



Supplement of

Impact of deoxygenation and hydrological changes on the Black Sea nitrogen cycle during the Last Deglaciation and Holocene

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Table S1: Outline of the seven ^{14}C dates used in the production of the age-model for core 64PE418 and their calibrated ages. The ^{14}C and calibrated age of 142.5 cm is shown but was excluded from the age-depth model due to an age reversal.

Core	Depth (cm)	Material	Radiocarbon age (^{14}C yr BP)	$\pm 1\sigma$	Calendar age (cal yr BP)	$\pm 2\sigma$
64PE418 ^a	24.5	TOC	2010	30	435 ^{c,e}	115
KNR134-08-BC17 ^b	39.0	TOC	3640	70	2145 ^{c,e}	205
64PE418 ^a	76.5	TOC	5795	35	4870 ^{c,e}	170
64PE418 ^a	118.5	TOC	9110	50	9328 ^{d,f}	128
64PE418^a	142.5	TOC	11650	60	12720^{d,g}	50
64PE418 ^a	158.5	TOC	9670	50	9975 ^{d,f}	205
64PE418 ^a	183.5	TOC	12380	70	13358 ^{d,g}	123
64PE418 ^a	217.5	TOC	17420	110	19270 ^{d,h}	250

a ^{14}C dates from this study

b ^{14}C dates from Jones & Gagnon, 1994

c Calibrated with the Marine20 curve (Heaton et al., 2020)

d Calibrated with the IntCal20 curve (Reimer et al., 2020)

e R-age of 600 years applied (Kwiecien et al., 2008)

f R-age of 800 years applied (Kwiecien et al., 2008)

g R-age of 900 years applied (Kwiecien et al., 2008)

h R-age of 1450 years applied (Kwiecien et al., 2008)

