Rapid onset of ocean anoxia shown by high U and low Mo isotope compositions of sapropel S1

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Abstract

Authigenic uranium isotope compositions of Holocene sapropel S1 (δ²³⁸Uauth = +0.10 to +0.52‰: ODP core 967; 2550 mbsl) are significantly higher than the proposed upper boundary (+0.2‰) associated with the transport-porewater diffusion model for sediment uranium uptake. It is shown that these high δ²³⁸Uauth values are compatible with rapid initial slowdown of thermohaline overturning and the development of an anoxic water column. These conditions would favour U uptake in an organic-rich floccule layer overlying the sediment-water interface.
The high $\delta^{238}U_{\text{auth}}$ values correlate with low $\delta^{98}Mo_{\text{auth}}$ values (+0.02 to -0.88‰), interpreted to reflect weakly euxinic conditions controlled by thiomolybdate–molybdate solution equilibria. The S1 data contrast markedly with published data from last interglacial sapropel S5 from the same core, which show $\delta^{238}U_{\text{auth}}$ and $\delta^{98}Mo_{\text{auth}}$ characteristics compatible with a restricted euxinic basin due to progressive slowdown in the thermohaline circulation. The U-Mo isotope data for S1 are similar to a range of published paleo-settings. Sapropels are therefore shown to be useful templates for the unravelling of the interplay between productivity and deep-water renewal times in ancient settings.
Introduction

The redox-sensitive behavior and associated isotope fractionations of molybdenum (Mo) and uranium (U) have led to a prominent role for their sedimentary and isotope geochemistry in the evaluation of ancient ocean redox conditions. Both elements can show strong authigenic (seawater-derived) enrichment in marine organic carbon-rich sediments, accompanied by distinctive isotope signatures (e.g. Asael et al., 2013; Brüske et al., 2020; Kendall et al., 2015).

Uranium isotopes in anoxic and organic carbon-rich marine sediments (expressed as $\delta^{238}$U, parts per thousand deviation from the CRM145 standard) generally show values considerably heavier than contemporary seawater (-0.39‰; Andersen et al., 2017). This isotope enrichment is compatible with partial reduction of U$^{+6}$ to U$^{+4}$. In modern organic carbon-rich sediments, authigenic $\delta^{238}$U values rarely exceed +0.2‰, equivalent to a $\Delta^{238}$U$_{\text{sediment-water}}$ of $\sim$+0.6‰, approximately half the estimated full isotope fractionation accompanying U reduction (Andersen et al., 2017). This has been interpreted in terms of a diffusion-reaction-transport model combining U reduction in the semi-closed sediment system, limited by U diffusion from bottom water through pore waters (Andersen et al., 2014). However, an increasing number of ancient organic carbon-rich sediments show authigenic $\delta^{238}$U values higher than +0.2‰, suggesting redox-driven U isotope fractionation closer to that expected in an open system ($\Delta^{238}$U $>$0.6‰), and pointing towards U reduction outside the sediments (e.g. Brüske et al., 2020; Cheng et al. 2020; Kendall et al. 2020).

In addition, coupled measurements of molybdenum isotope compositions (expressed as $^{98}$Mo/$^{95}$Mo, parts per thousand deviation from NIST 3134 +0.25; Nägler et al., 2014) in these high $\delta^{238}$U organic carbon-rich sediments, generally show $\delta^{98}$Mo significantly lower than the modern seawater value of $\sim$+2.3‰ (e.g. Cheng et al. 2020; Kendall et al. 2020). Near seawater
\(\delta^{98}\)Mo values are proposed to reflect euxinic water conditions, where dissolved \([\text{H}_2\text{S}]_{\text{aq}}\) exceeds a ‘switch point’ (~11µM for modern seawater) at which seawater \(\text{MoO}_4^{2-}\) becomes irreversibly and near-quantitatively converted to a highly particle reactive tetra-thiomolybdate (\(\text{MoS}_4^{2-}\)) species (Erickson and Helz, 2000; Arnold et al., 2004). Euxinic waters with \([\text{H}_2\text{S}]_{\text{aq}}\) below the switch point, may lead to Mo deposition with significantly lower \(\delta^{98}\)Mo values because Mo removal occurs from isotopically fractionated oxy-thiomolybdate species coexisting with molybdate (Neubert et al., 2008; Kerl et al., 2017). An alternative mechanism for the generation of isotopically light Mo relates to the delivery of authigenic Mo to sediments via an Fe-Mn oxide particulate shuttle (Kendall et al., 2017).

