

Mediterranean oceanography and North African climate over the Pliocene

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Abstract

Mediterranean basin sediments are excellent archives of 1) high-latitude climate change and 2) North African environmental evolution. First, the semi-enclosed nature of the basin amplifies high-latitude climatic signals recorded in the sediments. Second, the episodic formation of organic-rich layers (sapropels) during past North African humid periods allows the reconstruction of past Green Sahara Periods alternating with North African dry periods. In this thesis, I employ a multi-proxy reconstruction (stable oxygen isotope, environmental magnetic and X-ray fluorescence scanning data) for eastern Mediterranean Ocean Drilling Program (ODP) Site 967, to investigate Mediterranean oceanography and North African climate during the past 5.3 Myr (million years), especially focusing on the Pliocene.

Prior to the Miocene-Pliocene (M/P) transition (5.3 Myr ago), the Mediterranean was isolated from the global ocean due to tectonic restriction of the Atlantic-Mediterranean gateway, in an event called the ‘Messinian salinity crisis’. The 600,000-year long salinity crisis led to a kilometre-scale drawdown of the Mediterranean, resulting in massive evaporite deposition and brine formation. It had been suggested that a catastrophic megaflood due to Gibraltar sill collapse re-established normal marine conditions in the Mediterranean immediately following the M/P boundary.

The presence of an unusually lengthy sapropel (the ‘mystery sapropel’) is recognized in the eastern Mediterranean, at the M/P boundary, while an equivalent is absent in the western Mediterranean. Using physical oceanographic modelling, it is elaborated that an energetic flood transferred most of the western basin Messinian brines across the Sicily sill, yielding salinity stratification in the eastern basin, while normal marine conditions established in the western basin. With additional data from ODP Site 969, it is further explained how the eastern basin initially became stratified and oxygenated, due to a ~1,500-m-high, turbulent and aerated cascade that entered eastern basin. Stratification delayed the establishment of normal marine conditions by ~33,000 years, during which the mystery sapropel was deposited. While the accumulated salts were diffused into outflow that transported them back to the Atlantic, the eastern basin water column shifted from an oxidizing to a reducing redox state. Once the salt export allowed the resumption of convective deep-water formation, eastern Mediterranean deep waters became oxygenated again.

A second marked transformation occurred following the Early-Mid Pliocene transition (3.4-3.2 Myr), when eastern Mediterranean organic carbon burial intensified, due to a shift to greater

nutrient inputs. It is hypothesized that these inputs resulted from an increase in arid:humid contrast between alternating North African dry-wet episodes. A co-occurrence of various environmental shifts is recognized over the mid-latitudes of both hemispheres. Using paleoclimate modelling, it is shown that the Earth's shift from unipolar to bipolar glaciation resulted in strengthening and shifting of key components in the atmospheric circulation, leading to the observed global-scale phenomena.

Furthermore, using climate modelling results and terrestrial weathering indices, this work recognizes the existence of a Pan-North African humid period prior to the Early-Mid Pliocene transition (3.8-3.4 Myr). The lengthy humid period may have resulted in the oldest known early hominin migration to the Chad basin, ~2,000 km west of their origin in east Africa. Finally, a Mediterranean box model is used to show that the North African monsoon was modulated by orbital eccentricity with remarkably stable amplitudes over the past 5 Myr.

In summary, this thesis combines proxy data with numerical and climate modelling to explore major Mediterranean oceanographic and North African climatic transitions, and their relation to Pliocene global environmental evolution.

Key contributions of this thesis to the field of research:

- The mode of termination of the Messinian salinity crisis had remained a matter of debate even after 5 decades of research. This work strongly supports a catastrophic termination of the salinity crisis.
- This work discovers and documents a previously unknown 33,000-year-long transition period in the Mediterranean from an evaporitic basin to a normal marine basin.
- Most earlier paleoclimate modelling efforts were focused on either the Early Pliocene warm period, or the Mid Pliocene warm period. This work reveals global-scale environmental changes across the Early to Mid-Pliocene transition, suggesting the importance of further studies in a more continuous fashion rather than focussed on time slices.
- This work reveals a 400,000-year-long Pan-North African humid period, which suggests the importance of vegetation changes on early hominin migration.
- This work modifies an existing Mediterranean box model, to estimate the stratification strength during periods of past North African monsoon intensification over the past 5 million years.

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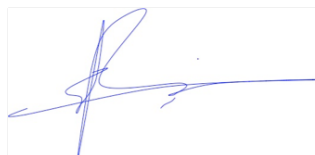
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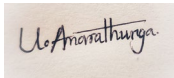


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Part 4: Comments and Conditions– Delegated Authority

I approve this change of thesis format. SF.

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CHAPTER 1

Introduction and Thesis Outline

1.1 Introduction

1.1.1 Background

The Pliocene Epoch, which extends from 2.58 to 5.33 million years (Myr), has been identified as a useful approximation for the future of global climate¹⁻³. Atmospheric CO₂ concentrations during the Pliocene were similar to those of the present, with temperatures more than 2°C above pre-industrial levels^{4,5} (Fig.1). Globally significant tectonic and oceanographic events occurred across the Pliocene, including the closure of Panamanian and Indonesian seaways, tectonic uplift of the Rocky Mountains and the end of a permanent El Niño-like state in the equatorial Pacific^{6,7}. These events combined with a decrease in the atmospheric CO₂ concentration, resulted in the gradual onset of Northern Hemispheric glaciations (NHG) since ~3.4 Myr, culminating in deep NHG from ~2.75 Myr⁸⁻¹⁰ (Fig. 1). Studying these major global events may provide insights valuable for the development of solutions to the impacts of modern climate change.

The Mediterranean region is considered to be an excellent natural laboratory for palaeoclimate research, due to its unique position on the transition between the subtropical high-pressure belt over North Africa and the temperate westerlies over central and western Europe, and its sensitivity to climate change as a land-locked marginal basin with restricted exchange with the open ocean^{11,12}. Conspicuous sediment cycles including organic-rich layers (sapropels) in the Mediterranean show a remarkably stable relationship with insolation maxima, during orbital precession minima, which provides uniquely detailed age control to Mediterranean sediment sequences (Fig. 1). Superimposed on this steady rhythm, the Mediterranean basin went through a series of regionally and globally significant transformations through the Pliocene epoch¹³⁻¹⁵. In the late Miocene, the Mediterranean basin's connection with the Atlantic Ocean became restricted, resulting in the 630,000-year Messinian Salinity Crisis (MSC), during which the basin was partially desiccated due to reduced Atlantic inflow^{13,16}. Revival of the Mediterranean after the MSC, marking the onset of the Pliocene (5.33 Myr), occurred when the Zanclean megaflood abruptly refilled the basin after the Gibraltar sill collapse¹³. Another milestone in Mediterranean evolution took place in the Mid Pliocene, when the frequency of Mediterranean organic-rich layer (sapropel) deposition intensified (with increased magnitude of organic carbon burial) at ~3.2 Myr¹⁴ (Fig. 1). Simultaneously, Mediterranean outflow (MO) to the North Atlantic significantly increased, according to evidence from the Gulf of Cadiz¹⁵.