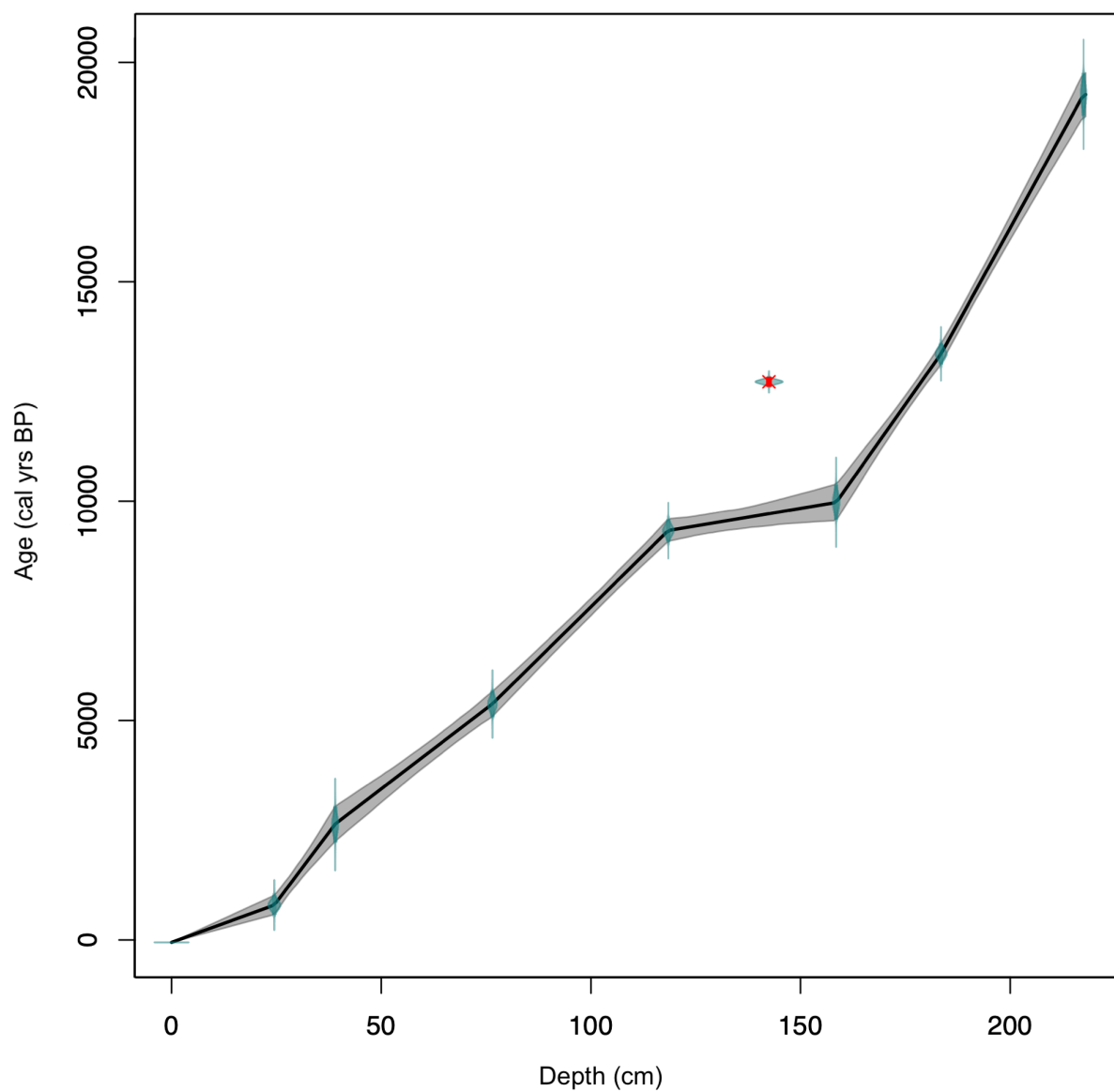


Figure S1: Age-depth model for core 64PE418, created using seven ^{14}C dates, six from core 64PE418 and one from KNR134-08-BC17 (Jones & Gagnon, 1994). Red dot shows the one excluded ^{14}C date at 142.5 cm due to an age-reversal.

