# Evidence for the presence of an oxygen depleted Sapropel Intermediate Water across the Eastern Mediterranean during Sapropel S1

Eleen Zirks<sup>1</sup>, Michael D. Krom<sup>1,2\*</sup>, Dongdong Zhu<sup>1</sup>, Gerhard Schmiedl<sup>3</sup>, Beverly N.

Goodman-Tchernov<sup>1</sup>

1 Leon H. Charney School of Marine Sciences, University of Haifa, Israel

2 Morris Kahn Marine Research Centre, Department of Marine Biology, Charney School of Marine Sciences, University of Haifa, Israel; and School of Earth and Environment,

Leeds University, Leeds, UK.

3 Center for Earth System Research and Sustainability, Institute for Geology, University of Hamburg, Germany

SUPPLEMENTARY INFORMATION

- Includes supplementary tables SI1 and SI2
- Deeper introduction about the studied sediment cores from the EMS
- Explanation how <sup>14</sup>C ages were corrected
- Calculation about the residence time of SIW in the EMS

## SUPPLEMENTARY INFORMATION

During our survey of cores across the EMS which had data which could be used to identify an interruption (Ba/Al, TOC or benthic foraminifera), we observed a clear pattern of the interruption at 8.2 ka BP in the cores sampled between 500 and 1800m and no interruption either above 500m or below 1800m. Specifically of the 18 cores which were sampled between 500 and 1800m, 16 showed evidence of the interruption. There was one core adjacent to the Libyan coast (562MC) which had Ba/Al data and showed no evidence of an interruption at 8.2 ka BP. This core was taken in the southern Ionian Sea at a considerable distance from the other cores and possible reasons for their exceptional behavior is described in the main text. There were 3 cores, which were used to define the

change in the start of S1 with depth (figure 4; MD84627, MD84641 and MD84639) which did not have any data which could be used to potentially identify an interruption.

Both shallow cores (AMC99-1 and SL31) showed no evidence of an interruption at 8.2 ka BP.

Of the 13 deep cores considered in this study, 10 cores showed no evidence of an interruption. Two cores, LC31 (2300m) and LC25 (3129m) had decreases in Ba/Al in the middle of the S1 sapropel signal. However, this decrease coincided with depths which have been interpreted by the original authors as small slumps, which they use to explain the entire changes in geochemical properties including Ba/Al. These decreases in Ba/Al are thus not due to re-oxidation so the data was not taken into consideration as cores which could be used to represent the 8.2 ka BP interruption.

There remained one core 967D sampled at 2563m which seemed to represent an exception to this general rule.<sup>1</sup> This core which appears to have an interruption as indicated by a drop in Ba/Al at ~8.2 ka BP. However, the Ba/Al decrease in core 967D does not have any associated change in RSTM (V, Mo, or U) which typically has been

found in others cores showing an increase in oxygen content due to the 8.2 ka interruption.<sup>2–4</sup> There is no obvious explanation for this anomaly.

## How was <sup>14</sup>C corrected

For cores MD84641, MD84639, MD84650 and MD84627, it was not mentioned in the original paper whether the <sup>14</sup>C measurements had been corrected or not.<sup>5</sup> It is normal practice in papers where a <sup>14</sup>C correction has been applied to state this explicitly and to note what reservoir age had been applied. We have contacted the authors of this paper (Calvert and Fontugne). Calvert replied that he could not remember the <sup>14</sup>C measurements had been corrected or not. He forwarded to email to Fontugne who has not replied. We therefore considered it likely that the ages were not corrected and we therefore calibrated them using the Marine13 curve of Calib 7.0.4, applying a reservoir age of 400 years.<sup>6</sup>

**S1 Table**. Core locations of all the cores summarized in this study.

Core locations of all the cores summarized in this study indicating whether they have evidence or not (Y or N) for an interruption in S1 sapropel at ~8.2 ka BP. The criteria used to identify the interruption are the presence/absence of BF (benthic foraminifera), TOC (Total Organic carbon), Ba/Al a minimum value showing a decrease of >30% from the maximum and an increase in RSTM (redox sensitive trace metals such as V, Mo and/or U). Locations marked with N\* are locations with a small slump.