Though this combination of high \(\delta^{238}\)U and low \(\delta^{98}\)Mo is observed in a range of ancient sediments, an understanding of the specific biogeochemical and oceanographic settings that cause it is hindered by the lack of well-studied modern analogs. The periodic deposition of organic carbon-rich sediments (sapropels) in the Eastern Mediterranean (EM) sea provide a means to study the behavior of this coupled redox proxy system. In particular, the study of sapropels of different intensity at different times in the same physical setting allows the identification of signatures driven by different climatic and oceanographic forcing mechanisms.

**Authigenic U and Mo isotopes in Sapropels S1 and S5**
This study investigates the contrasting U and Mo isotope systematics of EM sapropels S1 from the Holocene and S5 from the last interglacial (abbreviated ‘S1’ and ‘S5’ in the following), sampled in ODP core 967 (SI, Fig. S1). Sapropel S5 (~128.3-121.5 ka) shows strong authigenic enrichment of U and Mo, coupled to progressive \(\delta^{98}\)Mo\text{auth} increase (1.2-1.8 to +2.0-2.3‰) and \(\delta^{238}\)U\text{auth} decrease (+0.10 to -0.15‰), from the beginning to the end (Andersen et al., 2018).
Modelling of the S5 $\delta^{238}$U indicates a progressive 10-fold decline in the deep EM thermohaline overturning circulation. A study of S1 (10.8-6.1 ka) has shown that it is less strongly developed than S5, with weakly sulfidic bottom water conditions interpreted from low $\delta^{98}$Mo values (Azrieli-Tal et al., 2014), although anoxic conditions were regionally prevalent at water depths >1800m (de Lange et al., 2008).

Here, we report additional U isotope measurements for S1, allowing a direct comparison of the U and Mo isotope systematics for S1 and S5 (methods, age models and additional data are summarized in SI). The S1 samples show lower U concentrations (10-40 ppm) than S5 (25-150 ppm), but high $\delta^{238}$U values, reaching +0.35 to +0.5‰ in the lower and middle zones at 127-116 cm (Fig. 1). Thus, both the U concentration and $\delta^{238}$U patterns in S1 differ significantly from S5. Calculated authigenic U ($U_{auth}$) and Mo ($Mo_{auth}$) concentrations in the S1 profile show that detrital contributions are only significant in the background sediments, whereas authigenic contributions dominate in S1 (85-96%). High $U_{auth}$ concentrations are correlated with high $\delta^{238}U_{auth}$ values (>+0.2‰) and high $Mo_{auth}$ concentrations with low $\delta^{98}Mo$ values (Fig. 1). Peak $\delta^{238}U_{auth}$ values (127-116 cm) vary from +0.41 ± 0.06 ‰ to +0.52 ±0.06‰, whereas $\delta^{238}U_{auth}$ values of -0.7 to +0.1‰ occur before and after S1 and in the first sample at its start (130cm), indicating that a significant proportion of the $U_{auth}$ may be associated with U deposited directly with organic matter, carrying low $\delta^{238}U_{auth}$ (Andersen et al., 2017), in addition to in situ U reduction (see SI for details).

Controls on U and Mo isotope fractionation in S1 and S5

Sapropels S1 and S5 show contrasting behavior in their $\delta^{238}U$-$\delta^{98}Mo$ systematics, which may relate to different climatic and oceanographic mechanisms creating sediment and/or seawater anoxia. Firstly, the timing of peak sapropel development, as expressed in redox sensitive trace
metal profiles, represents a key difference between the two sapropels. Whereas redox-sulfide sensitive proxies for S1 (S, Fe/Al, V/Al, Mo/Al, As/Al) indicate rapid and early development to maximum intensity at ca 120 cm, the same proxies show that S5 developed more slowly, only reaching maximum values in the upper sapropel (SI, Fig. S2). The higher concentrations of redox sensitive trace metals (e.g. U and Mo concentration profiles; Fig. 1) also demonstrate the more reducing character of S5. In contrast, the two sapropels do not show any systematic differences in [TOC] at peak sapropel conditions (Fig. 1), and they have similar calculated organic carbon accumulation rates (OCAR) of 261 ± 36 mg/cm².ky for S1 and 178 ± 48 mg/cm².ky for S5 (see SI for details).