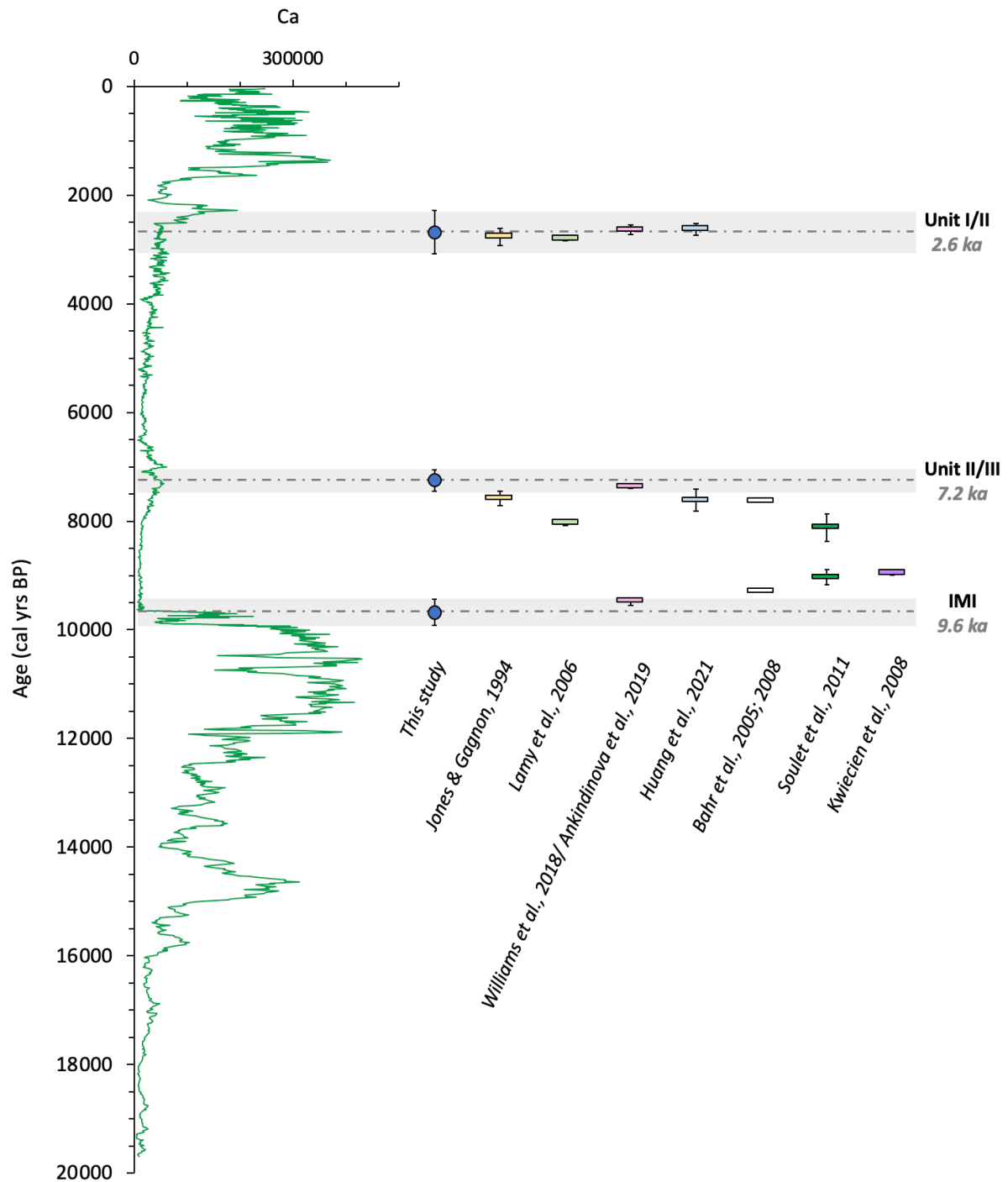


Figure S2: Calibrated ^{14}C ages of the key transitions in core 64PE418 over the Holocene (grey dashed lines, with error shown by grey band), and alignment with the previously published calibrated ages of these boundaries from existing studies (Jones & Gagnon, 1994; Lamy et al., 2006; Williams et al., 2018; Akindinova et al., 2019; Huang et al., 2021; Bahr et al., 2005; 2008; Soulet et al., 2011; Kwiecien et al., 2008), also highlighting their errors. Ca record from this study is also shown, in green.

Table S2. Identifying characteristics of the compounds reported in this study. AEC = assigned elemental composition, Δ mmu = (measured mass – calculated mass) x 1000 as calculated for extract from 1000 m depth. CFI = characteristic fragment ion(s). 135 cm

	Retention time (min)	Accurate mass ($[M+H]^+$)		AEC	Δ mmu	CFI
		Calculated	Observed			
Crenarchaeol ^a	66.8	1292.2444	1292.2452	C ₈₆ H ₁₆₃ O ₆	0.8	n/a
Isorenieratene ^a	28.6	528.3751 ^e	528.3754 ^e	C ₄₀ H ₄₈	0.3	133.1012, 436.3123
BHT-34S ^a	20.41	529.4615 ^f	529.4610	C ₃₅ H ₆₁ O ₃	0.5	163.148, 191.179
BHT-x ^a	20.82	529.4615 ^f	529.4636	C ₃₅ H ₆₁ O ₃	2.1	163.148, 191.179
H C ₂₆ diol ^a	10.2	577.4674	577.4677	C ₃₂ H ₆₅ O ₈	0.3	361.3826, 379.3930, 398.4033, 415.4141
H C ₂₈ diol ^b	12.0	605.4987	605.4995	C ₃₄ H ₆₉ O ₈	0.8	389.4138, 407.4224, 425.4348, 443.4454
H C ₂₈ triol ^c	9.2	621.4936	621.4933	C ₃₄ H ₆₉ O ₉	0.3	387.3973, 405.4085, 423.4189, 441.4308, 459.4402
H C ₃₀ triol ^c	11.1	649.5249	649.5247	C ₃₆ H ₇₃ O ₉	0.2	451.451, 469.4615, 487.4721
P C ₃₀ diol ^d	14.1	603.5198	603.5194	C ₃₅ H ₇₁ O ₇	0.4	417.4456, 435.4558, 453.4673, 471.4760
P C ₃₀ triol ^d	11.7	619.5143	619.5148	C ₃₅ H ₇₁ O ₈	0.5	415.4293, 433.4400, 451.4504, 469.4611, 487.4718
P C ₃₂ triol ^d	13.3	647.5456	647.5458	C ₃₇ H ₇₄ O ₈	0.2	443.4605, 461.4713, 479.4815, 497.4922, 515.5029

^aData from depth 135 cm

^bData from depth 130 cm

^cData from depth 160 cm

^dData from depth 13 cm

^e $[M]^+$ ion in place of $[M+H]^+$

^f $[M+H]^+-H_2O$ ion in place of $[M+H]^+$

References:

Ankindinova, O., Hiscott, R.N., Aksu, A.E and Grimes, V. 2019. High-resolution Sr-isotopic evolution of Black Sea water during the Holocene: Implications for reconnection with the global ocean. *Marine Geology*, **407**, 213-228.