Core	Latitude N	Longitude	Wate	Interruptio	BF	тос	Ba/Al	RSTM	Referenc
		E	r	n					е
AMC99-1	45°51.013'	14°45.011'	260	N	n	n		n	3
SL31	38°56.000'	25°00.000'	430	N	n				7,8
PS009PC	32°07.700'	34°24.400'	552	Υ		v	v	v	9
INVAS12-	41°30.004'	17°10.013'	570	Υ	у	у		у	3
KN3	36°40.600'	27°12.030'	607	Υ		у	n	У	4
P362/2-33	31°40.500'	29°45.000'	700	Υ		у	у		10
SL123	35°45.330'	27°33.340'	728	Υ	у				7
MP50PC	39°29.000'	18°31.000'	775	Υ		у	у	у	4
MNB-3	39°13.000'	24°58.000'	800	Υ		у			11
MD9502	34°46.000'	34°28.000'	860	Υ			у		12
MD84639	33°39.600'	32°42.000'	870						5
9509	32°01.000'	34°16.000'	884	Υ		у	у	у	2,13
SL112	32°44.520'	34°39.020'	892	Υ	у				7
966	33°47.790'	32°42.048'	937	Υ		n	у		14
9501	34°32.000'	33°59.000'	980	Υ		у	у		2,13
MD90-971	41°18.000'	17°37.000'	1010	Υ		y	y	y	15
ST04-1	41°27.008'	17°31.001'	1085	Υ	у	у		у	3
SL148	39°45.200'	24°05.800'	1094	Υ	у				7
<u>Z</u> 1	39°15.186'	19°51.995'	1160	Υ		y			16
MD84627	32°13.800'	33°45.000'	1184						5

	I	I	1	1	1	1		I	
MD84641	33°01.800'	32°37.800'	1375						5
562MC	32°46.000'	19°11.000'	1390	N			n	n	17,18
LC21	35°40.000'	26°35.000'	1522	Υ	у	у	у	у	8,15
MD04-2722	33°06.000'	33°30.000'	1780	Υ			n	у	19
BP18	33°10.000'	20°16.700'	1850	N		n	n		18
SL125	33°39.400'	24°33.000'	1946	N			n	n	18
BP10	33°22.200'	20°16.700'	2108	N		n	n		18
971C	33°42.800'	24°42.100'	2152	N			n	n	18
969	33°50.320'	24°53.000'	2210	N		n	n		14
MC12	33°23.700'	25°01.300'	2211	N		n	n	n	12,20
LC31	34°59.760'	31°09.810'	2300	N*	-		-		8
MD84650	33°40.200'	31°27.000'	2360						5
T87-26B	34°44.000'	16°48.000'	2415	N			n		12
967D	34°04.253'	32°43.531'	2563	?		n	у	n	1
MC07	34°19.200'	20°02.700'	2703	N		n	n	n	12,20
MC7S	34°19.200'	20°02.700'	2703	N		n	n	n	12,20
LC25	32°36.000'	27°23.000'	3129	N*			_		12
SL114	35°17.200'	21°24.500'	3390	N	n	n	n		7,21
964	36°15.630'	17°45.000'	3670	N		n	n		14

**S2 Table**. Details of sediment cores from SE Levantine used to show the evolution of the OMZ.

Core	Latitude N	Longitude	Water	Dated	S1 (ka	S1 identified	Referenc
		E	depth	by	BP)	by	е
PS009P	32°07.700'	34°24.400'	552	<sup>14</sup> C,	6.5-10.1	Ti/Al, Ba/Al,	22
С				<sup>210</sup> Pb		V/Al ratios,	
SL123	35°45.330'	27°33.340'	728	tephr	7.2-10.1	sediment	23,24
				а		color, diversity	
MD8463	33°39.600'	32°42.000'	870	<sup>14</sup> C	8.1-9.7	sediment	5
9509	32°01.000'	34°16.000'	884	δ <sup>18</sup> Ο	7.4-9.5	increased	25

