

The establishment of euxinic conditions in the Holocene Black Sea

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Sample preparation and analysis

Trace metal and major element analyses were performed at the ICBM, Oldenburg (Germany), according to the following protocol:

Sediment samples were freeze-dried and ground with an agate planetary ball mill before being analyzed by X-Ray Fluorescence (XRF) for major and minor elements, by infrared (IR) spectroscopy for total carbon (TC) and total sulfur (TS) and by CO₂-Coulometry for total inorganic carbon (TIC). The amount of total organic carbon (TOC) was calculated as the difference between TC and TIC.

For XRF analysis 0.7 g of dried and ground sample were mixed with 4.2 g Li₂B₄O₇ and 1.0 g (NH₄)₂NO₃ (oxidizing agent) and fused to borate glass beads at 1350 °C in platinum crucibles. These beads were analyzed with a Philips PW-2400 WD-XRF spectrometer (calibrated with 53 geostandards and checked for accuracy by random measurements of acid digested samples using an iCap 6000 Inductively Coupled Plasma Optical Emissions Spectrometer).

For TC and TS analyses a given amount of dried and ground sample (50-100 mg) was mixed with V₂O₅ (oxidizing agent) and combusted in an O₂ stream. The resulting CO₂ and SO₂ were

measured with an ELTRA CS-500 IR-spectrometer. For TIC analysis 5 ml 2 M HClO₄ were added to 50-100 mg of dried and ground sample, and the evolving CO₂ was measured in a coulometric cell (UIC CM-5012; carrier gas: N₂).

All analytical results were cross-checked by parallel analysis of in-house and international reference materials (olivine basalt GSR-3, carbonate rock GSR-6). The relative standard deviations (RSDs) for our XRF-measurements are <5% for major and <8% for trace elements, while the RSDs for TC, TIC and hence TOC are <1% and for TS <5%.

Because carbonate and organic carbon contents vary significantly in Black Sea sediments, we use element/Al ratios to compensate for dilution effects. In the following, the Fe/Al and Ca/Al ratios are given as [wt. %/wt. %], while the trace metal/Al ratios are defined as [ppm/wt. %].

The original data will be published in PANGAEA (www.pangaea.de; doi in progress).

Iron isotope analysis

Samples for iron isotope analysis were processed at the Institute of Marine and Coastal Sciences, Rutgers University, USA. Dried sediments were fully digested by standard acid digestion techniques (HF–HNO₃–HCl) and iron was purified by passing sample solutions through an anion exchange resin, using standard protocol (Severmann et al., 2006). Iron isotope measurements were performed at the Woods Hole Oceanographic Institute ICP facility, Massachusetts, USA, using a Thermo Fisher Neptune multiple-collector ICP mass spectrometer, following the procedure of Arnold et al. (2004). Purified samples were introduced into the mass spectrometer as 200 – 500 ppb iron solutions, mixed with equal amounts of copper standard of known isotope composition (NIST-976 copper isotope standard), which was measured simultaneously for mass bias correction. Bracketing standards were measured after every second sample for additional mass bias control. Isotope ratios of ⁵⁶Fe/⁵⁴Fe and ⁵⁷Fe/⁵⁴Fe are reported using standard delta notation. Measured ratios are normalized relative to igneous rocks, which have an average

isotope composition of $\delta^{56}\text{Fe} = 0 \pm 0.10\text{‰}$ (2σ) (Beard et al., 2003). On this scale the isotope composition of the international iron isotope reference material IRMM-014 is -0.09‰ for $\delta^{56}\text{Fe}$. The average external precision for $\delta^{56}\text{Fe}$ was typically better than $\pm 0.10\text{‰}$ (2σ) for all samples. Several standard reference materials of known isotope composition, including SDO-1 (Devonian black shale) BIR-1 (basalt) and SCo-1 (Upper Cretaceous silty marine shale) were measured routinely for each sample batch, and values agreed well with previous measurements and published values.