The δ⁹⁸Mo_auth of S1 shows a significant early drop towards the low values of ~ -0.8‰ at peak sapropel conditions, followed by a rise to ~ 0‰ (Fig. 1). The low S1 δ⁹⁸Mo values have been interpreted to represent Mo uptake from isotopically fractionated oxy-thiomolybdate species at bottom water sulfide levels below that at which Mo is effectively and quantitatively converted to tetra-thiomolybdate (Azrieli-Tal et al., 2014). The production of thiomolydates requires sulfate reduction, driven by biological productivity and long deep-water replacement times. Non-quantitative conversion of Mo to thiomolybate requires low sulfide and sequestration of more sulfidised species to the sediment, e.g., by colloidal FeMo(VI)S₄ (Helz and Vorlicek, 2019). Low sulfide levels and non-quantitative conversion of molybate to thiomolydates can result in light sedimentary Mo without invoking a Fe-Mn shuttle, via non-quantitative Mo removal from bottom waters, in a similar way as suggested for a range of modern semi-closed basins also showing authigenic δ⁹⁸Mo values below seawater (Bura-Nakic et al. 2018). In S5, with more intense sulfate reduction resulting from protracted thermohaline overturning slowdown and high OCAR, the δ⁹⁸Mo_auth are close to the seawater values (Andersen et al., 2018).
In contrast to S5, S1 is characterized by high δ²³⁸U, higher than expected from reduction of seawater-derived U in a semi-closed sediment-porewater system (Andersen et al., 2014). Post-sapropel oxidative burndown leading to diagenetic redistribution of previously deposited isotopically fractionated U downwards, could provide a mechanism for creating high δ²³⁸U. However, the expression of the oxidative burndown in S1 is distinct and sharp for all the redox sensitive metals. There is no evidence for downwards U diffusion and reprecipitation (e.g. a gradient in U/Al and δ²³⁸U with depth - see SI for details). Alternatively, U isotope reactive-transport modelling has suggested that high δ²³⁸U could be a consequence of low sedimentation rates and high productivity in reducing sediments (Lau et al., 2020). However, the similar sedimentation rates for S1 and S5, also make this an unlikely process given their very different δ²³⁸U signatures (Fig. 1). Direct U reduction in the water column, followed by scavenging and transport to the sediments, is another mechanism that could lead to high δ²³⁸U (e.g., Brüske et al., 2020, Kendall et al. 2020). But the stronger uptake of redox-sensitive metals in S5 than S1 (Fig. 1) would likely favour high δ²³⁸U in S5, not S1.

Another model for providing a greater expression of the Δ²³⁸U_{water-sediment} involves U reduction promoted by an organic-rich floccule layer overlying the consolidated sediment (Andersen et al., 2017; Cheng et al., 2020). The formation of an organic-rich floccule layer is likely to occur in settings with high biological productivity and organic-carbon flux. However, the combined Mo-U data for S1 require a further condition: light Mo isotopes require the partial conversion of Mo to thiomolybdate, and therefore mildly [H₂S]ₐq levels. Redox-sensitive element data for S1 (Figs 1 and 2) make a strong case for rapid early development of euxinia, which could promote deposition of such an organic-rich floccule layer. High resolution simulations of intermediate and deep-water circulation suggest that enhanced Nile discharge could have
triggered rapid shutdown of EM overturning circulation (Vadsaria et al., 2019). The early thermohaline circulation slowdown would potentially promote the development of mildly sulfidic waters.

Outlook: the U-Mo isotope proxy applied to ancient sediments

Both S1 and S5 show inverse correlations between $\delta^{238}\text{U}_{\text{auth}}$ and $\delta^{98}\text{Mo}_{\text{auth}}$ (Fig. 2). However, temporally, the trends go in opposite directions. For S5, the end-point of the correlation is defined by maximal euxinic conditions at the end of the sapropel. In S1, the end-point of the correlation is represented by the early sapropel peak. This difference in temporal progression for S1 and S5 is likely to reflect the fundamentally different modes of Mo and U incorporation into the sediments. Whilst the S5 data likely records progressive slowdown and increasingly euxinic conditions throughout the entirety of sapropel formation (Andersen et al. 2018), S1 seems to require rapid short-lived euxinia caused by early thermohaline slowdown. These two scenarios provide a potential framework for the interpretation of paleoredox evolution. Using the sapropel data, it is possible to delineate three general behaviours (Fig. 2). The first (1) represents mildly euxinic sediments typical of S1, with U and Mo uptake associated with an organic floccule layer. The second (2) is associated with non-quantitative U and Mo uptake in more intensely euxinic conditions and with porewater U reduction. The third (3) involves strongly euxinic sediments moving towards near-quantitative Mo and U uptake, as seen in S5 and in modern restricted basins with variable deep-water overturning rates (Fig. 2).