SL112	32°44.520'	34°39.020'	892	<sup>14</sup> C	6.5-9.6	sediment	26
9501	34°32.000'	33°59.000'	980	<sup>14</sup> C,	8.2-9.5	increased	25
MD8462	32°13.800'	33°45.000'	1184	<sup>14</sup> C	6.4-9.2	sediment	5
MD8464	33°01.800'	32°37.800'	1375	<sup>14</sup> C	7.2-8.9	sediment	5

# Estimate of residence time for SIW during S1a

It is possible to carry out a rough calculation of the residence time of water in the Levantine basin during S1a by assuming that SIW was formed in the central Aegean Sea at a similar location to the location where CDW was formed in the 1980's/1990's and where Cretan Intermediate water was formed.<sup>27</sup> At steady state during S1a, the average dissolved oxygen content based on the benthic foraminifera fauna was 40 mmoles/m<sup>3</sup> at SL123 location.<sup>24,28</sup> If the descending water was at 100% oxygen saturation at modern salinity and temperature values (38 ppt, 15C) and since the water descends during the winter phytoplankton bloom (30 mgC/m<sup>3</sup>), the net oxygen supplied to the intermediate water would be 225 mmolesO<sub>2</sub>/m<sup>3</sup>. The water thus lost 185 mmolesO<sub>2</sub>/m<sup>3</sup> in transit from its source in the central Aegean Sea to SL123, which is a distance of ~250km (250 x 10<sup>3</sup>) m). Considered that the total volume of water being fluxed was 500m deep by 100km in

cross sectional area (5 X  $10^7$ m³). Finally, it is assumed that the loss of oxygen rate (OUR) is similar to that calculated for the present day intermediate/deep water of 0.7 mmoles/m³/y.<sup>27</sup>

OUR = 
$$J * (C_{init} - C_{SL123})/V$$

Where OUR is the oxygen removal rate at 1500m modified for the shallower depth (500-1800m) considered here, J is the water flux,  $C_{init}$  is the net oxygen content of the descended water and  $C_{SL123}$  is the oxygen content at SL123 estimated from benthic foraminifera fauna, and V is the total volume of water being transferred across the Aegean Sea and fluxing into the Levantine basin at the straits of between Rhodes and Crete.<sup>27</sup>

Rearranging J = OUR x V 
$$/(C_{init} - C_{SL123})$$

$$J = 0.7 \times 250 \times 10^{3} \times 500 \times 100 \times 10^{3} / 185 \text{ m}^{3}/\text{y}$$

$$J = 0.11 \times 10^{12} \text{ m}^{3}/\text{yr}$$

The area of the Levantine basin is 320000 X 10<sup>3</sup> m<sup>2</sup>

Assume that 80% is below 500m, then the total volume of the SIW is

$$= 333 \times 10^{12} \text{ m}^3$$

The residence time of water during the peak of S1a is thus: Volume of SIW in the Levantine basin/flux of water flowing in from the Aegean

Or 333 x 
$$10^{12}$$
 m<sup>3</sup>/0.11 x  $10^{12}$  m<sup>3</sup>/y

Residence time for S1a is ~3000 years and is ~2400 years for S1b where the estimated dissolved oxygen at SL123 was ~80 mmoles/m³.