Constructing the composite geochemical core log (CGCL)

All cores used for the construction of the CGCL originate from the euxinic section of the water column in different parts of the Black Sea. The four GeoB cores follow a transect through the western basin, the cores from sites 8, 14, and 22 were recovered in the north-western part and off the eastern Anatolian coast (Fig. 1). Several major element and metal proxies in these seven gravity cores (Fig. DR-1 and DR-2) were combined to a single composite core log (Fig. 2 and DR-3) following a three-step procedure:

- 1) The depth scale of each core was adjusted to a reference core by linear interpolation between five adjustment points chosen based on litho-/chemostratigraphic similarities: a) Unit II/III and b) Unit I/II boundaries (on the basis of lithology, TOC and CaCO_3 profiles, according to Arthur and Dean, 1998; Ross and Degens, 1974), c) Fe/Al peaks, d) Mo maxima and e) TOC maxima. This was done to compensate for variations in sedimentation rate respectively dilution.
- 2) Proxy data were combined and mean values plus standard deviations were calculated for each interpolated 1 cm depth interval by a MATLAB routine.
- 3) The resulting composite profiles underwent a two-point-average smoothing to remove part of the scatter.

The age model of the CGCL is based on the average thickness of each unit and the average ages of the Unit I/II and Unit II/III boundaries as defined by lithological and geochemical criteria from the literature in seven cores across the Black Sea (Arthur and Dean, 1998; Bahr et al., 2006; Bahr et al., 2005; Jones and Gagnon, 1994; Lamy et al., 2006; Major et al., 2002; Ross and Degens, 1974; Verleye et al., 2009; see also Table DR-1). The mean ages of around 2.7 ka for the Unit I/II and 7.6 ka for the Unit II/III boundaries are valid for the whole basin because relatively rapid paleoenvironmental changes (as indicated by distinctive peaks in the geochemical records) occur at different sampling locations. The chronology of core GeoB 7608 (Fig. DR-1), which is also incorporated in our CGCL, was established by Bahr et al. (2005, 2006).

Inventory calculation based on Mo enrichment

We assume an anoxic water column of 2,000 m depth with an average Mo concentration of 4 $\mu\text{g/l}$ (equivalent to an absolute Mo content of 8 g/m^2) (Nägler et al., 2011), while the average Mo concentration of oxic seawater (salinity: 35) is $\sim 10 \mu\text{g/l}$ (Martin and Whitfield, 1983). The Black Sea Unit II sapropel is on average 30 cm thick, has a density of 1.5 g/cm^3 , a porosity of 60%, and an average Mo content of 80 mg/kg, leading to a total Mo content ($P_{\text{Mo t}}$) of 14 g/m^2 . Thus, roughly twice the water column Mo inventory was incorporated into the basin-wide Unit II sapropel. Consequently, assuming quantitative Mo removal, the water column Mo inventory had to be replenished at least twice over the duration of the sapropel formation (see also Table DR-2).

Estimates of past seawater inflow over the Bosphorus sill into the Black Sea are based on the Mo contents in each 1-cm interval of the CGCL. The sedimentary parameters (porosity, density, Mo content and sediment thickness) are taken from the calculation above. At an average sedimentation rate of 0.0065 cm/a for Unit II sediments, each 1-cm interval of the CGCL corresponds to about 150 a. The sedimentary parameters and the Mo contents may be used to

calculate the total Mo inventory of each basin-wide sediment layer, which is equivalent to a specific volume of seawater required to provide the total amount of Mo. We assume a dilution of the inflowing Mediterranean seawater equivalent to today's Black Sea deep water salinity (22), resulting in a Mo concentration in the water column of about 6.7 µg/l. Dividing the total Mo inventory in a basin-wide sediment interval by this Mo concentration results in the volume of seawater required per m² per year. To compare with today's situation, the seawater inflow of 305 km³/a has to be divided by the anoxic basin area of approx. 300,000 km², resulting in 1.0 m/a water exchange (Özsoy and Ünlüata, 1997.) Multiplication by the Black Sea basin area (413,000 km²) leads to the total influx of seawater (F_{sw}) into the Black Sea per year (see also Table DR-2).