Trend (1), seen in S1, is very similar to recent published combined $\delta^{238}\text{U}_{\text{auth}} - \delta^{98}\text{Mo}_{\text{auth}}$ data from Cambrian and Devonian organic carbon-rich sediments (Cheng et al. 2020; Kendall et al. 2020). These sediments show high $\delta^{238}\text{U}$ values (up to +0.6‰), combined with low $\delta^{98}\text{Mo}$ (down to -0.1‰). Also, Ediacaran organic–rich mudstones (Kendall et al., 2015) and the
Paleoproterozoic Zaonega Formation shales (Asael et al., 2013) show an inverse correlation which parallels the type 1 (S1) trend. Limited Black Sea unit II data (Brüske et al., 2020) show similarly high $\delta^{238}$U$_{auth}$ (~ +0.55‰) to S1, while $\delta^{98}$Mo$_{auth}$ (+1.23‰) is relatively higher (Fig. 2). All these localities exhibit similar negatively correlated $\delta^{238}$U-$\delta^{98}$Mo values as seen in S1, but at variable trajectories and with different $\delta^{98}$Mo values. This observation may be partly attributed to variable seawater $\delta^{98}$Mo over time, but it would also depend on the [H$_2$S]$_a$ levels and the specific stability of the oxythiomolybdate species in each setting.

A key observation is that although high productivity in upwelling-type settings has been suggested to be the critical driver for high $\delta^{238}$U in organic carbon-rich sediments (Cheng et al., 2020), this does not fit well with the observations in this study. Although high productivity is an important factor it is not the defining one (e.g. S1 and S5 have similar [TOC] contents and calculated OCAR, yet show completely contrasting behavior in the U and Mo isotope systematics). From the sapropel data it may be inferred that the specific conditions that favour combined high $\delta^{238}$U$_{auth}$ with low $\delta^{98}$Mo$_{auth}$ require both a high particulate to water ratio (e.g. organic flocule layer) and (low) [H$_2$S]$_a$ levels, to aid the reduction of U and formation of oxythiomolybdates, followed by Mo and U scavenging by particulate/organic matter to the sediments. In the case of S1 this likely occurs via rapid thermohaline slowdown combined with high productivity and formation of an organic flocule layer. In other settings with high productivity in upwelling zones, the development of [H$_2$S]$_a$ bottom water plumes as observed on the Peru margin (Schunk et al., 2013), combined with an organic flocule layer, could also provide the right condition for high $\delta^{238}$U$_{auth}$ with low $\delta^{98}$Mo$_{auth}$ in organic carbon-rich sediments. The paleo-examples discussed here show that conditions that favour these S1 type $\delta^{238}$U-$\delta^{98}$Mo sediment systematics likely occurred across a large part of Earth history. Yet, in inferring paleoproxy evolution from U and Mo isotope trends, it is the data systematics from
individual settings that are important, as opposed to direct comparison of exact $\delta^{238}$U and $\delta^{98}$Mo compositions between settings. Based on this study, the careful and combined analysis of $\delta^{238}$U-$\delta^{98}$Mo systematics in organic carbon-rich sediments is critical to providing the most robust way of identifying localized isotope effects for both systems and, thus, oceanographic conditions during sediment deposition.

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References


Figure 1. Depth profiles for sapropels S1 (top) and S5 (bottom). The S5 data are from Andersen et al. (2018), the S1 Mo data from (Azrieli Tal et al., 2014). Dashed lines indicate the position of the sapropel boundaries as determined from Ba/Al ratios. The TOC profile in S1 indicates post-sapropel oxidation in the upper 4cm (see SI). A potential post-deposition ventilation event at ~116cm (8ka) is marked with weakly stippled line for S1. Vertical lines in the isotope panels represent approximate seawater compositions. Note the larger scale-bars for S5 than S1 for the U (x2) and Mo (x4) concentrations.
Figure 2. $\delta^{98}\text{Mo}_{\text{auth}}$ vs $\delta^{238}\text{U}_{\text{auth}}$ crossplots for sapropels (main plot), as well as four Proterozoic to Devonian organic-rich shales (Asael et al., 2013; Cheng et al. 2020; Kendall et al., 2015; Kendall et al., 2020). The main plot shows S1 (blue, filled samples 130-116cm, stippled 116-110cm), sapropel S5 (orange) and background sediments. Compositions for modern-day seawater and average deep sediments in Cariaco Basin and Black Sea Unit I/II (cores 12GGC/70GGC and 32MUC24, respectively; Brüske et al., 2020) are also shown. Correlated linear relations for the sapropels from start towards peak sapropel maxima are shown by the arrows for S1 and S5. The four paleo-data sets (converted to authigenic compositions - see SI), identify high $\delta^{238}\text{U}$ values combined with low $\delta^{98}\text{Mo}$, and generally similar evolutions to the S1 trend in the main plot (S5 and S1 trends marked by stippled lines).
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Supplementary Information

