

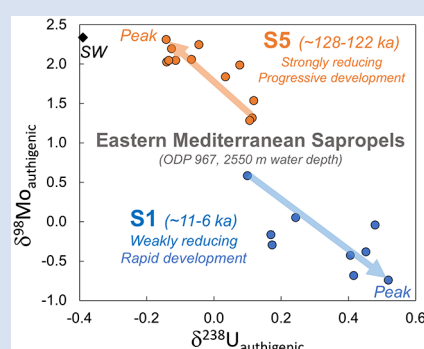
# Rapid onset of ocean anoxia shown by high U and low Mo isotope compositions of sapropel S1

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## Abstract



Authigenic uranium isotope compositions of Holocene sapropel S1 ( $\delta^{238}\text{U}_{\text{auth}} = +0.10$  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  $\delta^{238}\text{U}_{\text{auth}}$  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  $\delta^{238}\text{U}_{\text{auth}}$  values correlate with low  $\delta^{98}\text{Mo}_{\text{auth}}$  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  $\delta^{238}\text{U}_{\text{auth}}$  and  $\delta^{98}\text{Mo}_{\text{auth}}$  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 palaeo-

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.

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## Introduction

The redox sensitive behaviour 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; Kendall *et al.*, 2015; Bröske *et al.*, 2020).

Uranium isotopes in anoxic and organic carbon-rich marine sediments (expressed as  $\delta^{238}\text{U}$ , 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  $\text{U}^{+6}$  to  $\text{U}^{+4}$ . In modern organic carbon-rich sediments, authigenic  $\delta^{238}\text{U}$  values rarely exceed  $+0.2$  ‰, equivalent to a  $\Delta^{238}\text{U}_{\text{sediment-water}}$  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  $\delta^{238}\text{U}$  values higher than  $+0.2$  ‰, suggesting redox-driven U isotope fractionation closer to that expected in an open system ( $\Delta^{238}\text{U} > +0.6$  ‰), and pointing towards U reduction outside the sediments (e.g., Bröske *et al.*, 2020; Cheng *et al.*, 2020; Kendall *et al.*, 2020).

In addition, coupled measurements of molybdenum isotope compositions (expressed as  $^{98}\text{Mo}/^{95}\text{Mo}$ , parts per thousand deviation from NIST 3134 at  $+0.25$ ; Nägler *et al.*, 2014) in these high  $\delta^{238}\text{U}$  organic carbon-rich sediments, generally show  $\delta^{98}\text{Mo}$  significantly lower than the modern seawater value of  $\sim +2.3$  ‰ (e.g., Cheng *et al.*, 2020; Kendall *et al.*, 2020). Near seawater  $\delta^{98}\text{Mo}$  values are proposed to reflect euxinic water conditions, where dissolved  $[\text{H}_2\text{S}]_{\text{aq}}$  exceeds a 'switch point' ( $\sim 11$   $\mu\text{M}$  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  $\delta^{98}\text{Mo}$  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 a Fe-Mn oxide particulate shuttle (Kendall *et al.*, 2017).

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Though this combination of high  $\delta^{238}\text{U}$  and low  $\delta^{98}\text{Mo}$  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 analogues. The periodic deposition of organic carbon-rich sediments (sapropels) in the Eastern Mediterranean (EM) sea provide a means to study the behaviour 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.