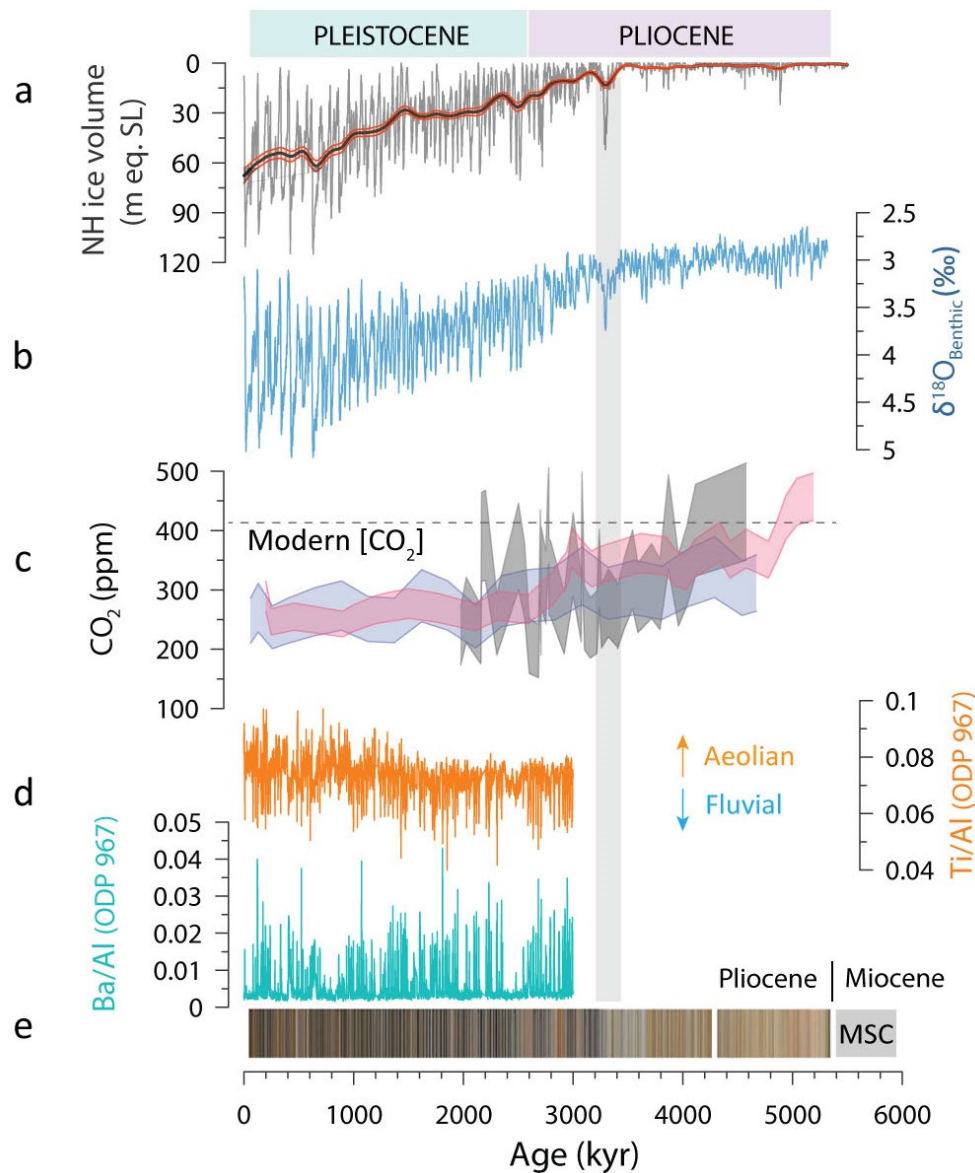


Figure 1| Plio-Pleistocene global climate evolution and major Pliocene environmental transitions of the Mediterranean. **a**, Northern Hemispheric ice volume changes. The thick black line indicates a 60-kyr moving average (to highlight the long-term variability), with lower and upper 95% confidence intervals shaded in orange. The increase in mean ice volume across the 3.4-3.2 Myr interval is highlighted with the vertical grey bar. **b**, Global open-ocean benthic $\delta^{18}\text{O}$ stack¹⁷, showing a long-term trend to positive values due to the increase in global ice volume. **c**, Alkenone and Boron isotope-based global CO_2 estimates through the past 5 Myr. Boron-based reconstruction is highlighted in grey¹⁸. Alkenone-based reconstructions are pink¹⁹ and purple⁵. **d**, Existing Eastern Mediterranean ODP Site 967 Ba/Al and Ti/Al records. Ba/Al is a proxy for original organic carbon burial. Higher Ti/Al values indicate more aeolian sediment input under dry conditions. **e**, ODP Site 967 sediment record, which extends back to the Miocene-Pliocene boundary. MSC, Messinian Salinity Crisis. Sudden intensification of the frequency of sapropel preservation (~ 3.2 Myr), follows the increase of Northern Hemispheric ice volume across 3.4-3.2 Myr period. To understand this, this thesis elaborates records for the Early Pliocene that complete the existing time-series back to 5.3 Myr.

1.1.2 Modern Mediterranean circulation

The Mediterranean Sea is connected to the Atlantic Ocean at the shallow and narrow Strait of Gibraltar. The Strait of Sicily (Fig. 2) plays an important role in the production of specific water masses in the region, at which the Mediterranean is divided into two sub basins as eastern and western basins. Modern Mediterranean circulation can be discussed in terms of three major water masses; surface, intermediate, and deep waters^{11,20}. In order to compensate for the saline subsurface outflow and net evaporative freshwater loss from the Mediterranean, surface Atlantic water (AW) flows into the basin through the Strait of Gibraltar²¹. Surface inflow of less-salty AW is then mixed with a proportion of upwelled Mediterranean Intermediate Water (MIW), forming Modified Atlantic Water (MAW)¹¹. Via complex surface flow patterns, MAW enters the eastern Mediterranean through the Strait of Sicily^{20,22}. Enhanced evaporation and winter cooling in the Levantine basin of the eastern Mediterranean initiate vertical convection that forms Levantine Intermediate Water (LIW)¹¹. The salty and relatively warm LIW flows westward, through the Strait of Sicily and into the western Mediterranean¹¹. The eastern and western Mediterranean sub-basins have their own sources of deep water formation, which are known as Eastern Mediterranean Deep Water (EMDW) and Western Mediterranean Deep Water (WMDW), respectively. Composed of contributions from EMDW and especially from WMDW, Mediterranean Intermediate Water (MIW or LIW) flows to the Atlantic Ocean beneath the surface inflow through the Strait of Gibraltar. The dense plume and eddies of Mediterranean outflow are known in the eastern North Atlantic as Mediterranean Outflow Water (MOW)^{11,20,23}.

1.1.3 The Messinian Salinity Crisis

The MSC is considered as one of the most abrupt global-scale environmental transformations since the demise of the dinosaurs ~66 Myr ago²⁴. Tectonically driven gradual restriction of the Mediterranean-Atlantic gateway (since ~7.3 Myr) led to the deposition of massive evaporates in the Mediterranean^{13,16}. The onset of the MSC (5.97 Myr) is marked by the initiation of gypsum-marl couplets in shallow (marginal) Messinian basins of the Mediterranean¹⁶. During the first stage of the MSC, up to 16 gypsum-marl couplets were deposited^{16,25}. During the second stage (5.6-5.55 Myr), the MSC reached its peak, as the Atlantic-Mediterranean gateway restriction maximized, likely terminating the outflow entirely^{16,25}. Seismic records reveal the presence of a basin-wide Messinian erosional surface formed during MSC peak, due to subaerial erosion^{13,16}. Significantly reduced (or completely blocked) Atlantic inflow led to a

km-scale desiccation of the basin, leading to the formation of massive halite and gypsum deposits beneath dense Messinian brines^{16,25}. The final MSC stage is composed of two sub-stages; upper evaporite phase (5.55-5.42 Myr) and the Lago Mare phase (5.42-5.33 Myr)^{16,26,27}. The gypsum-marl couplets formed within the upper evaporite phase were interpreted to have formed due to precession-driven climate oscillations¹⁶. The Lago Mare phase has been controversial even after 5 decades of research on the MSC²⁷. Paleontological and biogeochemical evidence indicative of substantial dilution of the Mediterranean by Paratethyan waters, suggest that the eastern and western basins were reconnected prior to the ending of the MSC^{26,27}. However, seismic records and sedimentological evidence suggest that the Mediterranean was still at a massive drawdown immediately prior to MSC termination, which led to the catastrophic Zanclean megaflood, which may have refilled the Mediterranean within 2 years^{13,24,28}.

1.1.4 Mediterranean Sapropels

The eastern Mediterranean is sensitive to both low- and mid-latitude climate processes, and is a particularly valuable archive of African monsoon variability^{11,29,30}. During the North African summer monsoon, Inter Tropical Convergence Zone (ITCZ) migrates northward, delivering intense precipitation over the Sahel region^{31–33}. The extent to which the monsoon front penetrates northward is governed by the intensity of solar radiation received by the North African land mass, which has changed throughout geological history^{11,34}. Insolation depends on variations in Earth's orbital parameters; precession, obliquity and eccentricity^{11,35,36}. Enhanced summer insolation during precession minima caused more monsoon precipitation to reach the eastern Mediterranean as runoff from the Nile and other (now dry) fossil rivers along the North African margin^{37,38}. The northward monsoon expansion and intensification also changed vegetation patterns, transforming present-day desert in to grassland and wooded grassland; hence, these past humid periods are known as Green Sahara Periods (GSPs) or African Humid Periods (AHPs)^{34,37,39,40}.

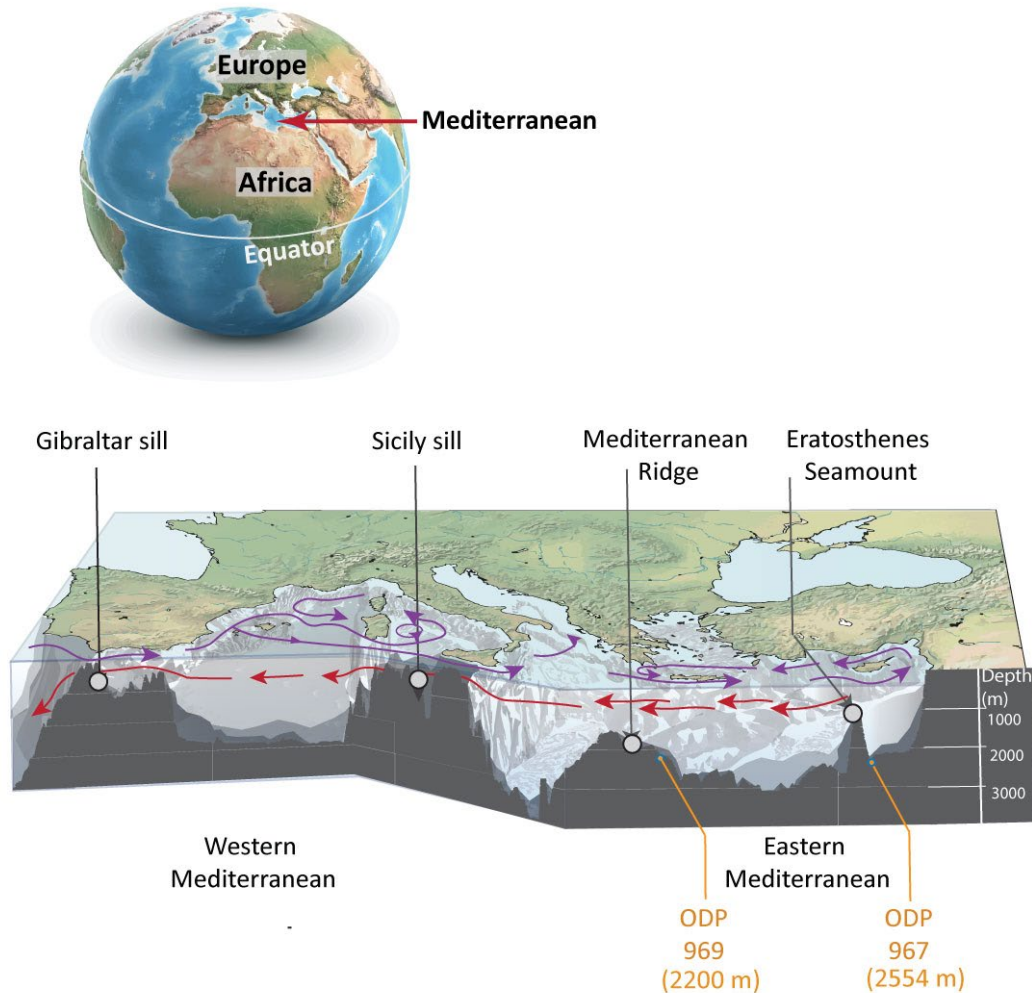
Astronomically driven increase of African monsoon runoff into the eastern Mediterranean has been recognized from negative stable oxygen isotope values ($\delta^{18}\text{O}$) measured on planktonic foraminiferal shells^{11,41–43}. Enhanced freshwater runoff led to a surface-layer buoyancy increase in the basin, which in turn led to curtailed deep water formation in the eastern Mediterranean^{42,44}. The runoff also increased nutrient transport into the basin. Combined, this resulted in bottom water anoxia, which induced the deposition of organic-rich layers known as

sapropels. Sapropels can be visually identified as dark, laminated beds in marine sediment cores, and contain higher organic carbon (C_{org}) contents than background sediments, typically between 1 and 10% ^{refs.11,42,44}. However, visual identification of Mediterranean sapropels becomes difficult where they have undergone post-depositional oxidation. A useful proxy for the identification of oxidized sapropels is the Ba/Al ratio, as sapropels are characterized by high Ba/Al contents due to increased organic carbon burial during their formation^{30,45,46}. Barium is usually deposited as biogenic barite ($BaSO_4$) which is considerably immobile in sediments compared to organic carbon; hence, it is thought to reflect the original C_{org} content^{11,47}. In addition, redox-sensitive trace metals indicative of low bottom water oxygen contents (e.g., V, Mo) and calcophilic elements such as Fe and Ni that attest to iron sulphide mineral formation, are enriched in Mediterranean sapropels⁴⁸. Moreover, environmental magnetic measurements can provide useful parameters in identifying oxidized sapropels. Post-depositional reoxygenation of bottom waters leads to the diagenetic formation of fine-grained magnetite at the top of the sapropel (termed as the ‘oxidation front’) that is indicative by higher than background anhysteretic remanent magnetization (ARM) levels^{47,49,50}. In summary, Mediterranean sapropels are characterized by high Ba/Al, V, Mo, Fe, Ni levels and high ARM values at the oxidation front where sapropel oxidation has occurred.