The Supplementary Information includes:

1. Methods
2. Age model and sapropel event definitions
3. Organic carbon sediment accumulation rates
4. Authigenic U and Mo concentration and isotope estimates
5. Authigenic $\delta^{238}$U and $\delta^{98}$Mo estimates - estimating the contribution of U and Mo directly associated with organic matter

- Figures S1 to S4
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1. Methods

The samples from sapropel S1 were taken from ODP core 967D, drilled at a water depth of 2550m south of Cyprus, at the base of the northern slope of the Eratosthenes Seamount (Emeis et al., 1998) (Fig. S-1). This study uses the dried and sieved <63μm fraction of the samples analysed by Scrivner et al. (2004) and Vance et al. (2004) for Nd isotope measurements in foraminifera (ODP 967D-1H1, covering S1 and depths immediately above and below). The S5 data of Andersen et al. (2018) used in this study were also measured on the dried and sieved <63 μm fraction of the samples analysed by Scrivner et al. (2004) for Nd isotopes in foraminifera (ODP 967C-H5). Previous studies using the <63 μm fractions indicate that they provide a representative record of the elemental and isotope geochemistry of sapropels (Box et al., 2011; Azrieli-Tal et al., 2014). Sample preparation and U isotope measurements were conducted at the facilities of the Bristol Isotope Group, University of Bristol, United Kingdom, while chemical analyses of major and trace element chemical analyses (wt.% and μg/g, respectively) were made using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at the Geological Survey of Israel after low temperature ashing and sodium peroxide digestions. Errors on single values (1σ) are from ±5 % to ±7 % for ratios. Total organic carbon (TOC) data (for the bulk sediment) are taken from Vance et al. (2004). For samples missing a direct TOC
measurement, the TOC is estimated as an average of the two bracketing samples with available TOC data.

**Figure S-1**  Vertical salinity profile (top) through the present-day Mediterranean basin (bottom). The position of core ODP 967 (2550 m water depth) is marked (star). Present-day deep-waters are well oxygenated due to thermohaline circulation driven by surface water evaporation and high salinity in the EM. The periodic formation of organic carbon-rich sapropels correlated with high northern hemisphere summer insolation during minima in the ca 21 ka orbital precession cycle. Significantly slower deep-water renewal rates in the EM would have played an important role in the formation of sapropels and are consistent with the suppression of overturning during high insolation periods, due to increased water body stratification resulting from higher riverine freshwater input under enhanced monsoon forcing. Diagram generated in Ocean Data View (https://odv.awi.de).

Details of the molybdenum and uranium isotope analyses, including standards, calibration procedures, and error treatments, are given in Azrieli-Tal *et al.* (2014) and Andersen *et al.* (2018). In brief, for the uranium isotope work in this study, samples (10-50 mg) were dissolved in steps involving concentrated HNO₃, HF, HCl and H₂O₂. At the first dissolution step, in HNO₃ and HF, the IRMM3636 \(^{236}\text{U}/^{233}\text{U}\) double spike was added, aiming for a \(^{236}\text{U}/^{235}\text{U}\) of ~4. After heating, fluxing and subsequent drying steps using 6 M HCl (x2) and a 7 M HNO₃ + 30% H₂O₂ mixture were completed, samples were re-dissolved in 10 ml of 3 M HNO₃ in preparation for U-Teva chromatographic chemistry, following protocols given in Andersen *et al.* (2014; 2018). Purified U fractions were dried and prepared for mass spectrometry in 2% (v/v) HCl aiming for 100-200 ppb U. Full procedural chemistry blanks were <20 pg of U. Uranium isotopic analyses were carried out at the University of Bristol, using a ThermoQuest Neptune instrument operating at low mass resolution (M/ΔM ~500) by means of a CPI (Amsterdam, The Netherlands) PFA nebulizer and spray chamber fitted to a CETAC Aridus. The set-up and measurement protocols were as outlined in Andersen *et al.* (2014; 2015). All
Faraday cups were equipped with $10^{11} \, \Omega$ resistors, apart from the cup for $^{238}\text{U}$ ($10^{10} \, \Omega$). Measurements were conducted with “standard” sampler and “X” type skimmer cones. Typical sample ion beam intensities were ~1 nA for $^{238}\text{U}$ using ~50 ng U per analysis. Measurements of two unknowns were bracketed with the CRM-145 uranium standard, spiked in similar fashion as the unknowns. The in-house CZ-1 uraninite standard, processed through U-Teva chemistry and periodically measured in a similar fashion to the sediment samples, yielded $\delta^{238}\text{U}$ of $-0.055\pm0.032 \, (\pm 2 \text{S.D.})$ for ten repeats, in excellent agreement with previously published compositions for this standard (Stirling et al., 2007; Andersen et al., 2015). The $^{234}\text{U}/^{238}\text{U}$ ratios were measured simultaneously with the $^{235}\text{U}/^{238}\text{U}$, and the $^{234}\text{U}/^{238}\text{U}$ data are reported as $\delta^{234}\text{U}$, the $^{234}\text{U}/^{238}\text{U}$ relative to secular equilibrium in part per thousand using the half-lives of Cheng et al. (2013). The external reproducibility for the CZ-1 standard is used as the uncertainty estimate for each of the unknowns (Andersen et al., 2014; 2015; 2018). Sample data, including depth information, chemical element concentrations, and isotopic compositions used in this study are presented in Table S-1.

