04	0.99	-0.24	±0.05	-0.37	±0.08	2+2	-0.64	±0.12	-0.97	±0.19	2+2	-1.01	-0.53
Station 14 (2218m)																	
0-2	euxinic	2.64	4.43	0.60	1.06	-0.13	±0.15	-0.15	±0.22	2	-0.72	±0.13	-1.03	±0.09	4	(42.11)	(20.89)
4-6	euxinic	2.69	3.86	0.70	1.26	-0.15		-0.20		1	-0.65	±0.06	-1.03	±0.01	2	-2.19	-1.02
8-10	euxinic	1.64	2.12	0.77	0.87	-0.21		-0.27		1	-0.71	±0.07	-1.07	±0.11	3	-1.64	-0.91
10-12	euxinic	1.27	1.59	0.80	0.68	-0.24	±0.02	-0.37	±0.00	2							-0.93
12-14	euxinic	2.51	3.34	0.75	1.17	-0.34	±0.09	-0.57	±0.06	2	-0.72	±0.12	-1.12	±0.14	2+2	-1.63	-1.62
14-16	euxinic	2.19	2.76	0.79	1.10	-0.22	±0.02	-0.33	±0.05	2							-0.85
16-18	euxinic	2.47	3.36	0.73	1.25	-0.13		-0.15		1	-0.78	±0.09	-1.18	±0.16	1+1	-2.12	-0.68
18-20	euxinic	1.81	2.39	0.76	0.85	-0.18	±0.00	-0.28	±0.01	2							-0.84
20-22	euxinic	1.84	2.34	0.79	0.67	-0.22	±0.03	-0.36	±0.03	2							-0.89
22-24	euxinic	2.28	3.40	0.67	0.85	-0.17	±0.04	-0.26	±0.06	2+2							-1.56
Standard reference materials																	
IRMM-014						-0.09	±0.03	-0.36	±0.26	18							
BIR-2						-0.04	±0.03	-0.28	±0.27	18							
Grav IRMM-014 -1ä [2]						-1.13	±0.02			17							
BHVO-1						0.03	±0.04	-0.15	±0.05	2							
Sco-1						-0.01	±0.01	-0.20	±0.06	2							
SDO-1						-0.05	±0.12	-0.27	±0.10	3+2							
SGR-1						-0.04	±0.02	-0.24	±0.01	2							
TAG [3]						-0.99	±0.09	-1.64	±0.16	2+3							

[1] Number of repeat isotope analysis, where multiple entries (e.g. 2+2) indicates that powdered samples were re-processed through entire chemical procedure.

[2] Gravimetric standard was made from IRMM-014 and enriched ^{54}Fe enriched tracer. The true δ^{56}Fe of the gravimetric standard is -1ä relative to IRMM-014.

[3] In-house standard made from mettaliferous hydrothermal sulfide sediments.

References

Anderson R. F., Lyons T. W., and Cowie G. L. (1994) Sedimentary record of a shoaling of the oxic/anoxic interface in the Black Sea. *Mar. Geol.* **116**, 373-384.

Arnold G. L., Weyer S., and Anbar A. D. (2004) Fe isotope variations in natural materials using high mass resolution multiple collector ICPMS. *Anal. Chem.* **76**, 322-327.

Arthur M. A., Dean W. E., Neff E. D., Hay B. J., King G. M., and Jones A. D. (1994) Varve calibrated records of carbonate and organic carbon accumulation over the last 2000 years in the Black Sea. *Global Biogeochem. Cycles* **8**, 195-217.

Beard B. L., Johnson C. M., Skulan J. L., Nealson K. H., Sun H., and Cox L. (2003) Application of Fe isotopes to tracing the geochemical and biochemical cycling of Fe. *Chem. Geol.* **195**, 87-117.

Calvert S. E. and Karlin R. E. (1991) Relationships between sulphur, organic carbon, and iron in the modern sediments of the Black Sea. *Geochim. Cosmochim. Acta* **55**, 2483-2490.

Canfield D. E., Lyons T. W., and Raiswell R. (1996) A model for iron deposition to euxinic Black Sea sediments. *Am. J. Sci.* **296**, 818-834.

Crusius J. and Anderson R. F. (1992) Inconsistencies in accumulation rates of Black Sea sediments inferred from records of laminae and ^{210}Pb. *Paleoceanography* **7**, 215-227.

Huerta-Diaz M. A. and Morse J. W. (1992) Pyritization of trace metals in anoxic marine sediments. *Geochim. Cosmochim. Acta* **56**, 2681-2702.

Hurtgen M. T., Lyons T. W., Ingall E. D., and Cruse A. M. (1999) Anomalous enrichments of iron monosulfide in euxinic marine sediments and the role of H_2S in iron sulfide transformations; examples from Effingham Inlet, Orca Basin, and the Black Sea. *Am. J. Sci.* **299**, 556-588.

Jones G. A. and Gagnon A. R. (1994) Radiocarbon chronology of Black Sea sediments. *Deep-Sea Res.* **41**, 531-557.

Lyons T. W. (1991) Upper Holocene sediments of the Black Sea: Summary of Leg 4 box-cores (1988 Black Sea Oceanographic expedition). In *Black Sea Oceanography* (ed. E. Izdar and J. W. Murray), pp. 401-441. Kluwer.

Lyons T. W. (1997) Sulfur isotope trends and pathways of iron sulfide formation in the upper Holocene sediments of the anoxic Black Sea. *Geochim. Cosmochim. Acta* **61**, 3367-3382.

Lyons T. W. and Berner R. A. (1992) Carbon-sulfur-iron systematics of the uppermost deep-water sediments of the Black Sea. *Chem. Geol.* **99**, 1-27.

Lyons T. W. and Severmann S. (2006) A critical look at iron paleoredox proxies based on new insights from modern euxinic marine basins. *Geochim. Cosmochim. Acta* **70**, 5698-5722.

Lyons T. W., Berner R. A., and Anderson R. F. (1993) Evidence for large pre-industrial permutations of Black Sea chemocline. *Nature* **365**, 538-540.

Poulton S. W. and Raiswell R. (2005) Chemical and physical characteristics of iron oxides in riverine and glacial meltwater sediments. *Chem. Geol.* **218**, 203-221.

Ross D. A., Degens E. T., and MacIlvaine J. (1970) Black Sea: recent sedimentary history. *Science* **170**, 163-165.

145   Taylor S. R. and McLennan S. M. (1985) *The Continental Crust: Its Composition and*
146   *Evolution*. Blackwell.
147   Wilkin R. T. and Arthur M. A. (2001) Variations in pyrite texture, sulfur isotope
148   compositions, and iron systematics in the Black Sea: Evidence for the late
149   Pleistocene to Holocene excursions of the O_2-H_2S redox transitions. *Geochim.*
150   *Cosmochim. Acta* **65**, 1399-1416.
151
152