There are many assumptions in this calculation which makes the result only a rough estimate. However, this value compares with the modern LDW residence time of 100-150 years which has an oxygen saturation value of ~60%.<sup>27</sup> It does suggest that at the peak

of anoxicity during S1 the flow of water into the Levantine basin (and presumably also into the Adriatic) was much slower than at present but not the zero flow into the deep water which resulted in anoxicity/euxinia.<sup>29</sup>

## REFERENCES SI

- (1) Azrieli-Tal, I.; Matthews, A.; Bar-Matthews, M.; Almogi-Labin, A.; Vance, D.; Archer, C.; Teutsch, N. Evidence from Molybdenum and Iron Isotopes and Molybdenum—Uranium Covariation for Sulphidic Bottom Waters during Eastern Mediterranean Sapropel S1 Formation. *Earth Planet. Sci. Lett.* 2014, 393, 231–242. https://doi.org/10.1016/j.epsl.2014.02.054.
- (2) Matthews, A.; Azrieli-Tal, I.; Benkovitz, A.; Bar-Matthews, M.; Vance, D.; Poulton, S. W.; Teutsch, N.; Almogi-Labin, A.; Archer, C. Anoxic Development of Sapropel S1 in the Nile Fan Inferred from Redox Sensitive Proxies, Fe Speciation, Fe and Mo Isotopes. *Chem. Geol.* 2017, 475 (October), 24–39. https://doi.org/10.1016/j.chemgeo.2017.10.028.

- (3) Tesi, T.; Asioli, A.; Minisini, D.; Maselli, V.; Dalla Valle, G.; Gamberi, F.; Langone, L.; Cattaneo, A.; Montagna, P.; Trincardi, F. Large-Scale Response of the Eastern Mediterranean Thermohaline Circulation to African Monsoon Intensification during Sapropel S1 Formation. *Quat. Sci. Rev.* 2017, 159, 139–154. https://doi.org/10.1016/j.guascirev.2017.01.020.
- (4) Filippidi, A.; Triantaphyllou, M. V.; De Lange, G. J. Eastern-Mediterranean Ventilation Variability during Sapropel S1 Formation, Evaluated at Two Sites Influenced by Deep-Water Formation from Adriatic and Aegean Seas. *Quat. Sci. Rev.* 2016, 144, 95–106. https://doi.org/10.1016/j.quascirev.2016.05.024.
- (5) Fontugne, M. R.; Arnold, M.; Labeyrie, L.; Paterne, M.; Calvert, S. E.; Duplessy, J.
   C. Paleoenvironment, Sapropel Chronology and Nile River Discharge during the
   Last 20,000 Years as Indicated by Deep-Sea Sediment Records in the Eastern
   Mediterranean. In Late Quaternary Chronology and Paleoclimates of the Eastern
   Mediterranean; Bar-Yosef, O., Kra, R. S., Eds.; Radiocarbon 36, 1994; pp 75–89.
- (6) Stuiver, M.; Reimer, P. J. Extended 14C Data and Revised Calib 3.0 14C Age

- Calibration Program. *Radiocarbon* **1993**, *35* (1), 215–230.
- (7) Schmiedl, G.; Kuhnt, T.; Ehrmann, W.; Emeis, K.-C.; Hamann, Y.; Kotthoff, U.; Dulski, P.; Pross, J. Climatic Forcing of Eastern Mediterranean Deep-Water Formation and Benthic Ecosystems during the Past 22 000 Years. *Quat. Sci. Rev.* 2010, 29 (23–24), 3006–3020. https://doi.org/10.1016/j.quascirev.2010.07.002.
- (8) Abu-Zied, R. H.; Rohling, E. J.; Jorissen, F. J.; Fontanier, C.; Casford, J. S. L.; Cooke, S. Benthic Foraminiferal Response to Changes in Bottom-Water Oxygenation and Organic Carbon Flux in the Eastern Mediterranean during LGM to Recent Times. *Mar. Micropaleontol.* 2008, 67 (1–2), 46–68. https://doi.org/10.1016/j.marmicro.2007.08.006.
- (9) Hennekam, R.; Jilbert, T.; Schnetger, B.; De Lange, G. J. Solar Forcing of Nile Discharge and Sapropel S1 Formation in the Early to Middle Holocene Eastern Mediterranean. *Paleoceanography* 2014, 29 (5), 343–356. https://doi.org/10.1002/2013PA002553.
- (10) Blanchet, C. L.; Tjallingii, R.; Frank, M.; Lorenzen, J.; Reitz, A.; Brown, K.; Feseker,