2. Age model and sapropel event definitions

The age model for S1 (10.8 to 6.1 ka) is taken from de Lange et al. (2008) and from Grant et al. (2012) for S5 (128.3 to 121.5 ka). The upper and lower boundaries assigned to the sapropels S1 and S5 are determined from their Ba/Al and TOC profiles (130-106 cm and 103.5-74 cm, respectively; Azrieli-Tal et al., 2014; Andersen et al., 2018, see Figure S-2). Whereas the TOC and Ba/Al boundaries coincide in S5, the TOC profile in S1 indicates post-sapropel oxidation (burndown) in its upper 4 cm (106-110 cm) (Fig. S-2). Sapropel geochemical data for S1 sensu stricto are thus recorded from ~110 to 130 cm. Furthermore, a short-lived oxidation event commencing at ~116 cm is also evident from the molybdenum isotope, Fe/Al and Ba/Al data (Azrieli- Tal et al., 2014). This likely correlates with a re-ventilation event related to the 8 ka northern hemisphere cold climate event recorded in other EM S1 sapropels (Casford et al, 2003). This injection of oxygen by re-ventilation has been recognised in number of sapropel S1 samples and is shown to affect (in addition to Ba/Al) redox sensitive metal ratios such as Fe/Al, As/Al and V/Al (Hennekam et al., 2014 ; Tachikawa et al., 2015 ; Filippidi and de Lange, 2019). The preservation in ODP967 of this re-ventilation signal (which has lead researchers to classify S1 into early (S1a) and late (S1b) segments) is not consistent with post-sapropel diagenetic remobilization of reduction sensitive metals from upper S1b into lower S1a. Specifically for U, a re-distribution profile would be expected to show increasing U/Al from the top and down to a zone of maximum reduction within S1a, similar to observed in modern reducing sediments with increasing uptake of reduced U at depth (e.g. Abshire et al., 2020). The lack of such U (Fig 1) or U/Al (Fig. S-2) profile, combined with the TOC and Ba/Al profiles for S1 and S5, is compatible with the early/late peak sapropel development evident in redox sensitive elements (Fig. S-2). This is also true for EM S1 and S5 TOC, Ba/Al and redox metal sapropel profiles determined in other studies (e.g., Gallego-Torres et al., 2007; 2010).
Figure 5-2  Depth profiles of selected proxies (TOC, S, Ba/Al, Fe/Al, U/Al, Mo/Al, V/Al, As/Al) for sapropel S1 (top layer) and sapropel S5 (lower layer). (Data sources for this figure and main text Figure 1, S1: Azrieli-Tal et al., 2014; Vance et al., 2004; this study; S5: Andersen et al., 2018; Emeis et al., 1998 – see table S-1). Stippled lines represent sapropel boundaries. The additional dashed line at 116 cm in S1 represents the commencement of the 8 ka reventilation event, and the yellow shading defines the unaltered sapropel below the depth to which the effects of the post-sapropel burndown were felt. The data clearly show the different timing of the peak increase in redox sensitive proxies early in S1 vs. late in S5. Note the different scales between S1 and S5 for a range of elemental and ratios (S, Ba/Al, U/Al, Mo/Al, V/Al, As/Al).

3. Organic carbon sediment accumulation rates

Organic carbon accumulation rates (OCAR) at peak sapropel conditions were calculated using the equation OCAR = 1000 * TOC * ρ * LSR mg/cm².ky (Gallego-Torres et al., 2007; Algeo et al., 2013; Schoepfer et al., 2015), where ρ is the dry sediment density and TOC is the mean TOC wt. fraction (g/g). Mean TOC fraction (Fig. S-2) and standard deviation (SD) data are 0.0382 ± 0.0028 for peak S1 data (126-118 cm) and 0.0316 ± 0.0.77 for peak S5 data (94-76 cm). S1 and S5 have similar thicknesses at ODP 967 (24 vs 29.5 cm), but the longer duration of S5 (6.8 vs 4.7 ky) means that it has a slightly lower linear sedimentation rate (LSR) of 4.3 cm/ky compared to 5.1 cm/ky for S1). The ρ values are taken from S1 and S5 data at EM ODP site 964 (1.34 ±0.08 and 1.31 ± 0.03 g/cm³, respectively (Gallego-Torres et al., 2007)).