Bahr, A., Lamy, F., Arz, H., Kuhlmann, H and Wefer, G. 2005. Late glacial to Holocene climate and sedimentation history in the NW Black Sea. *Marine Geology*, **214**, 309-322.

Bahr, A., Lamy, F., Arz, H., Major, C., Kwiecien, O and Wefer, G. 2008. Abrupt changes of temperature and water chemistry in the late Pleistocene and early Holocene Black Sea. *Geochemistry, Geophysics, Geosystems*, **9**, 1-16.

Jones, G.A and Gagnon, A.R. 1994. Radiocarbon chronology of Black Sea sediments. *Deep-Sea Research* **1**, **41**, 531-557.

Heaton, T.J., Köhler, P., Butzin, M., Bard, E., Reimer, R.W., Austin, W.E.N., Bronk Ramsey, C., Grootes, P.M., Hughen, K.A., Kromer, B., Reimer, P.J., Adkins, J., Burke, A., Cook, M.S., Olsen, J and Skinner, L.C. 2020. Marine20—The Marine Radiocarbon Age Calibration Curve (0–55,000 cal BP). *Radiocarbon*, **62**, 779–820. doi.org/10.1017/RDC.2020.68

Huang, Y., Zheng, Y., Heng, P., Giosan, L and Coolen, M.J.L. 2021. Black Sea paleosalinity evolution since the last deglaciation reconstructed from alkenone-inferred Isochrysidales diversity. *Earth and Planetary Science Letters*, **564**, 1-9.

Kwiecien, O., Arz, H.W., Lamy, F., Wulf, S., Bahr, A., Röhl, U and Haug, G.H. 2008. Estimated Reservoir Ages of the Black Sea Since the Last Glacial. *Radiocarbon*, 50, 99-118.

Reimer, P.J., Austin, W.E.N., Bard, E., Bayliss, A., Blackwell, P.G., Bronk Ramsey, C., Butzin, M., Cheng, H., Edwards, R.L., Friedrich, N., Grootes, P.M., Guilderson, T.P., Hajdas, I., Heaton, T.J., Hogg, A.G., Hughen, K.A., Kromer, B., Manning, S.W., Muscheler, R., Palmer, J.G., Pearson, C., van der Plicht, J., Reimer, R.W., Richards, D.A., Scott, E.M., Southon, J.R., Turney, C.S.M., Wacker, L., Adolphi, F., Büntgen, U., Capano, M., Fahrni, S.M., Fogtmann-Schulz, A., Friedrich, R., Köhler, P., Kudsk, S., Miyake, F., Olsen, J., Reinig, F., Sakamoto, M., Sookdeo, A and Talamo, S. 2020. The IntCal20 Northern Hemisphere Radiocarbon Age Calibration Curve (0–55 cal kBP). *Radiocarbon*, **62**, 725–757. doi.org/10.1017/RDC.2020.41

Soulet, G., Ménot, G., Lericolais, G and Bard, E. 2011. A revised calendar age for the last reconnection of the Black Sea to the global ocean. *Quaternary Science Reviews*, **30**, 1019-1026.

Lamy, F., Arz, H.W., Bond, G.C., Bahr, A and Pätzold, J. 2006. Multicentennial-scale hydrological changes in the Black Sea and northern Red Sea during the Holocene and the Arctic/North Atlantic Oscillation. *Paleoceanography & Paleoclimatology*, **21**, 1-11.

Williams, L.R., Hiscott, R.N., Aksu, A.E., Bradley, L.R., Horne, D.J and Stoica, M. 2018. Holocene paleoecology and paleoceanography of the southwestern Black Sea shelf revealed by ostracod assemblages. *Marine Micropaleontology*, **142**, 48-66.