Inventory calculations for Fe enrichment in shelf sediments

To estimate the excess Fe content (Fe_x) in the deep basin sediments we calculated the Fe_x after eq. 1 for every cm interval of the CGCL.

$$\text{Equation (1): } Fe_x = Fe - \left(Al \times \frac{Fe}{Al_{bg}} \right)$$

where Fe and Al are the iron and aluminum contents, respectively, in the sample and $Fe/Al_{bg} = 0.51$ is the minimum Fe/Al ratio of all Unit III samples with a total sulfur content <0.1% (n = 230), representing the iron background value excluding an overprinting by diagenetic Fe sulfides. In a second step, the percentage of the Fe_x fraction relative to the total Fe was calculated. To eliminate scatter, a two-point-average smoothing was applied to the data, resulting in Fig. DR-4. This simple inventory calculation shows that 14-27% (mean value: 22%) of the Fe in the Fe-enriched sapropel sediments must originate from elsewhere.

The accumulation rates of total Fe in the basin sediment were calculated by using the Fe content per 1-cm interval of the CGCL, the sediment properties from above, and an average

sedimentation rate of 0.0155 cm/a (65 a/cm) for Unit I. The calculations were performed by using the same method as for the Mo budget.

The Fe inventory of the basin sapropel (M_{Fe}) was calculated by integrating the total Fe contents per m² at 1-cm intervals in the CGCL for Units I and II separately. To correct for the dilution by the spatially varying sedimentation rates in the Black Sea basin during deposition of both units, accumulation rates were multiplied by factors of 1.3 and 1.9 for Unit I and II, respectively. These modified accumulation rates were multiplied by the Black Sea basin area to estimate the total amount of Fe enriched in the sapropel layer ($M_{Fe} = 6.8 \times 10^9$ t; see also Table DR-2). The estimated excess Fe fraction (1.8×10^9 t) of this iron inventory represents 17% of the Fe_x from the average Holocene Black Sea sediments, and 22% of the Fe enriched layer in Unit I and II.

A simple inventory calculation shows that shelf sediments provide enough Fe to explain the enrichments in the deep basin sapropel: We calculated from Fe/Al ratios that the sapropel contains on average ~22% Fe_x . Multiplying this excess Fe with the basin-to-shelf area ratio ($170,000 \text{ km}^2 / 140,000 \text{ km}^2 = 1.21$) results in ~27% of Fe_x that must have been mobilized from the shelf. We investigated three cores from the suboxic shelf with an average Fe concentration of 3 wt. %. Since sediment accumulation rates are at least four times higher on the shelf compared to the basin, we calculate a maximum loss of ~0.2 wt. % of the shelf Fe inventory due to the Fe shuttle model. Owing to the locally variable Fe content of Black Sea shelf sediments, this loss may be insignificant.

In addition to the Fe inventory, the fraction f of mobilized Fe_x was calculated by Fe isotope mass balance, using equation (2) transposed to f_{Fe_x} :

$$\text{Equation (2):} \quad \delta^{56}Fe_{\text{total}} = f_{Fe_x} \times \delta^{56}Fe_x + (1 - f_{Fe_x}) \times \delta^{56}Fe_{\text{weath}}$$

$\delta^{56}Fe_x$ was calculated following the equation of Severmann et al. (2008) for samples with Fe enrichment, and separately for samples with Fe/Al background values. $\delta^{56}Fe_{\text{weath}} \approx 0 \pm 0.05\text{‰}$ is

the average Fe isotope composition of weathering input diluting the Fe enrichments. On the basis of equation (2), the $\delta^{56}\text{Fe}_{\text{total}}$ value of the Fe/Al peaks may be explained by a 36% contribution of Fe_x mobilized from the shelf sediments. This value is in line with the overall calculated Fe_x fraction of >20%.

Supplementary Table DR-1: Age model for Black Sea basin sediments using average boundary ages from the literature.