Similar to the enhanced freshwater inflow due to monsoon intensification, aeolian dust supply into the Mediterranean Sea is also controlled by orbital variations^{47,51}. Dust supply minima are related to the periods of enhanced monsoon precipitation^{14,35,36,51}. Dust supply maxima, in contrast, are related to intervening periods of enhanced aridity. Dust contents in eastern Mediterranean sediments can be characterized using Ti/Al and hematite contents. Sapropels typically contain low values of the sedimentary Ti/Al ratio, which reflects a decrease in Ti-rich Saharan dust input and an increased (Al-rich) riverine input^{36,52,53}. Conversely, intervening arid periods are characterized by Ti/Al maxima. Magnetic measurements also provide valuable information about palaeoceanographic and climatic conditions during sapropel formation^{46,51,54}. For example, isothermal remanent magnetization (IRM) variations agree closely with the Ti/Al variations, indicating depleted/enhanced aeolian hematite input to the Mediterranean from Sahara, respectively^{37,51}.

North African arid-humid cycles have existed throughout at least the past 8 Myr³⁷. Eastern Mediterranean sediment records provide an undisturbed archive of Mediterranean oceanography and North African climate evolution, back to the Miocene/Pliocene boundary (5.33 Myr). Prior to that, the Mediterranean was (partly) desiccated¹³. However, existing core-

scanning XRF and high-resolution environmental magnetic data extended back only to 3 Myr, and the lack of detailed earlier data hinders the development of a sound understanding of Mediterranean and North African climatic evolution through the most important Pliocene



transformations, and their global implications.

Figure 2| The Mediterranean Basin. Location of the Mediterranean Basin between North African landmass and Europe is shown in the upper diagram. Lower conceptual diagram shows the locations of Gibraltar and Sicily sills, and the locations of the two Ocean Drilling Program sites (ODP sites 967 and 969) discussed in the theses. Purple arrows indicate the Mediterranean surface circulation, where Atlantic inflow waters enter the western Mediterranean and continues flowing to the eastern Mediterranean across the Sicily sill. Levantine intermediate water is formed in the easternmost Mediterranean due to evaporation, which sinks to a 200-600m depth and flows to the west. With contributions from eastern and western Mediterranean deep waters, Levantine intermediate waters (red arrows) ultimately enter the Atlantic Ocean as a sub-surface flow at the Strait of Gibraltar. Deep water formation is not shown in the diagram. See Rohling et al., (2015)¹¹ for a review.

1.1.5 Objectives

In this project, the Pliocene evolution of the Mediterranean basin is studied using sediment cores retrieved during Ocean Drilling Program (ODP) Leg 160, from ODP Site 967 (Figs.1,.2). The earliest part of the sediment record (5.33 – 5.25 Ma) is studied in particular detail to understand the Mediterranean evolution during and immediately after the Zanclean megaflood, with additional data (including pollen, organic matter content, X-ray diffraction and biomarker analyses) from ODP Site 969 from the Mediterranean Ridge (Fig.2). A planktonic foraminiferal isotope record and an environmental magnetic record are generated using ODP Site 967 sediment record, for the period between 3 Ma and 5.3 Ma. X-ray Fluorescence (XRF) core scanning data for the same time interval aid in the reconstruction of North African climate variability and Mediterranean palaeoceanography through the Pliocene. Details of each thesis chapter involving aforementioned data generation are mentioned in the thesis outline.

1.2 Thesis Outline

This thesis is organized in six main chapters (excluding the introduction), that are written in the form of scientific papers. These chapters are presented in order of development of the project, instead of their chronological order.

Chapter 2 explores the Mediterranean refilling event (Zanclean megaflood, 5.33 Myr) that ended the Late Miocene desiccation phase of the Mediterranean (Messinian salinity crisis). Using proxy data, an anomalously lengthy sapropel is observed immediately after the Miocene/Pliocene boundary at ODP site 967, which is then recognized in all available deep eastern Mediterranean drilling sites. However, none of the western Mediterranean sites consisting of continuous sediment records across the M/P boundary contain an equivalent sapropel. Then, numerical modelling is used to explain the differences between eastern-western basins and the deposition of the anomalous sapropel in the eastern basin.

Chapter 3 investigates the second major Pliocene oceanographic transformation observed in eastern Mediterranean sediment records, using a multi-proxy reconstruction for ODP site 967 sediments. At ODP site 967, no sapropels are observed for 5.3-3.2 Myr period. Organic carbon burial abruptly intensifies at ODP site 967 at 3.2 Myr, resulting in frequent sapropel preservation afterwards. Intensified organic carbon burial with higher frequency of sapropel appearance is also observed in other deep Mediterranean ODP sites (ODP sites 964, 966 and

969). Reconstructed proxy data are then employed to evaluate the possible causes behind North African landscape transformation, which led to the observed 3.2 Myr intensification of organic carbon burial in the eastern Mediterranean.

Chapter 4 reveals an unusually lengthy period of sapropel absence in all available eastern Mediterranean sediment records, which also coincides with the period of maximum long-term freshwater input (based on site 967 stable oxygen isotope record) to the eastern Mediterranean (3.8-3.3 Myr). A proxy data compilation and climate modelling results are used to investigate this interval, which explain the North African climate/vegetation evolution in relation to global Early Pliocene warmth and the initiation of Northern Hemispheric glacials after 3.3 Myr.

Chapter 5 recognizes global environmental transformations across the Early-Mid Pliocene transition (3.4-3.2 Myr, with the M2 glaciation centered at 3.3 Myr), which occurred coeval to the North African landscape transformation discussed in chapters 3 and 4. Climate modelling is employed to evaluate the influence of global ice volume increase and subsequent atmospheric modifications across the 3.4-3.2 Myr transition on Northern and Southern Hemispheric ecosystems.

Chapter 6 presents a detailed analysis of the eastern Mediterranean Miocene/Pliocene boundary, using ODP sites 967 and 969 sediment records. This chapter combines multiple methods of data generation (biomarker, organic matter content, X-ray fluorescence, X-ray diffraction and pollen analyses) with numerical modelling, to reveal aspects on the MSC-terminating megaflood, that were not revealed in chapter 1.

Chapter 7 presents quantitative estimates of North African monsoon variability through past 5 Myr, using a Mediterranean box model that deconvolves ODP site 967 stable oxygen isotope record. This chapter describes the role of orbital eccentricity in modulating the North African monsoon over long time scales. Box model sensitivity tests are used to investigate the likely causes behind changing oxygen isotope values across globally important transitions, such as the intensification of Northern Hemispheric glaciation at ~2.6 Myr.

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CHAPTER 2

Sill-controlled salinity contrasts followed post-Messinian flooding of the Mediterranean

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The Mediterranean Sea was substantially disconnected from the global ocean in an event called Messinian Salinity Crisis (MSC; 5.97-5.33 million years ago (Myr)), resulting in a reduced Atlantic inflow and likely a terminated outflow. During the MSC, the Mediterranean was desiccated to more than 1.5 km below Atlantic level. At 5.33 Myr, collapse of the Gibraltar Sill initiated a megaflood (Zanclean megaflood), which may have refilled the Mediterranean within 2 years. This chapter investigates the immediate impact of the Zanclean megaflood on post-Messinian evolution of the Mediterranean.

Statement of Contribution

This thesis is submitted as a Thesis by Compilation in accordance with https://policies.anu.edu.au/ppl/document/ANUP_003405

I declare that the research presented in this Thesis represents original work that I carried out during my candidature at the Australian National University, except for contributions to multi-author papers incorporated in the Thesis where my contributions are specified in this Statement of Contribution.

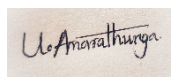
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Sill-controlled salinity contrasts followed post-Messinian flooding of the Mediterranean

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A mile-high marine cascade terminated the Messinian Salinity Crisis 5.33 Myr ago, due to partial collapse of the Gibraltar sill that had isolated a largely desiccated Mediterranean from the Atlantic Ocean. Atlantic waters may have refilled the basin within 2 years. Prevailing hypotheses suggest that normal marine conditions were established across the Mediterranean immediately after the catastrophic flooding. Here we use proxy data and fluid physics-based modelling to show that normal conditions were likely for the western Mediterranean (wMed), but that flooding caused a massive transfer of salt from the wMed to the eastern Mediterranean (eMed) across the Sicily sill, which became a hyper-salinity-stratified basin. Hyper-stratification inhibited deep-water ventilation, causing anomalously long-lasting organic-rich (sapropel) sediment deposition. Model-data agreement indicates that hyper-stratification breakdown by diapycnal diffusion required 26,000 years. An alternative hypothesis that Atlantic reconnection occurred after the Mediterranean had largely been refilled is inconsistent with our observations, as this would have led to hyper-stratification and sapropel formation in both basins. Our findings offer insight into the role of stratification in delaying the re-establishment of normal marine conditions following abrupt refilling of a previously desiccated ocean basin.