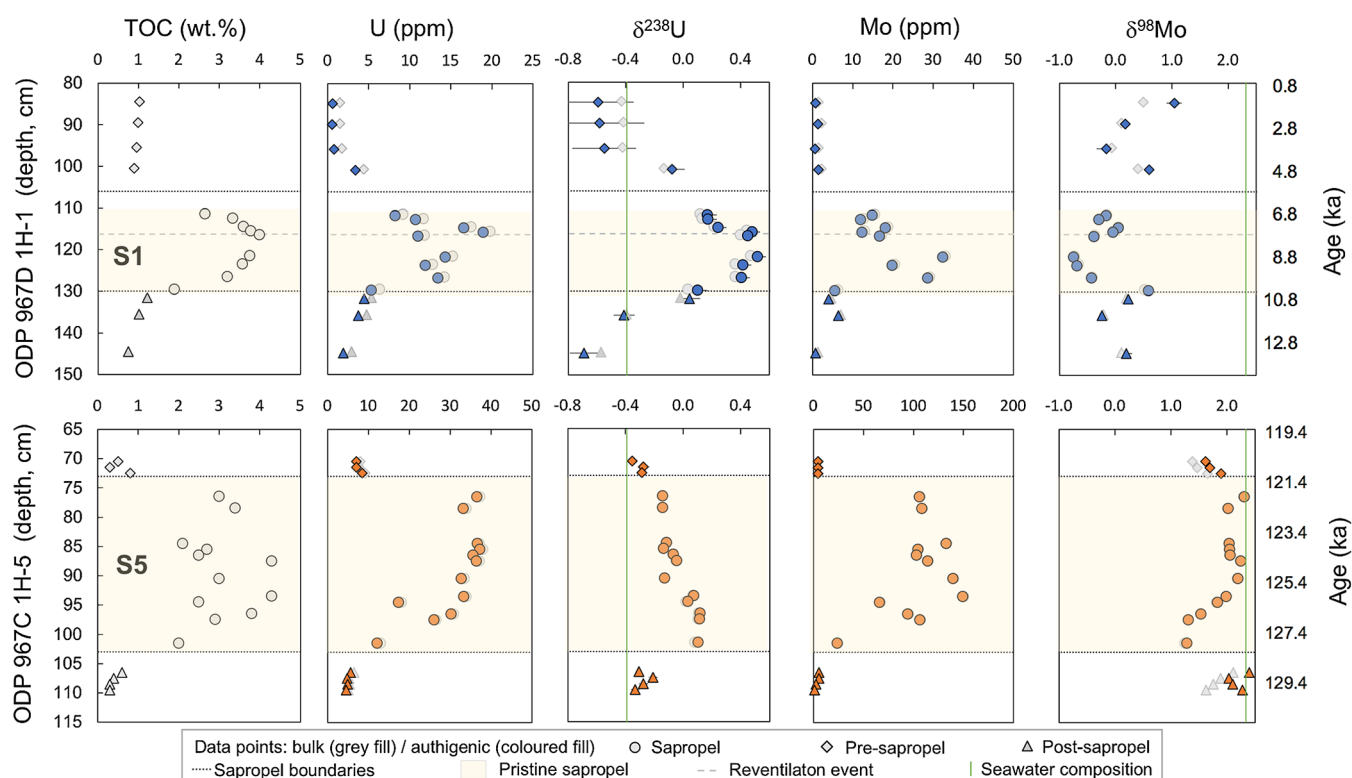
## Authigenic U and Mo Isotopes in Sapropels S1 and S5

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. S-1). Sapropel S5 (~128.3–121.5 ka) shows strong authigenic enrichment of U and Mo, coupled to progressive  $\delta^{98}\text{Mo}_{\text{auth}}$  increase (+1.2 to +2.3 ‰) and  $\delta^{238}\text{U}_{\text{auth}}$  decrease (+0.10 to −0.15 ‰), from the beginning to the end (Andersen *et al.*, 2018). Modelling of the S5  $\delta^{238}\text{U}$  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  $\delta^{98}\text{Mo}$  values (Azrieli-Tal *et al.*, 2014), although anoxic conditions were regionally prevalent at water depths >1800 m (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 summarised in SI). The S1 samples show lower U concentrations (10–40 ppm) than S5 (25–150 ppm), but high  $\delta^{238}\text{U}$  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  $\delta^{238}\text{U}$  patterns in S1 differ significantly from S5. Calculated authigenic U ( $\text{U}_{\text{auth}}$ ) and Mo ( $\text{Mo}_{\text{auth}}$ ) 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  $\text{U}_{\text{auth}}$  concentrations are correlated with high  $\delta^{238}\text{U}_{\text{auth}}$  values (> +0.2 ‰) and high  $\text{Mo}_{\text{auth}}$  concentrations with low  $\delta^{98}\text{Mo}$  values (Fig. 1). Peak  $\delta^{238}\text{U}_{\text{auth}}$  values (127–116 cm) vary from  $+0.41 \pm 0.06$  ‰ to  $+0.52 \pm 0.06$  ‰, whereas  $\delta^{238}\text{U}_{\text{auth}}$  values of −0.7 to +0.1 ‰ occur before and after S1 and in the first sample at its start (130 cm), indicating that a significant proportion of the  $\text{U}_{\text{auth}}$  may be associated with U deposited directly with organic matter, carrying low  $\delta^{238}\text{U}_{\text{auth}}$  (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 behaviour in their  $\delta^{238}\text{U}$ – $\delta^{98}\text{Mo}$  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



**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 4 cm (see SI). A potential post-deposition ventilation event at ~116 cm (8 ka) 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.