Age Unit I/II boundary [years]	Age Unit II/III boundary [years]	References
2,044 ± 7	7,869 ± 237	Arthur & Dean (1998)
	7,607 ± 40	Bahr et al. (2005, 2006)
2,720 ± 160	7,540 ± 130	Jones & Gagnon (1994)
2,760 ± 35	7,995 ± 55	Lamy et al. (2006)
3,330 ± 108	7,160 ± 108	Major et al. (2002)
3,090 ± 140	7,090 ± 180	Ross & Degens (1974)
3,050 ± 35	8,140 ± 50	Verleye et al. (2009)
2,760 ± 287	7,607 ± 316	Median

Supplementary Table DR-2: Parameters used for calculation of budgets

Sedimentary parameters	
Black Sea basin area	$A_{BS} = 413,000 \text{ km}^2$
Avg. density	$\rho = 1.5 \text{ t/m}^3$
Avg. porosity	$\Phi = 60\%$
Mass of 1 cm sediment layer	$m = \rho \cdot 0.01 \text{ m}^3 \cdot (1 - \Phi) = 0.006 \text{ t}$
Fe _{total} content of the sapropel in 1 cm interval	Fe _t [mg/kg]
Fe _{total} content of 1 cm layer per m ²	$C_{Fe} [\text{g}] = \text{Fe}_t \cdot m$
Mo _{total} content of the sapropel in 1 cm interval	Mo _t [mg/kg]
Mo _{total} content of 1 cm layer per m ²	$C_{Mo} [\text{g}] = \text{Mo}_t \cdot m$
Avg. sedimentation rate of Unit I	$SR_I = 0.0155 \text{ cm/a} \rightarrow 1 \text{ cm} = 65 \text{ a}$
Avg. sedimentation rate of Unit II	$SR_{II} = 0.0065 \text{ cm/a} \rightarrow 1 \text{ cm} = 154 \text{ a}$
Water column parameters	
Anoxic water column	$d_{wc} = 2000 \text{ m}$
Avg. Mo concentration	$\text{Mo}_{aq} = 4 \text{ } \mu\text{g/l}$
Mo content per m ²	$P_{\text{Mo aq}} = (\text{Mo}_{aq} \cdot d_{wc}) / 0.001 \text{ m}^2 = 8 \text{ g/m}^2$
Inflowing seawater Mo concentration (salinity of 22‰)	$\text{Mo}_{sw} = 6.7 \text{ } \mu\text{g/l}$
Seawater inflow estimates	$F_{SW} [\text{km}^3/\text{a}] = [(C_{Mo} / \text{Mo}_{sw}) / (1/SR)] \cdot A_{BS}$
Sapropel parameters	
Avg. thickness of Unit II sapropel layers	$d_{sap} = 30 \text{ cm}$
Correction factors for the average sedimentation rate of Unit I and II	$f_I = 1.9 \text{ and } f_{II} = 1.3$
Absolute Fe content of the Black Sea sapropel	$M_{Fe} = (f_I \cdot \Sigma C_{Fe \text{ Unit I}} + f_{II} \cdot \Sigma C_{Fe \text{ Unit II}}) \cdot A_{BS} = 6.8 \cdot 10^9 \text{ t}$
Avg. Mo content in the Unit II sapropels	$\text{Mo}_{t2} = 80 \text{ mg/kg}$
Mo content per m ²	$P_{\text{Mo t}} = [\rho \cdot (1 - \Phi) \cdot d_{sap}] \cdot \text{Mo}_{t2} = 14 \text{ g/m}^2$