- T.; Brückmann, W. High- and Low-Latitude Forcing of the Nile River Regime during the Holocene Inferred from Laminated Sediments of the Nile Deep-Sea Fan. *Earth Planet. Sci. Lett.* **2013**, *364*, 98–110. https://doi.org/10.1016/j.epsl.2013.01.009.
- (11) Gogou, A.; Bouloubassi, I.; Lykousis, V.; Arnaboldi, M.; Gaitani, P.; Meyers, P. A.
  Organic Geochemical Evidence of Late Glacial-Holocene Climate Instability in the
  North Aegean Sea. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 2007, 256 (1–2), 1–
  20. https://doi.org/10.1016/j.palaeo.2007.08.002.
- (12) Mercone, D.; Thomson, J.; Croudace, I. W.; Siani, G.; Paterne, M.; Troelstra, S. R. Duration of S1, the Most Recent Sapropel in the Eastern Mediterranean Sea, as Indicated by Accelerator Mass Spectrometry Radiocarbon and Geochemical Evidence. *Paleoceanography* 2000, 15 (3), 336–347. https://doi.org/10.1029/1999PA000397.
- (13) Box, M. R.; Krom, M. D.; Cliff, R. A.; Bar-Matthews, M.; Almogi-Labin, A.; Ayalon, A.; Paterne, M. Response of the Nile and Its Catchment to Millennial-Scale Climatic Change since the LGM from Sr Isotopes and Major Elements of East Mediterranean

- Sediments. Quat. Sci. Rev. 2011, 30 (3–4), 431–442. https://doi.org/10.1016/j.quascirev.2010.12.005.
- (14) Gallego-Torres, D.; Martinez-Ruiz, F.; Meyers, P. A.; Paytan, A.; Jimenez-Espejo, F. J.; Ortega-Huertas, M. Productivity Patterns and N-Fixation Associated with Pliocene-Holocene Sapropels: Paleoceanographic and Paleoecological Significance. *Biogeosciences* 2011, 8 (2), 415–431. https://doi.org/10.5194/bg-8-415-2011.
- (15) Mercone, D.; Thomson, J.; Abu-Zied, R. H.; Croudace, I. W.; Rohling, E. J. High-Resolution Geochemical and Micropalaeontological Profiling of the Most Recent Eastern Mediterranean Sapropel. *Mar. Geol.* 2001, 177 (1–2), 25–44. https://doi.org/10.1016/S0025-3227(01)00122-0.
- (16) Geraga, M.; Mylona, G.; Tsaila-Monopoli, S.; Papatheodorou, G.; Ferentinos, G. Northeastern Ionian Sea: Palaeoceanographic Variability over the Last 22 Ka. *J. Mar. Syst.* 2008, 74 (1–2), 623–638. https://doi.org/10.1016/j.jmarsys.2008.05.019.
- (17) Casford, J. S. L.; Rohling, E. J.; Abu-Zied, R. H.; Fontanier, C.; Jorissen, F. J.; Leng,

- M. J.; Schmiedl, G.; Thomson, J. A Dynamic Concept for Eastern Mediterranean Circulation and Oxygenation during Sapropel Formation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2003**, *190*, 103–119. https://doi.org/10.1016/S0031-0182(02)00601-6.
- (18) Reitz, A.; Thomson, J.; De Lange, G. J.; Hensen, C. Source and Development of Large Manganese Enrichments above Eastern Mediterranean Sapropel S1.

  \*Paleoceanography\* 2006, 21 (3), 1–17. https://doi.org/10.1029/2005PA001169.
- (19) Tachikawa, K.; Vidal, L.-A.; Cornuault, M.; Garcia, M.; Pothin, A.; Sonzogni, C.; Bard, E.; Menot, G.; Revel, M. Eastern Mediterranean Sea Circulation Inferred from the Conditions of S1 Sapropel Deposition. *Clim. Past* 2015, *11* (6), 855–867. https://doi.org/10.5194/cp-11-855-2015.
- (20) Thomson, J.; Higgs, N. C.; Wilson, T. R. S.; Croudace, I. W.; De Lange, G. J.; Van Santvoort, P. J. M. Redistribution and Geochemical Behaviour of Redox-Sensitive Elements around S1, the Most Recent Eastern Mediterranean Sapropel. *Geochim. Cosmochim. Acta* 1995, *59* (17), 3487–3501. https://doi.org/10.1016/0016-

7037(95)00232-O.