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. S-2). 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  $261 \pm 36$  mg/cm<sup>2</sup>-kyr for S1 and  $178 \pm 48$  mg/cm<sup>2</sup>-kyr for S5 (see SI for details).

The  $\delta^{98}\text{Mo}_{\text{auth}}$  of S1 shows a significant early drop towards the low values of  $\sim -0.8$  ‰ at peak sapropel conditions, followed by a rise to  $\sim 0$  ‰ (Fig. 1). The low S1  $\delta^{98}\text{Mo}$  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 near-quantitatively converted to tetra-thiomolybdate (Azrieli-Tal *et al.*, 2014). The production of thiomolybdates requires sulfate reduction, driven by biological productivity and long deep water replacement times. Non-quantitative conversion of Mo to thiomolybdate requires low sulfide and sequestration of more sulfidised species to the sediment, *e.g.*, by colloidal FeMo(VI)S<sub>4</sub> (Helz and Vorlicek, 2019). Low sulfide levels and non-quantitative conversion of molybdate to thiomolybdates can result in isotopically 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  $\delta^{98}\text{Mo}$  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  $\delta^{98}\text{Mo}_{\text{auth}}$  are close to the seawater values (Andersen *et al.*, 2018).

In contrast to S5, S1 is characterised by high  $\delta^{238}\text{U}$ , 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  $\delta^{238}\text{U}$ . 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  $\delta^{238}\text{U}$  with depth – see SI for details). Alternatively, U isotope reactive-transport modelling has suggested that high  $\delta^{238}\text{U}$  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  $\delta^{238}\text{U}$  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  $\delta^{238}\text{U}$  (*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  $\delta^{238}\text{U}$  in S5, not S1.

Another model for providing a greater expression of the  $\Delta^{238}\text{U}_{\text{sediment-water}}$  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 sulfidic levels. Redox sensitive element data for S1 (Figs. 1, S-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.

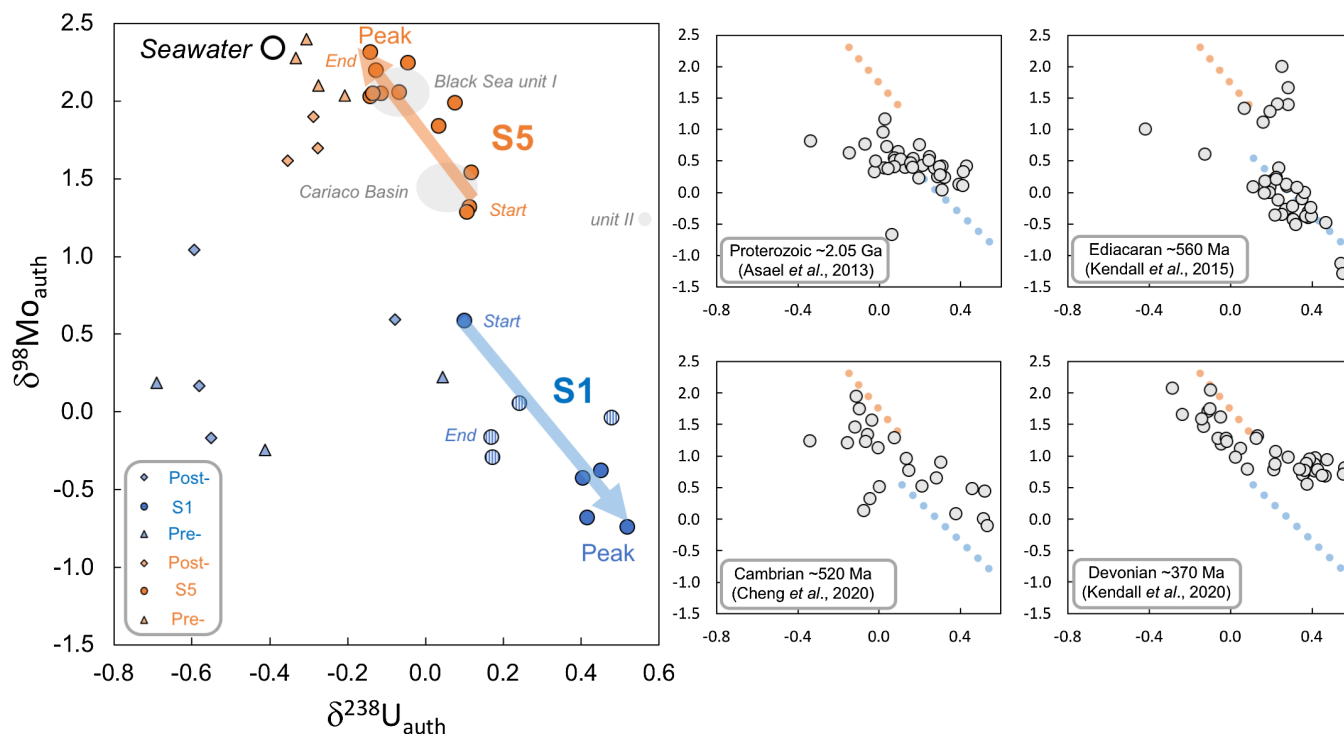
## Outlook: the U-Mo Isotope Proxy Applied to Ancient Sediments