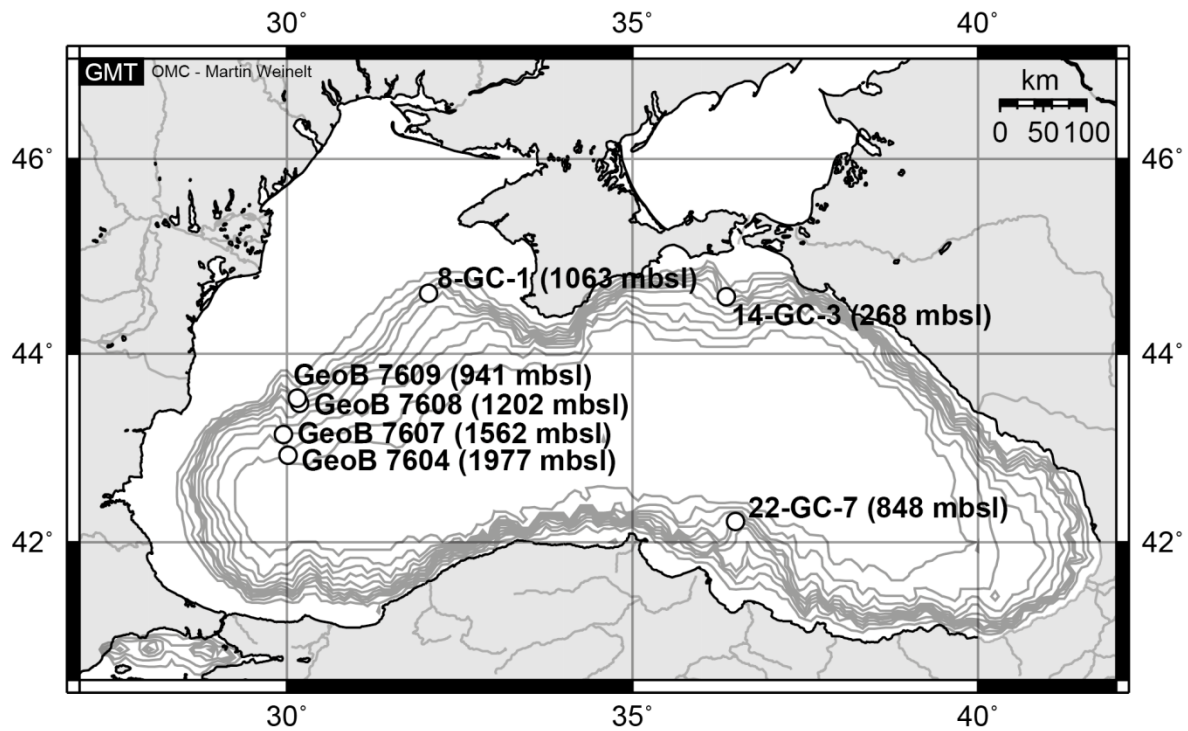


Figure DR-1: Map of the Black Sea with sampling locations. Sampling depths are noted in parentheses (created by OMC: http://www.aquarius.geomar.de/make_map.html; OMC copyright: M. Weinelt).