- (21) Slomp, C. P.; Thomson, J.; De Lange, G. J. Enhanced Regeneration of Phosphorus during Formation of the Most Recent Eastern Mediterranean Sapropel (S1).
  Geochim. Cosmochim. Acta 2002, 66 (7), 1171–1184.
  https://doi.org/10.1016/S0016-7037(01)00848-1.
- (22) Hennekam, R.; de Lange, G. J. X-Ray Fluorescence Core Scanning of Wet Marine Sediments: Methods to Improve Quality and Reproducibility of High-Resolution Paleoenvironmental Records. *Limnol. Oceanogr. Methods* 2012, *10*, 991–1003. https://doi.org/10.4319/lom.2012.10.991.
- (23) Ehrmann, W.; Schmiedl, G.; Hamann, Y.; Kuhnt, T.; Hemleben, C.; Siebel, W. Clay Minerals in Late Glacial and Holocene Sediments of the Northern and Southern Aegean Sea. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2007**, *249* (1–2), 36–57. https://doi.org/10.1016/j.palaeo.2007.01.004.
- (24) Kuhnt, T.; Schmiedl, G.; Ehrmann, W.; Hamann, Y.; Hemleben, C. Deep-Sea Ecosystem Variability of the Aegean Sea during the Past 22 Kyr as Revealed by

- Benthic Foraminifera. *Mar. Micropaleontol.* **2007**, *64* (3–4), 141–162. https://doi.org/10.1016/j.marmicro.2007.04.003.
- (25) Almogi-Labin, A.; Bar-Matthews, M.; Shriki, D.; Kolosovsky, E.; Paterne, M.; Schilman, B.; Ayalon, A.; Aizenshtat, Z.; Matthews, A. Climatic Variability during the Last ~90 Ka of the Southern and Northern Levantine Basin as Evident from Marine Records and Speleothems. *Quat. Sci. Rev.* 2009, 28 (25–26), 2882–2896. https://doi.org/10.1016/j.quascirev.2009.07.017.
- (26) Hamann, Y.; Ehrmann, W.; Schmiedl, G.; Krüger, S.; Stuut, J. B. W.; Kuhnt, T. Sedimentation Processes in the Eastern Mediterranean Sea during the Late Glacial and Holocene Revealed by End-Member Modelling of the Terrigenous Fraction in Marine Sediments. *Mar. Geol.* 2008, 248 (1–2), 97–114. https://doi.org/10.1016/j.margeo.2007.10.009.
- (27) Schlitzer, R.; Roether, W.; Oster, H.; Junghans, H. G.; Hausmann, M.; Johannsen,
   H.; Michelato, A. Chlorofluoromethane and Oxygen in the Eastern Mediterranean.
   Deep Sea Res. Part A, Oceanogr. Res. Pap. 1991, 38 (12), 1531–1551.

- https://doi.org/10.1016/0198-0149(91)90088-W.
- (28) Sen Gupta, B. K.; Machain-Castillo, M. L. Benthic Foraminifera in Oxygen-Poor Habitats. *Mar. Micropaleontol.* **1993**, *20*, 183–201.
- (29) De Lange, G. J.; Thomson, J.; Reitz, A.; Slomp, C. P.; Speranza Principato, M.; Erba, E.; Corselli, C. Synchronous Basin-Wide Formation and Redox-Controlled Preservation of a Mediterranean Sapropel. *Nat. Geosci.* 2008, 1 (9), 606–610. https://doi.org/10.1038/ngeo283.