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 palaeo-redox 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 Palaeoproterozoic 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  $\delta^{238}\text{U}_{\text{auth}}$  ( $\sim +0.55$  ‰) to S1, while  $\delta^{98}\text{Mo}_{\text{auth}}$  ( $+1.23$  ‰) is relatively high (Fig. 2). All these localities exhibit similar negatively correlated  $\delta^{238}\text{U} - \delta^{98}\text{Mo}$  values as seen in S1, but at variable trajectories and with different  $\delta^{98}\text{Mo}$  values. This observation may be partly attributed to variable seawater  $\delta^{98}\text{Mo}$  over time, but it would also depend on the  $[\text{H}_2\text{S}]_{\text{aq}}$  levels and the specific stability of the oxy-thiomolybdate 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  $\delta^{238}\text{U}$  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 behaviour in the U and Mo isotope systematics). From the sapropel data it may be inferred that the specific conditions that favour combined high  $\delta^{238}\text{U}_{\text{auth}}$  with low  $\delta^{98}\text{Mo}_{\text{auth}}$  require both a high particulate to water ratio (*e.g.*, the organic floccule layer) and (low)  $[\text{H}_2\text{S}]_{\text{aq}}$  levels, to aid the reduction of U and formation of oxy-thiomolybdates, 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





**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; Kendall et al., 2015; Cheng et al., 2020; Kendall et al., 2020). The main plot shows S1 (blue, filled samples 130–116 cm, stippled 116–110 cm), 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 palaeo-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).

high productivity and formation of an organic floccule layer. In other settings with high productivity in upwelling zones, the development of  $[\text{H}_2\text{S}]_{\text{aq}}$  bottom water plumes as observed on the Peru margin (Schunck et al., 2013), combined with an organic floccule layer, could also provide the right condition for high  $\delta^{238}\text{U}_{\text{auth}}$  with low  $\delta^{98}\text{Mo}_{\text{auth}}$  in organic carbon-rich sediments. The palaeo-examples discussed here show that conditions that favour these S1 type  $\delta^{238}\text{U}$ - $\delta^{98}\text{Mo}$  sediment systematics likely occurred across a large part of Earth history. Yet, in inferring palaeo-proxy 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  $\delta^{238}\text{U}$  and  $\delta^{98}\text{Mo}$  compositions between settings. Based on this study, the careful and combined analysis of  $\delta^{238}\text{U}$ - $\delta^{98}\text{Mo}$  systematics in organic carbon-rich sediments is critical to providing the most robust way of identifying localised isotope effects for both systems and, thus, oceanographic conditions during sediment deposition.

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## Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article2027>.



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