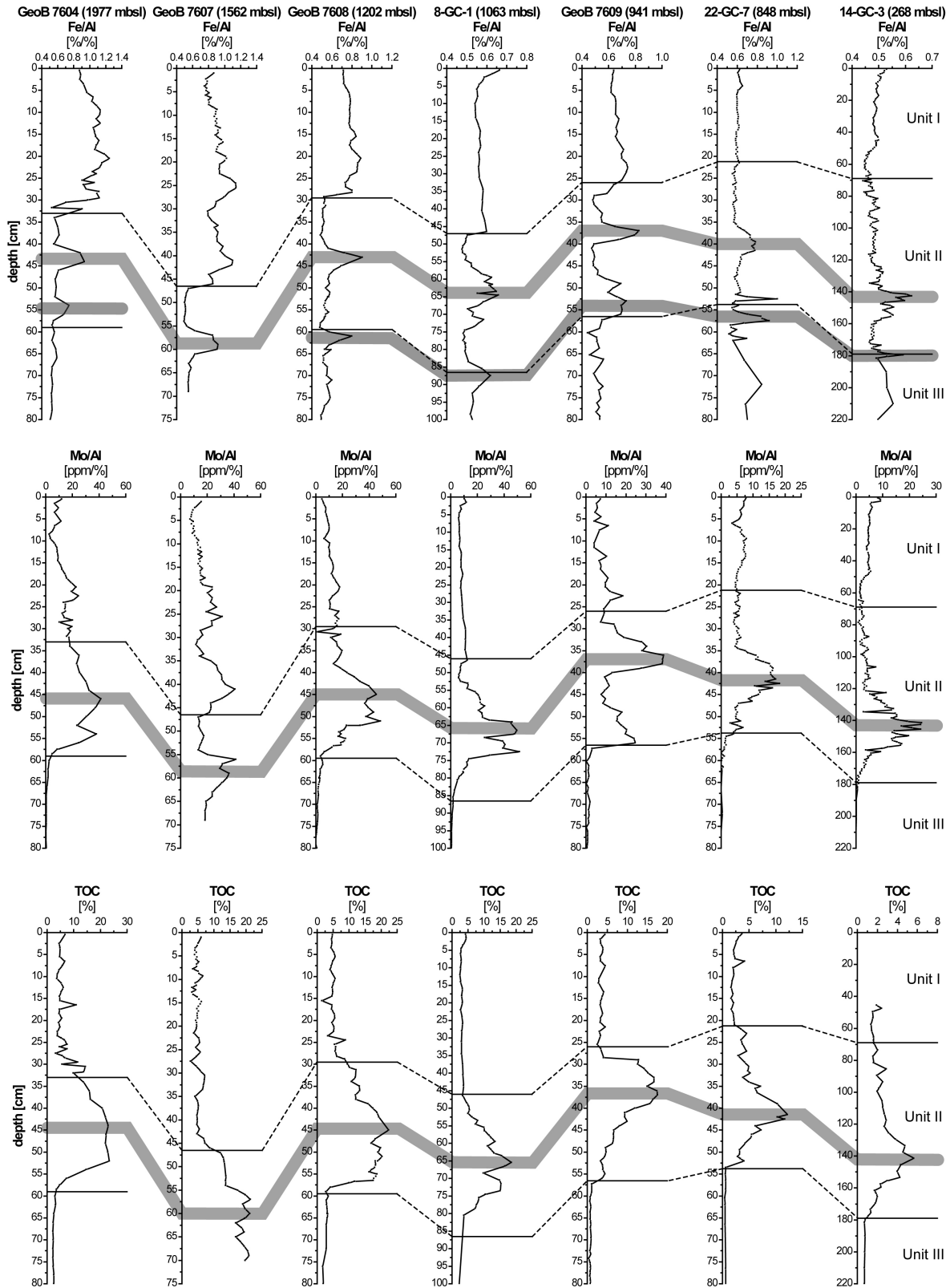


Figure DR-2: Depth profiles of Fe/Al, Mo/Al and TOC for the sampling locations shown in Fig. DR-1. The horizontal lines indicate the unit boundaries. The shaded bars highlight ubiquitous signals in the geochemical records. The original data will be published in PANGAEA (www.pangaea.de; doi in progress).