The 630,000-year Messinian Salinity Crisis (MSC) resulted from progressive closure of the connection(s) between the Mediterranean Sea and Atlantic Ocean ~5.96 Million years ago (Myr)¹⁻³. During the MSC, massive evaporite sequences were deposited. A phase of km-scale

Mediterranean drawdown occurred⁴, resulting in a basin-wide Messinian erosional surface⁵ and 2,500 m and 1,300 m deep Messinian canyons excavated beneath the Nile delta and the Rhône River mouth, respectively^{6,7}. It has long been inferred that Mediterranean sea levels were low, ~1,300 m to ~2,700 m below global sea level^{5,8–11}, prior to the earliest Pliocene (Zanclean) megaflood event that terminated the MSC. Alternatively, geochemical and paleobiological evidence from latest Messinian evaporites may imply elevated basin levels, attributing the drawdown to an older Messinian phase¹². In that scenario, increased Paratethyan and occasional Atlantic inflows are suggested to have largely refilled the Mediterranean¹³ (a shallow Mediterranean base level below Atlantic, with interconnected subbasins) with lower-salinity water overlying deep hypersaline fluids prior to complete Atlantic reconnection^{12–14}. We investigate the consequences of abrupt refilling of a partially desiccated basin (a kilometer-scale drawdown in the megaflood hypothesis) and address the alternative hypothesis in a sensitivity test (see Methods, Extended Data Figs. 6-8).

Evidence supporting the megaflood hypothesis

The megaflood hypothesis is based on seismic and borehole data from both the wMed and eMed^{15–17}. Critical evidence at the Strait of Gibraltar comes from a massive erosive channel in the Gibraltar arc/sill, which extends 390 km from the Gulf of Cadiz on the Atlantic side toward the deep Alboran Sea on the Mediterranean side; the so-called Zanclean channel³. Elongated megabar deposits detected alongside the main erosive channel in the eastern Alboran Sea have been related to the flooding event¹⁶. This sharply defined channel has maximum depth and width of 650 m and 15 km, respectively^{3,16}. The dimensions of this incision have led to model estimates of water fluxes of up to ~150 Sv (Sverdrup, $1 \times 10^6 \text{ m}^3 \text{ s}^{-1}$) during the Zanclean flood³.

The most plausible flood-water passage from the wMed into the eMed is the Noto Canyon, which was carved into the Malta escarpment^{15,16}. Upslope, this canyon comprises a 400 m deep and 4 km wide erosive channel, with Pliocene-Quaternary sediment infill¹⁵. At the Noto Canyon outlet, seismic stratigraphy in the western Ionian basin reveals a buried chaotic sediment body that extends over an 11,000 km² area, and reaches a 1,430–1,620 km³ volume^{15,16}. This unit has been interpreted as a megaflood deposit of material that was eroded, transported, and deposited during a catastrophic flooding event at the Miocene/Pliocene transition^{15,16}.

The Miocene/Pliocene boundary was drilled at several Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) sites in the deep Mediterranean¹⁸. It is characterized by a sharp

lithological change, which has been attributed to an abrupt return to open-marine conditions across the Mediterranean, terminating the MSC^{16,18,19}. However, where continuous records across the boundary are available, a major difference can be seen between Mediterranean sub-basins (Supplementary Table 1, Extended Data Fig. 1). In the wMed, complete records across the M/P transition from the Tyrrhenian Sea, Balearic margin, and Alboran Sea (Supplementary Table 1) reveal earliest Pliocene foraminifer-nannofossil oozes over Late Messinian evaporative sequences. This sequence suggests that normal marine conditions were established rapidly in the wMed following flooding (Supplementary Table 1). In contrast, eMed cores indicate deposition of a thick organic-rich layer (sapropel) in the earliest Pliocene, which was first detected in DSDP Site 376 from the Florence Rise and named the “mystery sapropel”²⁰. ODP Site 969 on the Mediterranean Ridge contains a similarly thick, laminated sapropel immediately above the flooding surface (Supplementary Table 1). Absence of benthic foraminifera in this sapropel indicates a lack of eMed deep-water ventilation/ oxygenation in the immediate flood aftermath, in contrast to better wMed ventilation²⁰.

More evidence for the mystery sapropel

At eMed ODP Site 967 (Eratosthenes seamount), late Messinian brecciated carbonates (with gypsum²¹) are overlain by dark grey to olive green earliest Pliocene sediments^{21,22}. Throughout the sediments younger than ~3.2 Myr at Site 967, colour reflectance records and oxygen isotope stratigraphy indicate a regular pattern of sapropel occurrence, visibly recognizable as dark layers^{21,23,24}. Between 3.2 Myr and 5.33 Myr, there are no visible sapropels, but there are red intervals resulting from post-depositional sapropel oxidation^{21,23,24} (Extended Data Fig.2). These red intervals contain similar Ba enrichments as sapropels, which are associated with organic matter burial and remained present even after post-depositional oxygenation^{25,26}; thus, Ba enrichment is a reliable proxy for original sapropel extents, and for detecting sapropels that were initially present but that were later oxidized^{25–28}. Throughout the last ~14 Myr, sapropel deposition (and associated Ba peaks) consistently occurred during high-amplitude precession-driven insolation maxima, where the amplitude is modulated by orbital eccentricity maxima^{29,30}.

Here we present core-scanning X-ray fluorescence (XRF) and magnetic data across the M/P boundary at ODP Site 967 (Supplementary Information) that corroborate the deposition of an organic-rich layer immediately following the M/P transition (Figure 1). From our results, this layer comprises two Ba peaks with lower (but still substantially elevated) Ba levels in between

(Figure 1). This Ba pattern is mirrored by two Ti/Al minima with an intervening maximum (Figure 1). In the eMed sapropel stratigraphy, these mirrored fluctuations are typical of two insolation maxima with an intervening minimum^{31–33}. Our chronology suggests that this organic-rich sediment deposition persisted over a 26,000-year period (Extended Data Fig. 3, Supplementary Table 2). Profiles of redox-sensitive elements and anhysteretic remanent magnetization (ARM) across the organic-rich layer (Figure 1) are also typical of sapropels^{25,26,28}. This 26,000-year interval represents the only Neogene example of a sapropel that extends through an insolation minimum; it breaks the well-understood relationship between sapropel deposition and African monsoon maxima associated with northern hemisphere insolation maxima^{29,34–37}. In this conventional mode, monsoon maxima caused extensive freshwater flooding into the Mediterranean^{36,38–40}, which drove both enhanced stratification (curtailing new deep-water ventilation/oxygenation) and enhanced organic export production^{29,41,42}. Meanwhile, the monsoon maximum suppressed wind transport of Ti-rich dust to the eMed^{26,31,43}. Extension of the sapropel at the M/P boundary across an African monsoon minimum (insolation minimum) is a clear indication of the operation of an additional mechanism that was unique to this event with respect to the entire Neogene.

Establishment of normal marine conditions

The terminal Messinian was a period of surface dilution that resulted from increased Paratethyan and riverine freshwater input (*Lago Mare* events), punctuated by local gypsum deposition during times of enhanced evaporation^{32,44,45}. In our main scenario, deep Mediterranean basins prior to the Zanclean flooding were filled with residual high-salinity brines that in places exceeded 2 km in thickness^{9,32,44}. Here, we consider ‘Late Messinian brines’ to have been derived from MSC Stage 2 fluid dilution (when halite precipitated in the wMed and eMed⁴⁵), including potential contributions from halite re-dissolution. We set the brine concentration to 140 PSU (see Methods for explanation on choice of brine salinity). A qualitative conceptual refill scenario can then be formulated based on energy- and mass-balance arguments (the alternative hypothesis starting with a largely refilled late-Messinian basin^{12–14} is addressed in a sensitivity test; see Methods). In the main scenario, the high-energy Atlantic floodwater cascading into a partially desiccated Mediterranean would have encountered and vigorously mixed with residual wMed brines, while the wMed filled to the height of the sill in the Strait of Sicily (Extended Data Fig. 4). Mixed wMed brine would then have broken through and cut the Noto Canyon, cascading into the eMed. Meanwhile, wMed sea level would have remained several hundred metres below Atlantic sea level, which

continued the Atlantic cascade through the Zanclean channel, mixing with wMed brines. Thus, we expect massive salt transfer from the steadily diluting wMed into the filling eMed. Once eMed and wMed sea levels equalized, the level across both basins would have risen in unison, until it equalized with Atlantic sea level across the Strait of Gibraltar. Approximately balanced Atlantic inflow and Mediterranean outflow then drove gradual excess salt removal from the Mediterranean. At this stage, stratification was much less pronounced in the wMed than in the eMed because of the prior wMed salt transfer into the eMed (as the latter filled). Inhibition of deep-water ventilation during this hyper-stratified brine-filled eMed period—accentuated by monsoon flooding during insolation maxima—may then explain the anomalously long duration of the “mystery sapropel” spanning two insolation maxima and an intervening minimum.

Our qualitative concept requires quantitative assessment, especially to evaluate whether the hypothesized mixing processes are realistic energetically and whether (and why) eMed stratification persisted for ~26,000 years, as derived from our XRF-based sapropel stratigraphy and insolation tuning (see Methods, Extended Data Fig. 3). For this purpose, we present a brine evolution model for the flooding event and its aftermath. Our model considers post-Messinian Mediterranean basin evolution in two successive phases: *(i)* the Flooding Phase and *(ii)* an Evolving Phase. The switch between phases occurred when Mediterranean sea level matched Atlantic sea level across the Strait of Gibraltar.