Calculated OCAR values at ODP 967 are: 261 ± 36 mg/cm².ky (S1); 178 ± 48 mg/cm².ky (S5). These values are comparable with average OCAR values calculated for the Black Sea (Schoepfer et al., 2015) and emphasize the fact that peak S1 has a high organic carbon flux, despite apparently lower deep-water sulfide levels than S5.

4. Authigenic U and Mo concentration and isotope estimates

Authigenic U (Uauth) and molybdenum (Mauth) were calculated from the U and Mo enrichment factors relative to Post Archaean Average Shale (PAAS; Taylor & McLennan, 1985) U/Al and Mo/Al ratios, which are taken to represent the detrital component (Thomson et al., 1999; Brumsack, 2006; Tribovillard et al., 2006). Such a calculation (Table S-1) shows that the detrital fraction (Udet) is a significant component of the background sediments: overlying post-
sapropel sediments $U_{\text{det}} \sim 50\%$ falling to $< 20\%$ within 5 cm of the boundary: $M_{\text{det}} \sim 50\%$
falling to $\sim 30\%$; underlying pre-sapropel sediments $U_{\text{det}} \sim 19-11\%$; $M_{\text{det}} \sim 46-15\%$. $U_{\text{auth}}$ and $M_{\text{auth}}$ fractions in S1 vary from 85% to 99%, with values $>96\%$ typical of peak sapropel conditions.

These detrital U estimates are consistent with the measured $\delta^{234}U$ (Table S-1). The Holocene age of the samples means that the age correction for the $\delta^{234}U$ is less than a few permil and the sapropels are likely to have experienced minimal $^{234}U$ nuclide redistribution, as has been observed in other sapropels (Gourgiotis et al., 2011), and is also likely the case for the S5 samples (Table S-1). The $\delta^{234}U$ values are high for S1 ($\sim 130-115\%$), slightly lower for pre-S1 ($\sim 110-100\%$) and lowest for post-S1 ($\sim 90-0\%$) sediments. While modern seawater has a $\delta^{234}U$ of $\sim 146\%$, the detrital material can be variable and deviate from secular equilibrium. It is therefore not possible to accurately estimate the authigenic U fraction in the absence of good estimates of the detrital terrigenous $\delta^{234}U$ composition. We note however that the $\delta^{234}U$ compositions from highest to lowest values of S1, followed by pre-S1 and then post-S1, are in good agreement with the order of high to low authigenic U based on U/Al.

The isotope composition of the authigenic Mo and U fractions is estimated using the elemental concentrations in combination with Mo and U isotope compositions for detrital terrigenous shales. Here, values of $\delta^{238}U = -0.3\%$ and $\delta^{98}Mo = 0\%$ were used for the detrital terrigenous sediments (Tissot & Dauphas, 2015; Andersen et al., 2017; Kendall et al., 2017; Andersen et al., 2018). Propagation of uncertainties on the authigenic composition was done by weighting the relative size of the detrital component following Andersen et al., (2014) and (2018), see Table S-1. Furthermore, authigenic $\delta^{238}U$ and $\delta^{98}Mo$ from literature data (Asael et al., 2013; Kendall et al., 2015; Cheng et al., 2020; Kendall et al., 2020) was reconverted in similar fashion to the sapropel data (apart from omitting the ‘carbonate’ correction for the authigenic U, see below) and using Mo-U isotope and Mo-U vs. Al ratios reported in these publications (Table S-1).

5. Authigenic $\delta^{238}U$ and $\delta^{98}Mo$ - estimating the contribution from U and Mo directly associated with organic matter

Andersen et al. (2014) suggested that authigenic U was dominated by two main fractions, (i) U from biogenic carbonates and (ii) U incorporated from in situ uranium reduction. Following calculations in Andersen et al. (2014), which assume that the [Ca] in bulk sediments is primarily from biogenic carbonates with $\sim 1$ ppm U, the relative U contribution from this carbonate source to the authigenic fraction can be estimated. This calculation shows that the biogenic carbonate U fraction constitutes $<3\%$ for S1 and $<20\%$ for surrounding sediments (Table S-1). Further, the $\delta^{238}U$ of the remaining authigenic U fraction may be estimated by subtracting the biogenic U carbonate fraction with $\delta^{238}U = -0.4\%$ (Andersen et al., 2014).