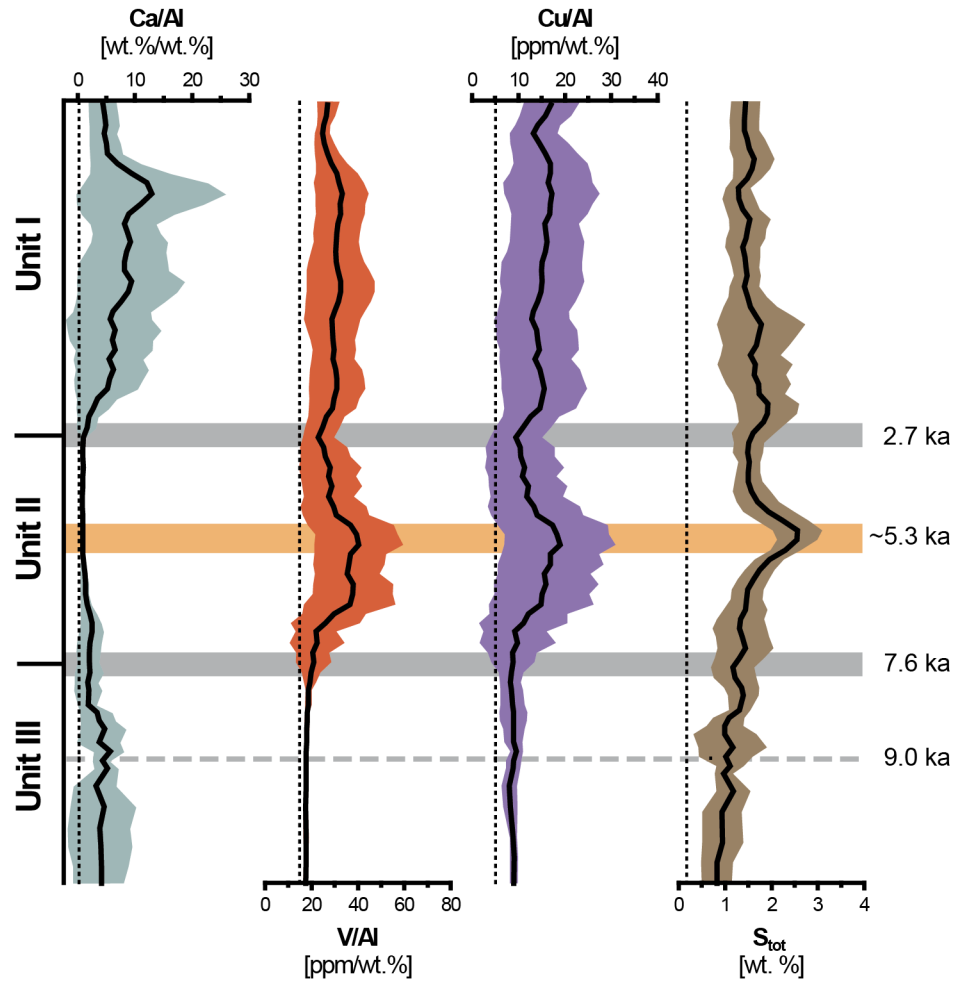


Figure DR-3: Composite geochemical core logs (CGCL) of Ca/Al, Cu/Al, V/Al, and S_{tot} . The vertical distribution patterns are based on element data of seven cores (see text and method section). The colored areas show the standard deviations. The vertical dashed lines represent average shale values. The dashed horizontal line displays the first ingress of Mediterranean seawater into the Black Sea basin (9.0 ka; Soulet et al., 2011). The beige bar depicts first establishment of shelf suboxia (~5.3 ka). The grey horizontal bars show the unit boundaries. The Ca/Al profile parallels the establishment of coccolithophorida communities in Unit I after completion of the limnic/marine transition. Cu/Al, V/Al, and S_{tot} display the development of euxinic conditions in the sedimentary archive, as do Fe/Al, Mo/Al, and TOC data. TOC indicates an increase in productivity and/or preservation during the transition phase (Unit II).

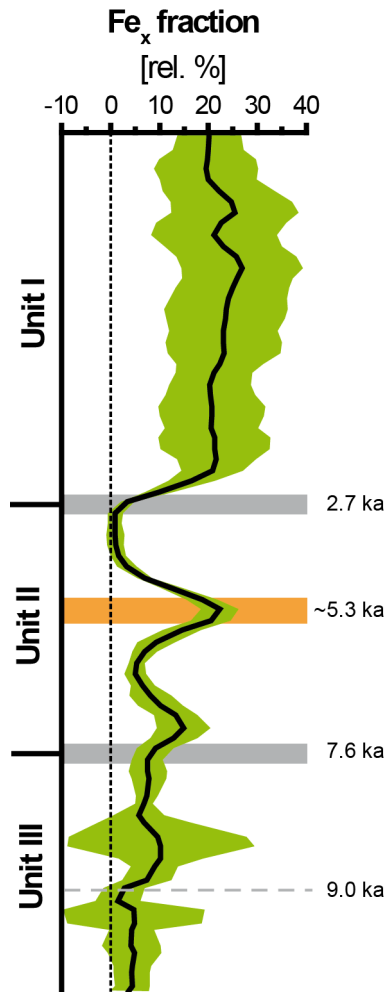


Figure DR-4: Percentage of the Fe_x fraction relative to total Fe in CGCL. The green area shows the standard deviation; the vertical dashed line shows the zero % Fe_x fraction, negative values are due to diagenetic Fe mobilization. This plot is based on the Fe/Al background value of 0.51 for Unit III samples with low S contents, thus excluding diagenetic Fe sulfide overprinting. The dashed horizontal line displays the first ingress of Mediterranean seawater into the Black Sea basin (9.0 ka). The beige bar depicts first establishment of shelf suboxia (~5.3 ka). The grey horizontal bars show the unit boundaries.

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