The flooding phase is characterized by release of enormous gravitational potential energy. This potential energy is converted to kinetic energy as Atlantic floodwaters cascade into the wMed, which we estimate may have exceeded 1.6×10^{19} J per day at peak flood (Supplementary Figure 1), or more than 500 times the kinetic energy dissipation at Niagara Falls in one year⁴⁶. This energy is sufficient to mix (most of) the existing wMed brines with Atlantic inflow, forming a deep mixed layer atop potential residual brine (Figure 2, see Methods). As the rising wMed sea level reached the crest of the Sicily Sill, mixed wMed waters started cascading into the eMed via Noto Canyon. Given a smaller channel cross-section in Noto Canyon than in the Zanclean channel, we find that an even more energetic flow entered the eMed than the wMed (Supplementary Figure 1). Note that our method calculates the minimum flow, restricted only by channel dimensions, and that more energy would have been available in reality because of the steep drop in this passage^{15,16}. A massive amount of wMed mixed brine was transferred into the eMed through Noto Canyon because the eMed volume is ~2.5 times greater than the wMed, while—at the same time—Atlantic inflow through the Zanclean channel continued to dilute the wMed mixed layer. We find that >95% of the wMed excess salt ended up in the

eMed, as this basin filled (Figure 2). Once eMed sea level reached the Sicily Sill, energy transfer across the sill diminished as the cascade terminated gradually. Later, while both basin levels rose together to the Atlantic level, enhanced mixing occurred only in the vicinity of the Gibraltar Sill, further diluting the western basin (Figure 2, Extended Data Figs. 4, 5).

At the flooding phase conclusion, dense (post-flood) brines had filled the eMed to the Sicily Sill. For the Mediterranean to return to normal marine conditions, the salt in this brine must have been transferred out of the basin, into the Atlantic Ocean. Eroding the deep brine layer required mixing across the interface separating the brine from shallower, inflow-dominated lower salinity waters. This mixing would have been governed by similar processes to those operating in the modern global ocean: diapycnal mixing due to wind forcing, tidal interaction with bathymetry, and internal wave breaking⁴⁷. These processes lead to estimated diapycnal diffusivity values within a $1\text{--}5 \times 10^{-5} \text{ m}^2\text{s}^{-1}$ range⁴⁸; we use this range to estimate mixing timescales and their uncertainties. The wide uncertainty range used here is derived from the competing effects of mixing inhibition owing to stronger stratification and enhanced mixing within a smaller basin (with greater boundary interactions).

We model the evolving phase using diapycnal diffusivity in the stated range to remove salt by mixing. We obtain timescales of 10,000–40,000 years (Figure 3b). The ~26,000-year duration estimated from our proxy data agrees well with this range and corresponds to a diapycnal diffusivity of $2 \times 10^{-5} \text{ m}^2\text{s}^{-1}$. We calculate that this process would have released more than $7 \times 10^{16} \text{ kg}$ of excess salt into the Atlantic Ocean within that time period, via Mediterranean outflow. Eventually, salt removal from the deeper eMed reduced stratification sufficiently to allow winter-cooled surface waters to attain densities conducive to new deep-water formation. This facilitated restart of deep-water ventilation and oxygenation, which ended the evolving phase marked by the “mystery sapropel.” Downward oxidation of reduced sapropel sediments under an oxygenated water column caused a “burn down” oxidation front in the upper 35 cm of the sapropel^{26–28,49,50} (Figure 1).

We propose that absence of a wMed sapropel following the flooding resulted from wMed brine transfer to the eMed during a high-energy mixing and refilling episode. Our sensitivity test evaluates an alternative ending to the MSC, starting with a deep water column of residual brine overlain by lower-salinity brackish waters that had refilled the basin before Atlantic reconnection^{12–14}. We find that there is insufficient energy in this scenario to remove brine from the wMed (Extended Data Figs. 6–8, see Methods), and a long phase of anoxic (sapropel)

deposition would be expected in both the wMed and eMed, which conflicts with available observations (Supplementary Table 1). This offers strong support for a partially desiccated Mediterranean state prior to Atlantic reconnection. To account for potential post-Messinian tectonic movements which may have affected the Sicily sill depth^{9,14}, and to test for the minimum wMed and eMed base level drops below Atlantic level required to validate our hypothesis, we perform additional sensitivity tests (Methods). Results of the analysis support available observations, further strengthening our hypothesis (Extended Data Figs. 9, 10).

We find that only a kilometer-scale base level fall in both basins at the terminal Messinian would have resulted in the observed proxy records and modelling outcomes. We conclude that the transition from a partially desiccated Mediterranean basin to normal marine conditions was much less rapid than basin refilling; the full transition took ~26,000 years, whereas flooding/refilling took only ~2 years (Figures 2, 3). The ~26,000-year timescale is corroborated quantitatively by our model, which suggests that a 10,000-40,000-year duration is expected. Throughout this time, hyper-stratified eastern Mediterranean conditions caused persistence of an anomalously long interval of organic-rich sediment deposition that extended through two precession-related insolation maxima and the intervening minimum.

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Author contributions

U.A. designed and led the study, and wrote the paper; U.A. developed the hypothesis and performed the modelling, with guidance from A.M.H. and E.J.R.; E.J.R., A.M.H., A.P.R., K.M.G. and D.H. contributed to data interpretation; K.M.G. calibrated scanning XRF data; S.G. performed WD-XRF analyses; X.Z. and P.H. assisted with magnetic measurements; D.L. performed XRF core-scanning; D.L. and T.W. developed the ODP967 composite depth splice; all authors contributed to manuscript development.

Competing interests. The authors declare no competing interests.

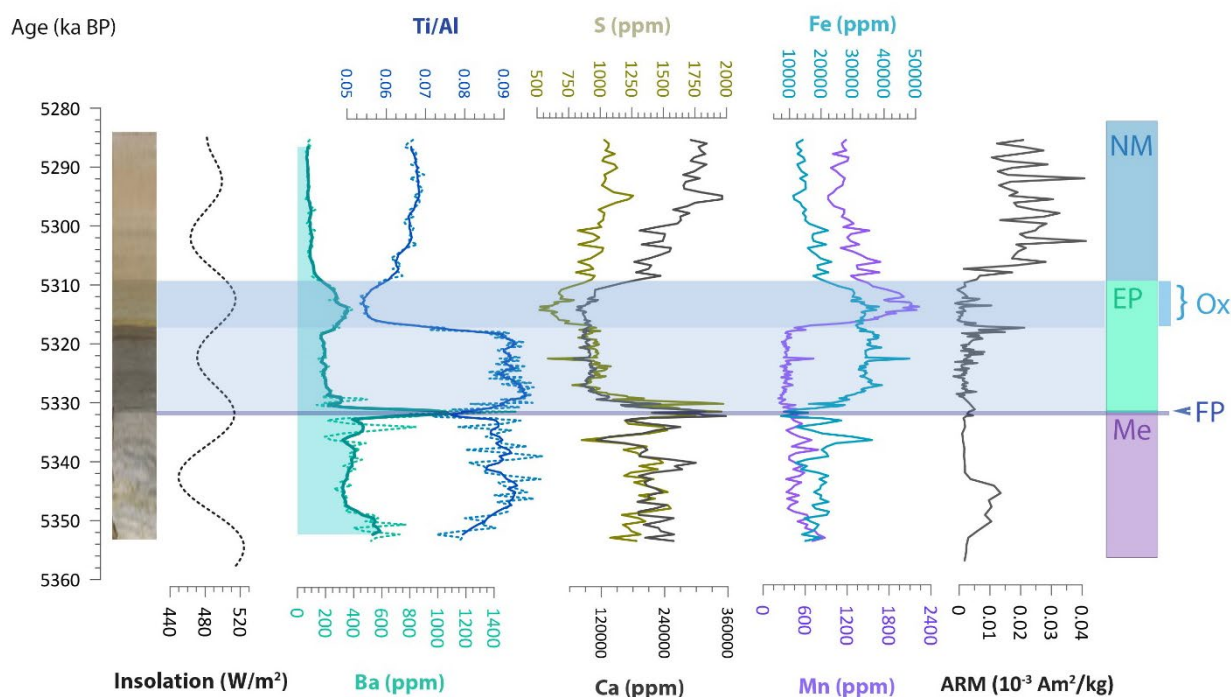


Figure 1| XRF core scanning and magnetic data across the Miocene/Pliocene boundary from ODP Site 967. The Miocene/Pliocene transition is tuned to the 65°N insolation maximum at 5.333 Myr (see Extended Data Fig. 3). Return to normal marine conditions is marked by a sudden jump in Ca concentration at around 5.307 Myr. Elevated Ba concentrations indicate organic matter preservation between the first two Pliocene insolation maxima (Mystery sapropel). The intervening insolation minimum records more than twice as high Ba concentrations compared to normal marine (NM) conditions. (For Ba and Ti/Al, dotted lines in the background indicate original XRF data. Thick lines are the 5-point moving average of the two records). The upper portion of the mystery sapropel has been oxidized as indicated by Mn, S, and ARM profiles (Ox). Me, Messinian; FP, Flooding Phase (Zanclean flooding surface); EP, Evolving Phase.