These calculations suggest that the greater part of $U_{\text{auth}}$ in these sediments is due to authigenic U addition rather than that associated with biogenic carbonates. In addition to U uptake from in situ U reduction (process ii), it has also been suggested that U may be directly associated with organic matter (OM) which could be a third (iii) potential important additional source of authigenic U accumulation in sediments. This OM-derived U, either directly incorporated or adsorbed, could carry isotopically light U to the sediments (Holmden et al., 2015; Hinojosa et al., 2016; Andersen et al., 2017; Abshire et al., 2020; Chen et al., 2020). Such a U fraction would be indistinguishable from the in situ uranium reduction component (process ii) in the calculations described above, and may drive the authigenic $\delta^{238}U$ pool towards lower
compositions, in instances when the relative OM deposition rate vs. *in situ* reduction rate is high.

Focusing on the pre-S1 and early part of the S1 data with relatively low [U]_{auth} in the sediments, 1/[U_{auth}] vs. δ^{238}U plots (Fig S-3a) show a systematic evolution from low δ^{238}U_{auth} (~ -0.6‰) at low [U_{auth}], to high δ^{238}U_{auth} (~ +0.5‰) at high [U_{auth}]. This pattern is consistent with an approximate mixing trend between authigenic OM-derived U (δ^{238}U ~ -0.6) and increasingly *in situ* U reduction. The 1/[U_{auth}] vs. δ^{238}U plots for the S1 and S5 and background sediment data (Fig S-3b) show that the post-S1 data also plot in the region that may be dominated by authigenic OM-derived U, but with significantly lower [U_{auth}]. Also, both the post- and pre-S5 data show moderate U enrichments, which could suggest a mixture between authigenic OM-derived U and *in situ* U reduction. On the other hand, Andersen et al. (2018) interpreted these samples to show U and Mo isotope systematics consistent with near quantitative uptake of U and Mo from porewaters. Both scenarios are possible. In contrast, both peak S1 and peak S5 appear to be completely dominated by authigenic *in situ* U reduction uptake, but with differently expressed U isotope fractionations as discussed in the main text.

**Figure S-3**  
(a) Cross-plots of δ^{238}U vs. 1/U_{auth} (ppm⁻¹) from pre-S1 and the early part of S1 (from 145 to 120 cm depth) and (b) all the data from S1/S5 and surrounding sediments. The δ^{238}U vs. 1/U_{auth} plot in (a) suggests that the data define a possible mixing trend between authigenic U associated with organic matter (δ^{238}U ~ -0.6‰ and low [U_{auth}]) and U formed by *in situ* reduction (δ^{238}U ~ +0.5‰ and high [U_{auth}]) at peak sapropel conditions.

Similar to the above discussion of the authigenic U uptake, although Mo associated with biogenic carbonate is low and therefore not important for authigenic calculations, the potential for OM-derived Mo has been suggested as a potential important source for Mo addition to organic carbon-rich sediments (e.g. McManus et al., 2002; King et al., 2018). Based on cross-plots of δ^{98}Mo vs. 1/[Mo_{auth}] (ppm) for the S1 and S5 and surrounding data (Fig. S-4) there are no trends evident in the data which could suggest that this is an important process for the observed δ^{98}Mo_{auth} in the organic carbon-rich sapropel sediments. There is, however, a difference in the δ^{98}Mo_{auth} compositions of the background sediments. The background sediments surrounding S1 have δ^{98}Mo_{auth} values in the range of suboxic sediments with low sulfide levels, where Mo uptake could be dominated by OM or adsorption on Fe oxides (e.g. McManus et al., 2002; Goldberg et al., 2009; Scholz et al., 2013; Matthews et al., 2017). On the other hand, S5 background sediments have δ^{98}Mo_{auth} values >+1.5‰, typical of sediments.
where authigenic Mo uptake occurs within sulfidic pore waters (Poulson-Brucker et al., 2009; 2012). 

![Figure S-4](image)

**Figure S-4** \( \delta^{98}\text{Mo} \) vs. \( 1/[\text{Mo}]_{\text{auth}} \) (ppm\(^{-1}\)) cross-plot for S1 and S5 and non-sapropel sediment data. No clear mixing trends are observed between post/pre-S1 or S5 and the peak S1 and S5 sediments.

**Supplementary Tables**

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Supplementary Information References


Hinojosa, J.L., Stirling, C.H., Reid, M.R., Moy, C.M. and Wilson, G.S. (2016) Trace metal cycling and 


