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A 10-fold decline in the deep Eastern Mediterranean thermohaline overturning circulation during the last interglacial period

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ABSTRACT

Present-day Mediterranean deep-waters are well oxygenated, but the episodic formation of organic-rich sediments (sapropels) indicates that this pattern was frequently perturbed in the past. Both high export productivity and disruption of the thermohaline circulation, leading to reduced deep-water ventilation, have been proposed to account for sapropel deposition and anoxia. The last interglacial sapropel S5 is considered one of the most strongly developed. Here, we apply the redox-sensitive Mo and U (elemental and isotope) systems to quantify the intensity of anoxic deep-water conditions in the Eastern Mediterranean Sea from ODP core 967 (2550 mbsl). Both U and Mo show strong authigenic enrichment, coupled to progressive increase in $\delta^{98}Mo_{auth}$ (+1.2–1.8‰ to +2.0–2.3‰) and decrease in $\delta^{238}U_{auth}$ (+0.10‰ to −0.15‰) from the beginning to the end of S5, suggesting increasing water column euxinia and removal fluxes of Mo and U. Based on modern euxinic basins, we show that sedimentary $\delta^{238}U_{auth}$ can be used to derive estimates of water column U depletion and, ultimately, deep-water renewal rates. These principles are first tested on the modern Black Sea, which yields calculated deep-water renewal times of $830^{+690}/_{-500}$ yrs, in good agreement with independent estimates. Applying these principles to the end of S5 suggests bottom-water U depletion of ~50% and deep-water renewal times of $1030^{+820}/_{-520}$ yrs. The significantly slower deep-water renewal rates in the Eastern Mediterranean Sea compared to today (~100 yrs) would have played an important role in the formation of sapropel S5 and are consistent with the proposed suppression of overturning during the last interglacial, due to increased stratification resulting from higher riverine freshwater input under enhanced monsoon forcing.

1. Introduction

The Mediterranean overflow system and outflow into the Atlantic plays a major role in Atlantic Meridional Overturning Circulation (AMOC) (Johnson and Stevens, 2000; Rogerson et al., 2012). In its current configuration, the Mediterranean Sea is characterized by large-scale thermohaline circulation in which the relatively low salinity inflow from the Atlantic is converted via high evaporation in the Eastern Mediterranean Basin into an intermediate-depth saline outflow (Levantine Intermediate Water) (Malanotte-Rizzoli and Bergamasco, 1989; Pinardi and Masetti, 2000; Rohling et al., 2015) (Fig. 1). Such a circulation pattern leads to the formation of well-oxygenated deep-water in both the Eastern and Western Mediterranean basins, separated by the straits of Sicily. In the past, however, the periodic formation of organic carbon-rich sediments, termed sapropels, suggests that the redox state of deep-waters changed (e.g., Rossignol-Strick, 1985; Rohling and Hilgren, 1991; Emeis et al., 1998; Emeis et al., 2000; Rohling et al., 2015).

Sapropels are associated with anoxic conditions in the deep ocean that allow the preservation of organic matter. Both higher export productivity, creating anoxia through enhanced consumption of oxygen, and disruption of oxygen supply via changes in the thermohaline circulation, have been proposed to account for the formation and preservation of organic matter (Rossignol-Strick, 1985; Rohling and Hilgen, 1991; Emeis et al., 2000; de Lange et al., 2008; Meyer and Kump, 2008). Pleistocene Mediterranean sapropels are unique sediments in that their periodicity is correlated with high northern hemisphere summer insolation during minima in the *ca.* 21 ka orbital precession cycle, and they are

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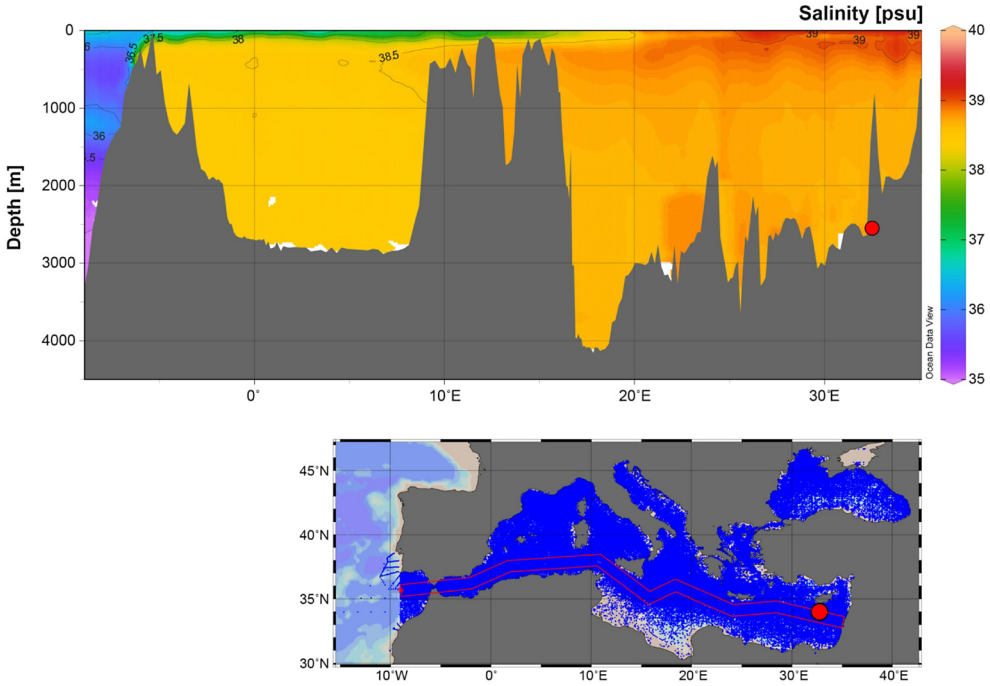