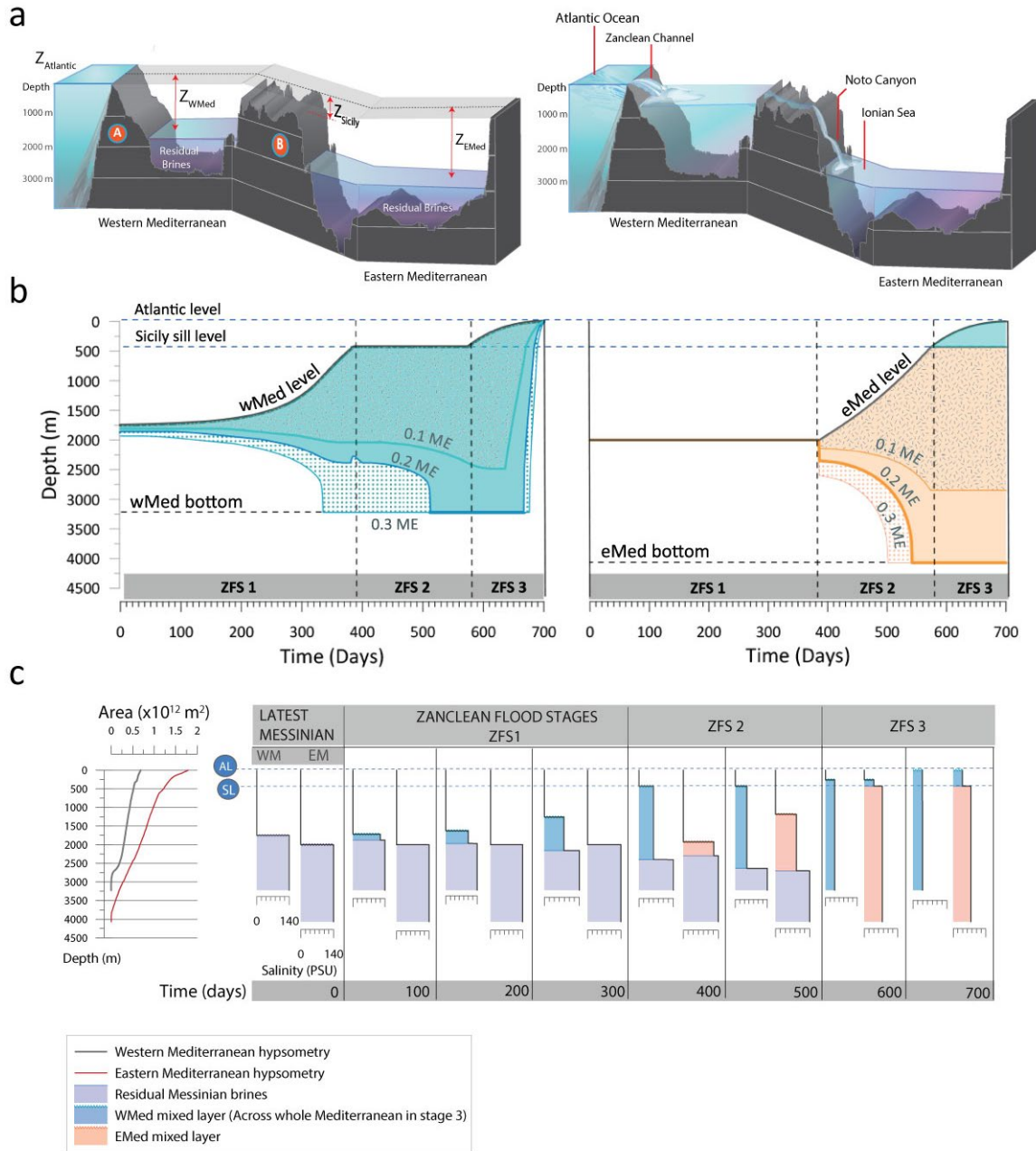


Figure 2 | Evolution of Mediterranean sub-basins during the Zanclean flood. **a**, Sketches of the basin configuration during the latest Messinian (left) and Flooding Phase (right). A = Camarinal Sill; B = Sicily Sill; Z_{wMed}/Z_{eMed} = Messinian drawdown in wMed/eMed; Z_{Sicily} = Depth to Sicily Sill; $Z_{Atlantic}$ = Atlantic Sea surface. **b**, Mixed layer evolution with time for western and eastern basins. Thick black line indicates sea-level rise in both basins with time (wMed and eMed levels). Coloured, hatched, and dotted backgrounds indicate the mixing extent at mixing efficiency (ME) = 0.2, 0.1 and 0.3, respectively. The difference between the basin level curve and the mixed-layer curve gives the mixed layer thickness at a given time. **c**, Reconstructed wMed and eMed hypsometry (left); salinity profile evolution (right) for wMed and eMed at each 100-day interval. Salinity profiles (thick black lines) are given in PSU (from 0 to 140 in each diagram). ZFS 1 terminates as the wMed level reaches the Sicily Sill; ZFS 2 terminates as eMed level reaches Sicily Sill; during ZFS 3 both basins rise to the Atlantic level simultaneously. ZFS, Zanclean flood stage; AL, Atlantic Level; SL, Sicily Sill Level; WM, Western Mediterranean; EM, Eastern Mediterranean.

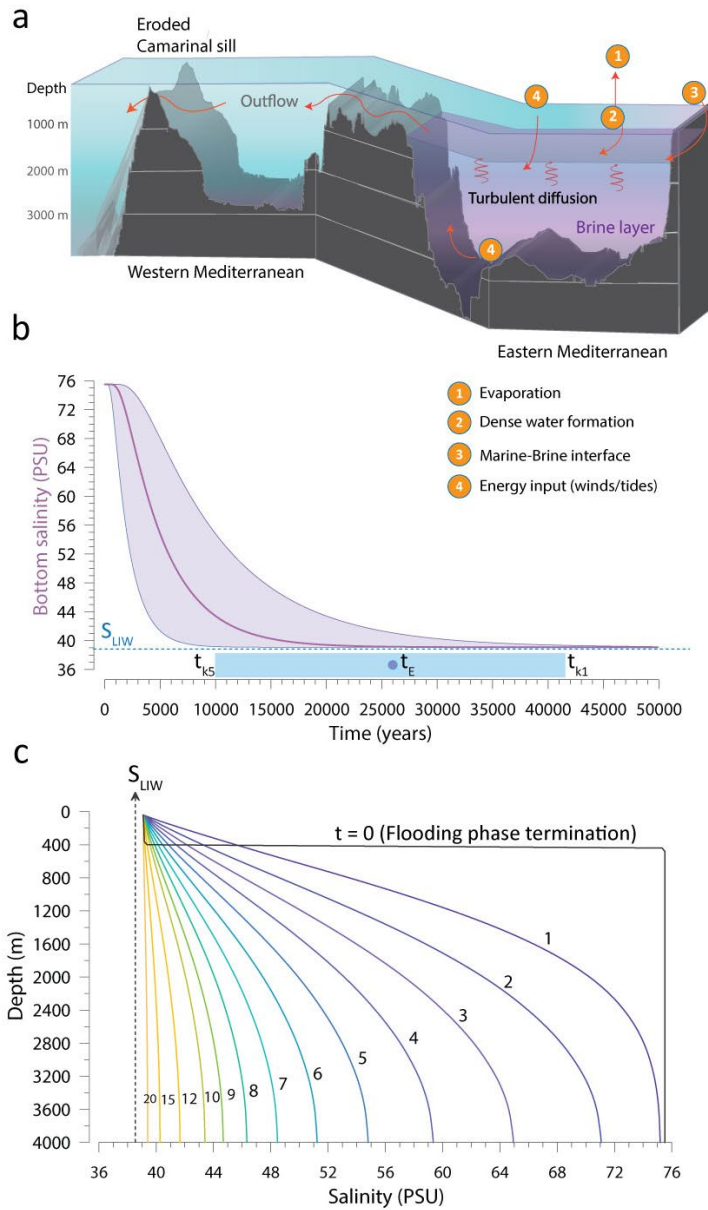


Figure 3 | Mediterranean evolution during the Evolving Phase (EP). **a**, A sketch of the main processes involved in brine removal from eMed during the EP. Here, the eMed brine layer formed at the end of the Flooding Phase, as a result of wMed salt transfer and mixing with eMed residual Messinian brines. This layer should not be confused with ‘residual Messinian brines’ that existed before the flood. **b**, Bottom salinity evolution with time. The thick line is the salinity evolution for diapycnal diffusivity $K_S = 2 \times 10^{-5} \text{m}^2 \text{s}^{-1}$. Upper and lower envelopes mark the evolution at diffusivities of $1 \times 10^{-5} \text{m}^2 \text{s}^{-1}$ and $5 \times 10^{-5} \text{m}^2 \text{s}^{-1}$, respectively. t_{k1} and t_{k5} are the durations taken to erode the brine at $1 \times 10^{-5} \text{m}^2 \text{s}^{-1}$ and $5 \times 10^{-5} \text{m}^2 \text{s}^{-1}$, respectively. The time window between t_{k1} and t_{k5} demarcates all possible time frames within mentioned diffusivity values. t_E is the duration recorded by proxy data (26,000 years). S_{LIW} , Levantine intermediate water salinity. **c**, Evolution of eMed salinity profile with time for $K_S = 2 \times 10^{-5} \text{m}^2 \text{s}^{-1}$. Numbers on each curve represent time evolved in thousand years (1 = 1,000 years, etc.)

METHODS

Bulk sediment geochemistry

We present X-ray fluorescence (XRF) core-scanner data from ODP Site 967 for the 5.12-5.35 Ma interval. Scanning was performed on archive core-sections at MARUM-University of Bremen on an Avaatech XRF core scanner. Core sections were covered with 4 mm-thick Ultralene film and measured at 50 and 30 kV with 0.55 mA current and with a Cu and Pd-thick filter, respectively, and at 10 kV with 0.035 mA current (no filter); count time for all runs was 7 s. Element ‘counts’ for the entire interval were converted into element concentrations by multivariate log-ratio calibration⁵¹, using new wavelength dispersive (WD)-XRF reference element concentrations. For these, 38 bulk sediment samples were chosen to cover a range of lithologies based on the XRF scan, then 1 cm³ dried ground sample was mixed with a lithium tetraborate/lithium metaborate flux and fused into 39 mm diameter beads. Major element abundances were analysed by WD-XRF using a Bruker S8 Tiger™ spectrometer at Geoscience Australia. Loss on ignition (LOI) was measured by gravimetry after combustion at 1000 °C. One in every ten samples was duplicated along with multiple analyses of 3 international standards (NCS DC70306, MAG-1, ML-2) and an internal basalt standard (WG1). Quantification limits for all major element oxides are <0.2% and reproducibility is within 1%.

Anhyseretic remanent magnetization (ARM)

ODP967 U-channel samples were sliced at 1-cm intervals into discrete non-magnetic 2×2×2 cm plastic cubes and measured for ARM on a 2-G Enterprises cryogenic magnetometer at the Australian National University. The ARM was imparted using an alternating field of 100 mT and a direct current bias field of 0.05 mT.

Mediterranean evolution

Evaporative Mediterranean drawdown during the Messinian left residual brines in the adjacent eMed and wMed basins, with thicknesses reaching more than 2 km in the deepest parts^{9,32,44}. We assume a water level drop of 2,000 m below Atlantic sea level in the eastern basin, and 1,750 m in the western basin prior to the megaflood^{5,8–10}. To relate Mediterranean refilling to the volume flux of the incoming flood, we use an intermediate reconstruction between Miocene and present-day Mediterranean hypsometry¹⁰. Before the flood, halite precipitation occurred at ~5.6 Myr in both basins at the Messinian Salinity Crisis (MSC) peak. The final MSC stage contains gypsum deposition punctuated by surface-water freshening events. A few drilling sites record gypsum below the flooding surface (Supplementary Table 1). Considering these

observations, we set Messinian residual brine salinity to gypsum saturation at the start of the flood (140 PSU⁵²). We test model outputs for a range of starting salinities (60-240 PSU) in a sensitivity test (Extended Data Figs. 9, 10).

The Flooding Phase

To determine the flood velocity entering the western basin from the Strait of Gibraltar, we use a flood incision model, following Garcia-Castellanos et al. (2009)³. This model computes the incision rate (dz_s/dt) at Camarinal Sill based on the following approach, where dt is the timestep and dz_s is the depth of erosion per time step:

$$\frac{dz_s}{dt} = k_b(\tau_b)^a, \quad (1)$$

where k_b and $a = 1.5$ are positive constants. To obtain a final sill incision depth (240 m^{ref. 3}), we calibrate k_b to $1.8 \times 10^{-4} \text{ m yr}^{-1} \text{ Pa}^{-a}$, where a is the constant mentioned above, while τ_b is the basal shear stress at the sill, which is computed using:

$$\tau_b = \rho_s g(z_s - z_0)S, \quad (2)$$

where ρ_s is seawater density, $(z_s - z_0)$ is the mean water depth at the sill, g is acceleration due to gravity, and $S = z_h/L$ is the ratio between head loss (z_h) and length of the erosive channel (L). Manning's formula³ is used to calculate the flow velocity:

$$v = \frac{1}{n} R_h^{\frac{2}{3}} S^{\frac{1}{2}}, \quad (3)$$

where v is the average flow velocity along the slope toward the Alboran basin, $n = 0.05$ is the roughness coefficient³ and R_h is the hydraulic radius of the passage between the Atlantic and Mediterranean³. Where channel width is substantially greater than the water depth, the hydraulic radius is approximated by $(z_s - z_0)$. Flood discharge flux into the Mediterranean (Q) is then calculated using:

$$Q = W(z_s - z_0)v, \quad (4)$$

where $W = k_w Q^{a_w}$ is the incision channel width, which increases to a final 14 km value at the end of the flood. Here $a_w = 0.5$ is a constant, and we impose $k_w = 1.1$ to obtain the final channel width (see Methods in Garcia-Castellanos et al. (2009) for details³).

This model predicts a peak discharge flux that exceeds 100 Sv at a velocity $> 40 \text{ ms}^{-1}$ at the Camarinal Sill³. In the initial flood stage, high-energy normal Atlantic seawater inflow

encounters much denser residual wMed brines. The extent of mixing between brine and flood waters depends on the kinetic energy of the flow that approaches the brine surface. Without mixing, a seawater layer (ρ_s) would form on top of the denser brine (ρ_b). In contrast, if complete seawater mixing occurred with the brine, a single intermediate density layer (ρ_m) would have formed. Mixing due to turbulent erosion of stratification can be accomplished with a large enough energy to overcome the potential energy, raising denser fluid parcels while lowering lighter parcels⁵³.

If complete mixing occurred in the basin, the centre of gravity of the system must be raised, resulting in a potential energy gain given by:

$$PE_{Final} - PE_{Initial} = PE_{Gain} = \int_0^{H+h} \rho_m g z dz A(z) - \left(\int_H^{H+h} \rho_s g z dz A(z) + \int_0^H \rho_b g z dz A(z) \right), \quad (5)$$

where PE_{Gain} represents the energy (per day) required for complete mixing, $A(z)$ is the basin surface area with depth (z), h is the thickness of the seawater layer flooded into the basin per timestep (per day), and H is the total brine column thickness prior to mixing.

Under the assumption of the Garcia-Castellanos et al. (2009)³ model that the slope of Atlantic water inflow into the wMed is constant over time, the flow velocity entering the brine surface in the western basin, v_{wMed} is v . The kinetic energy per day of this inflow (KE_{wMed}) is then calculated using:

$$KE_{wMed} = \frac{1}{2} \rho_s v_{wMed}^2 Q. \quad (6)$$

In our model, we calculate energy conversions at daily iterations, by integrating the energy expression in equation 6 over one-day intervals. Available potential energy of inflow into the wMed (at the sill), APE_{wMed} , is equal to $\rho_s g Q L_{wMed}$, where L_{wMed} is the vertical distance between the brine surface and the Camarinal Sill crest. As the Atlantic inflow descended down-slope, gravitational potential energy was released to kinetic energy, and was lost in processes such as Zanclean channel erosion and turbulent dissipation. Erosion along the slope will have resulted in a headward-migrating erosion wave along the channel that may have then triggered even higher flow and erosion rates, resulting in a more abrupt flood⁵⁴. Therefore, our calculations offer a minimum estimate of flow kinetic energy into the wMed.

Most of the inflow kinetic energy into the basin is lost to viscous turbulent dissipation. Laboratory experiments in stratified fluids suggest that ~20% of the turbulent energy loss goes

to irreversibly mixing the stratification (known as the mixing efficiency)^{55,56}. Thus, the energy available for basin mixing (KE_{Av}) can be given as:

$$KE_{Av} = \Gamma \cdot KE_{wMed}, \quad (7)$$

where $\Gamma \approx 0.2$ is the mixing efficiency. Full-depth mixing can occur only if $KE_{Av} > PE_{Gain}$. If available kinetic energy is less than that required to mix the entire brine column thickness (H), partial brine mixing will occur. The mixing extent can then be computed using energy arguments. For this purpose, we introduce a mixing depth (H_{Mix}). Where mixing is incomplete, equation 1 can be rewritten as:

$$KE_{Av} = PE_{GPar} = \int_{H+h-H_{Mix}}^{H+h} \rho_m g z dz A(z) - \left(\int_H^{H+h} \rho_s g z dz A(z) + \int_{H+h-H_{Mix}}^H \rho_b g z dz A(z) \right), \quad (8)$$

where PE_{GPar} is the potential energy gain during partial mixing. Hence, if available energy is insufficient to mix completely, mixing will be restricted to a brine depth of H_{Mix} . If the flow kinetic energy increases with time, H_{Mix} will increase accordingly, eventually completely mixing the brine when KE_{Av} exceeds PE_{Gain} .

We use the following approach to calculate the salinity evolution (S_m) of the mixed fluid:

$$S_m = \frac{Q_{S_{AW}} + Q_b S_b}{Q_m} = S_{wMed}, \quad (9)$$

where Q_b is the brine volume (per day) mixed in the basin, S_b is the brine salinity, and Q_m is the resultant volume of mixed fluid (per day). For salinity-density conversions, we include the Gibbs Sea Water (GSW) Oceanographic Toolbox functions into our model.

Once wMed sea level reaches the Sicily Sill (430 m below sea level), wMed mixed fluid spills into the eMed. We use equation (8) to compute the mixing extent in the eastern basin as it fills. Noto Canyon is considered to be the path of flood waters into the Ionian basin (eMed) during the megaflood¹⁵. To approximate the flow velocity approaching the eMed brine surface, we consider that the volume flux spreads across a channel of width b_{eMed} , in a fluid layer of depth d_{eMed} travelling at velocity v_{eMed} . The erosive channel detected at the upper Noto Canyon is 4 km wide; thus, we impose b_{eMed} to be a 4 km maximum. The present average channel depth is $400 \text{ m}^{\text{ref } 15,16}$ (d_{eMed}). Minimum flow velocity into the eMed is then given by:

$$v_{eMed} = \frac{Q}{A_{Noto}}, \quad (10)$$

where A_{Noto} is the present-day maximum cross-sectional area of the Noto Canyon erosive channel. In reality, flow velocity entering the eMed would have been higher due to the steep slope toward the end of the passage^{15,16}. The kinetic energy of flow entering the brine is:

$$KE_{eMed} = \frac{1}{2} \rho_s (v_{eMed})^2 Q. \quad (11)$$

Similar to the wMed approach, complete mixing is assumed if $1 > (\Gamma KE_{eMed})/PE_{Gain}$. As the eMed is filled, wMed waters mix continuously due to inflow through the Strait of Gibraltar. Equation (9) is used to calculate salinity evolution in both basins during this flood stage (S_{wMed} and S_{eMed} , respectively). The water flow cascading into the Ionian basin (eMed) terminates once the eMed level reaches the Sicily Sill level. Thereafter, both eMed and wMed levels rise simultaneously to the Atlantic level. In this final flood stage, mixing occurs due to flow along the Zanclean channel (Strait of Gibraltar), further diluting the western basin (thus, further decreasing S_{wMed}).

The Evolving Phase

During the first part of our model (*Flooding Phase*), most wMed salt was transferred into the eMed across the Strait of Sicily. As a result, the wMed had less saline waters, whereas the eMed filled with a denser brine layer up to the Sicily Sill (the reconstructed early Pliocene eMed volume with sea level equal to the Sicily Sill level is $2.04 \times 10^{15} \text{ m}^3$ ref. 10). For the Mediterranean to return to normal marine conditions, this enormous amount of brine should then have been redirected to the Atlantic Ocean.

The processes required to erode this deep, dense brine layer would have involved mixing across the interface separating it from inflowing waters. This mixing would occur due to the same set of processes that operate in the modern global ocean; namely, diapycnal mixing due to internal wave breaking^{47,57}. Generation of internal gravity waves results from a chain of processes including barotropic tidal flow over topography, variations in wind force at the ocean surface, lee waves produced by ocean currents, and eddies flowing over topography^{47,57}. The sum of all turbulent processes leads to an effective turbulent diffusivity of $K_S = 1-5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ refs. 48,57. By assuming a turbulent diffusivity in this range, we estimate the duration required to erode the deep layer. The salinity profile immediately after the flooding event consists of an upper Mediterranean seawater layer, and a deep brine layer below the sill depth. Mixing and advection is rapid in the x and y directions (horizontally); thus, a good approximation for salinity, S , at any time is that it depends on height, z , only. The diffusive timescale, t , can be estimated from the diffusion equation:

$$\frac{\partial S}{\partial t} = K_s \frac{\partial^2 S}{\partial z^2}. \quad (12)$$

To solve Eq. (12) numerically, we divide the domain into N equally spaced layers, each having thickness d_z . Basin hypsometry is characterized by the surface area (A_z) at each depth interval. The salt flux between adjacent layers is proportional to the local salinity gradient given by:

$$F \sim K_s \frac{\partial S}{\partial z}. \quad (13)$$

Evolution of salinity in the j^{th} layer of the domain is given by the flux divergence:

$$A^j \frac{\partial S^j}{\partial t} = \frac{K_s}{d_z} \left(A^{j+1} \left[\frac{S^{j+1} - S^j}{d_z} \right] - A^j \left[\frac{S^j - S^{j-1}}{d_z} \right] \right). \quad (14)$$

When this equation is further discretized in time, it can be shown that:

$$S_{\tau+1}^j = S_{\tau-1}^j + \frac{2K_s d_t}{d_z^2} \left(S_{\tau}^{j-1} - \left[\frac{A^{j+1}}{A^j} + 1 \right] S_{\tau}^j + \left[\frac{A^{j+1}}{A^j} \right] S_{\tau}^{j+1} \right), \quad (15)$$

where d_t is the time step and time levels are indicated by the subscript (τ). With use of these equations, we compute the salinity profile evolution until the basin reached modern eMed salinity values. Diffusive transport of salt from deeper layers to upper eastern basin layers will be balanced by salt transport to the wMed, and ultimately into the Atlantic Ocean via the Mediterranean outflow.