Fig. 1. Vertical salinity profile (top) through the Mediterranean basin (bottom). The position of the studied core ODP 967 is marked with the red dot. Generated in Ocean Data View (https://odv.awi.de). (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

particularly well developed during interglacials. The resultant organic carbon-rich sedimentary deposits are important and useful analogs for such sediments in deeper time in Earth history. In this paper, we explore the validity of disrupted thermohaline circulation as a forcing factor in the creation of anoxia. Enhanced monsoon-driven freshwater runoff into the surface of the Eastern Mediterranean, through the Nile or transient North African rivers, or both, have all been put forward as important factors in the creation of less saline surface water layers. This, in turn, may have led to partial stratification of the water body and disruption of the thermohaline circulation system (Rossignol-Strick et al., 1982; Emeis et al., 1998; Osborne et al., 2008; Bar-Matthews, 2014; Rohling et al., 2015). It is also recognized that some 'preconditioning' may have occurred, through the prior formation of anoxic deep-waters due to enhanced regional rainfall and sea level rise following glacial maxima (Grimm et al., 2015; Grant et al., 2016).

Geochemical proxies for redox conditions prevailing prior to and during sapropel formation, and following their termination as oxic conditions returned, include: organic biomarkers, elements sensitive to paleoproductivity and organic burial (e.g. barium) and redox-sensitive trace elements (RSTE, e.g. iron, manganese, vanadium, molybdenum, uranium) (Thomson et al., 1999; Cane et al., 2002; Rohling et al., 2006; de Lange et al., 2008; Almogi-Labin et al., 2009; Gallego-Torres et al., 2010). For instance, using a powerful combination of ^{14}C dating and RSTE profiles, de Lange et al. (2008) showed that basin-wide anoxic conditions prevailed during the formation of the latest (Holocene) sapropel, S1, at water depths >1800 m.

The stable isotope systems of the metals molybdenum and uranium, which fractionate during oxidation-reduction processes, can record distinctive isotope signatures during organic carbon-rich sedimentation (Barling et al., 2001; Arnold et al., 2004; Neubert et al., 2008; Weyer et al., 2008; Nägler et al., 2011; Andersen et al., 2014). In today's oxic oceans, the isotope composition of dissolved Mo (δ^{98}Mo +2.34‰, reported in delta-notation as δ^{98}Mo using the $^{98}Mo/^{95}Mo$ ratio normalized to NIST SRM 3134 standard +0.25 in parts per thousand; Nägler et al., 2014), dominated by the oxyanion molybdate species (MoO_4^{2-}), is thought to be fractionated relative to the Mo input to the ocean (δ^{98}Mo ∼+0.7‰; Archer and Vance, 2008) mostly because of the loss of Mo adsorbed to manganese oxides (δ^{98}Mo ∼ −0.7‰; Barling et al., 2001). In contrast, strongly euxinic (anoxic + sulfidic) water conditions result in near-quantitative uptake of Mo from seawater (either by scavenging to organic matter or through formation of a colloidal Fe–Mo–S species; Helz et al., 2011), driven by the transformation of molybdate to tetra-thiomolybdate (MoS_4^{2-}), with $MoS_4^{2-} \gg MoO_4^{2-}$ when concentrations of H_2S are above 11 µMol (e.g. Neubert et al., 2008). This leads to organic carbon-rich sediments acquiring a δ^{98}Mo value very close to that of seawater, as has been recognized in organic carbon-rich sediments deposited in the euxinic deep Black Sea (Neubert et al., 2008; Nägler et al., 2011; Wegworth et al., 2018). Intermittent or weaker (H_2S concentrations <11 µMol) euxinic conditions, on the other hand, may lead to isotopically lighter Mo in sediments due to isotope fractionation during incomplete MoO_4^{2-} to MoS_4^{2-} transformation (Poulson-Brucker et al., 2012; Kerl et al., 2017). In sub-oxic to anoxic conditions, Mo isotope signatures intermediate between those of seawater and the oxic end-member may also reflect the importance of adsorption of isotopically light Mo species on iron oxides and pyrite (Goldberg et al., 2009). Indeed, δ^{98}Mo values much lower than modern seawater, and inferred weakly euxinic to anoxic conditions, have been observed in middle Pleistocene sapropels and in the most recent Holocene sapropel S1 at 2550 m water depth (Scheiderich et al., 2010; Azrieli-Tal et al., 2014). δ^{98}Mo minima from seawater during the early diagenesis of sapropel S1 in the Nile Fan have also been explained by Mo isotope fractionation during the kinetically-controlled particulate uptake of porewater thiomolybdate species (Matthews et al., 2017).

The mechanism for authigenic uranium enrichment in reduced sediments differs from that of molybdenum: while Mo removal primarily occurs in a euxinic water column, the major U uptake has been shown to, instead, occur within the reducing sediment environment, mediated by metal- and sulfate-reducing bacteria (Anderson et al., 1989; Lovley et al., 1991; McManus et al., 2006). The isotope system of the uranium parents ($^{238}U/^{235}U$, given in typical delta-notation as δ^{238}U, which is the parts per thousand