Sensitivity test Part 1: Basin evolution for a largely refilled Mediterranean (alternative hypothesis)

The nature of the MSC termination has long been debated. One hypothesis is a catastrophic termination (the main scenario of this paper) that resulted from Camarinal Sill collapse in the Strait of Gibraltar^{3,11,15,16}. This hypothesis considers a km-scale drawdown of water in Mediterranean sub-basins prior to the reconnection. An alternative hypothesis interprets an almost-filled Mediterranean during the final MSC stage (Lago Mare), which was connected to the Atlantic and/or Paratethys prior to the termination^{12,14,58}.

Here we present a sensitivity test to evaluate the validity of our hypothesis (a partially-desiccated Mediterranean leading to catastrophic termination), compared to a scenario where the basin is filled to the Sicily Sill before the termination. We argue that the sapropel presence immediately after the Miocene/Pliocene boundary in eMed cores (Supplementary Table 1) resulted from basin stratification after the Zanclean megaflood. In contrast, no wMed sapropels

were found following the M/P boundary. We suggest that absence of a wMed sapropel resulted from brine transfer to the eMed during an abrupt refilling event.

If the present-day Black and Caspian Seas were completely emptied into the Mediterranean, this would result in a ~250 m thick layer at the Mediterranean surface¹³. This gives a high-end estimate of Paratethyan inflow to the Mediterranean if the two basins were connected during the Lago Mare phase. It has been suggested that gypsum precipitation resulted from evaporated Paratethyan surface waters (above denser residual brines) at a salinity of ~40 PSU⁵⁸. Therefore, we simulate emptying of a volume equivalent to the present-day Black and Caspian Seas into the Mediterranean and allow it to evaporate to a salinity of 40 PSU. If the top of such a layer sits at the crest of the Sicily Sill (430 m), it will be about 130 m in thickness (calculated using a reconstructed Mediterranean hypsometry¹⁰), and will extend below the sill crest to a depth of 560 m.

Numerical modelling has shown that halite precipitation during the MSC peak (Stage 2, 5.59-5.55 Ma) resulted from complete disconnection from the Atlantic⁵⁹. Complete isolation will result in basin drawdown due to excess evaporation that will come to equilibrium within a few thousand years (3 to 8 kyr)^{9,10}. The idea of a km-scale drawdown is also supported by the existence of a basin-wide Messinian Erosional Surface (MES)⁵ and deep canyons excavated beneath the Nile delta and Rhône River mouth^{6,7}. Similar to our main scenario, we assume a wMed deep brine layer at gypsum saturation (140 PSU) below 1750 m, which formed as a result of MSC stage 2 drawdown. From 560 m to 1750 m, we allow salinity to increase linearly from 40 to 140 PSU, to obtain a conservative estimate (Extended Data Fig. 6a).

Starting with this basin configuration, we compute wMed basin evolution (Extended Data Fig. 6b) during a refilling event resulting from inflow through the Strait of Gibraltar using the Flooding Phase model. Here we re-calibrate the channel width coefficient (k_w) to allow the inflow channel to evolve up to the same dimensions as in our main scenario. We then compare the refilling and basin evolution in both scenarios (Extended Data Fig. 6c). Our findings suggest that for a filled Mediterranean up to the crest of the Sicily Sill, reconnection with the Atlantic results in a much longer episode of refilling. The total kinetic energy released during such a scenario will be >50 times smaller compared to a catastrophic termination, which is insufficient to erode the deeper brine in the wMed and would result in persistence of a density-stratified wMed (Extended Data Fig. 6b, c). In that case, we argue that a sapropel should be expected in the wMed after Atlantic reconnection. Absence of a wMed sapropel provides

strong support for catastrophic MSC termination and for a drawn-down Mediterranean prior to Atlantic reconnection. We also test this scenario for even lower salinity profiles between a thin surface layer and deep brines (from 560 m to 1750 m), to assess if the flood energy was sufficient to erode wMed deep brines, if the mid-layer salinity was lower (Extended Data Fig. 7a, b). This test run confirms that the energy is insufficient to remove wMed deep brines even for a 100% mixing efficiency.

Sensitivity test Part 2: Basin evolution at initial salinities < 140 PSU (Main scenario)

In order to test the validity of our hypothesis in case the residual Messinian fluid salinity was lower than 140 PSU, we computed the salinity evolution of the wMed and eMed using the same approach in the Flooding Phase used for the main scenario. We use a range of salinities from 60 to 120 PSU. Then we use the Evolving Phase to determine the duration of brine removal at different initial salinities (Extended Data Fig. 7c, d). At salinities lower than 140 PSU, all wMed salt is transferred to the eMed, resulting in a salinity approximated by:

$$S_{eMed} = \frac{(V_{eMed(Sicily)} - V_{b(eMed)} - V_{b(wMed)}) \times S_{Atl} + (V_{b(eMed)} + V_{b(wMed)}) \times S_b}{V_{eMed(Sicily)}} \quad (16)$$

where S_{eMed} is the final eMed salinity below the Sicily Sill, $V_{eMed(Sicily)}$ is the total eMed volume at the Sicily Sill, $V_{b(eMed)}$ and $V_{b(wMed)}$ are the residual Messinian volumes in eMed and wMed, and S_b is the initial Mediterranean fluid salinity. For a range of initial residual Messinian brine salinities from 60 to 120 PSU, we find that the salt removal period varies between ~14,000 to 22,000 years.

Sensitivity test Part 3: Basin evolution at initial salinities > 140 PSU (Main scenario)

In order to test the validity of the hypothesis in case the residual Messinian salinities were > 140 PSU, we compute the salinity evolution of the wMed and eMed using Flooding Phase calculations for 160-240 PSU. We employ the Evolving Mode approach to estimate salt removal duration for both basins, when excess salt remains at the end of the flooding phase. If wMed stratification was less than the resulting winter water density, convective overturn would mix surface and deep waters, removing the additional salt. In the present-day wMed, surface salinities reach 38.0-38.4 PSU in winter, with reduced temperatures of 10-12 °C^{ref.29}. We assume a constant brine temperature of 20 °C during the flooding phase. Therefore, we calculate the sea water salinity at 20 °C for an equivalent wMed winter surface water density. We use this as a limit in determining the brine removal period in the evolving phase (Extended Data Fig. 8). Results of the sensitivity test indicate that all wMed salt would transfer to the

eMed up to initial brine salinities of 170 PSU. From 170 to 200 PSU, final mixed wMed waters have a higher-than-winter water density. Above 220 PSU, residual Messinian brines remain in the deep wMed, implying that flood energy was insufficient to erode the deep brines. Above 170 PSU initial salinity, we find that it would take about 4,000 to 12,000 years to remove wMed salt by diffusion. Combining the information from Sensitivity Test Parts 2 and 3, we conclude that our model results agree reasonably with the data for starting salinities across the 60-170 PSU range.

Sensitivity test Part 4: Basin evolution with the change of Sicily sill depth

To test the effect of Sicily sill depth on basin evolution during the flooding mode, we modified our model for shallower and deeper than present Sicily sill depth. For this, we employed ~0.7 and ~1.3 times the present sill depth (300 m and 560 m, respectively). We find that the flooding mode length reduces/increases when the Sicily sill depth is shallower/deeper than present. We find that independent of the sill depth, a majority of the wMed Messinian salt is transferred to the eMed across the sill (Extended Data Fig. 9). Our model suggests that as the sill gets shallower, there is slightly more salt remaining in the wMed, compared to the deeper sill setting. Detailed palaeomagnetic studies have shown that the Sicily sill may have been uplifted to its present depth during central to eMed wide middle-late Pliocene tectonic events^{24,60}. Modelling experiments have also suggested a deeper Sicily sill during the Messinian^{9,10,14}. Our model results would agree with these observations, as more wMed salt would be transferred to the eMed for a deeper sill.

Sensitivity test Part 5: Effect of the initial base level on basin evolution

We have assumed initial base levels for the wMed (1,750 m below Atlantic level) and the eMed (2,000 m) for our main scenario, based on available references. In sensitivity test part 1 (alternative scenario), we tested basin evolution when the Mediterranean is filled up to the Sicily sill. To test the effect of intermediate base levels, and to define a minimum base level which validates the hypothesis, we computed basin evolution by stepwise increasing the base level in 100 m increments in both basins. For each step of base level increase above the main scenario base levels, we filled both wMed and eMed with lower salinity waters following the steps of sensitivity test part 1. From 1,750 m up to 1,450 m base level in the wMed (2,000 to 1,700 m in the eMed), all the residual Messinian salt is transferred from wMed to the eMed. When the base level is increased above this point, excess salt tends to remain in the wMed. We have shown test results up to 1,250 m wMed base level; corresponding to a 1,500 m eMed base

level (Extended Data Fig. 10). A period of 2,500 to 4,500 years is required to remove the excess salt by diffusion when the wMed level is above 1,450 m.

Data availability

ODP Site 967 data from this study are available from Panagea (www.pangaea.de) under ‘Scanning XRF and environmental magnetic data across the Miocene-Pliocene boundary from ODP Site 967 (Eastern Mediterranean)’ and are also available as online Supplementary Data accompanying this article.

Code availability

All the figures in this manuscript are reproducible via Jupyter notebooks and instructions provided in the Github repository Med_evolution_megaflowd⁶¹ (<https://doi.org/10.5281/zenodo.6528768>).

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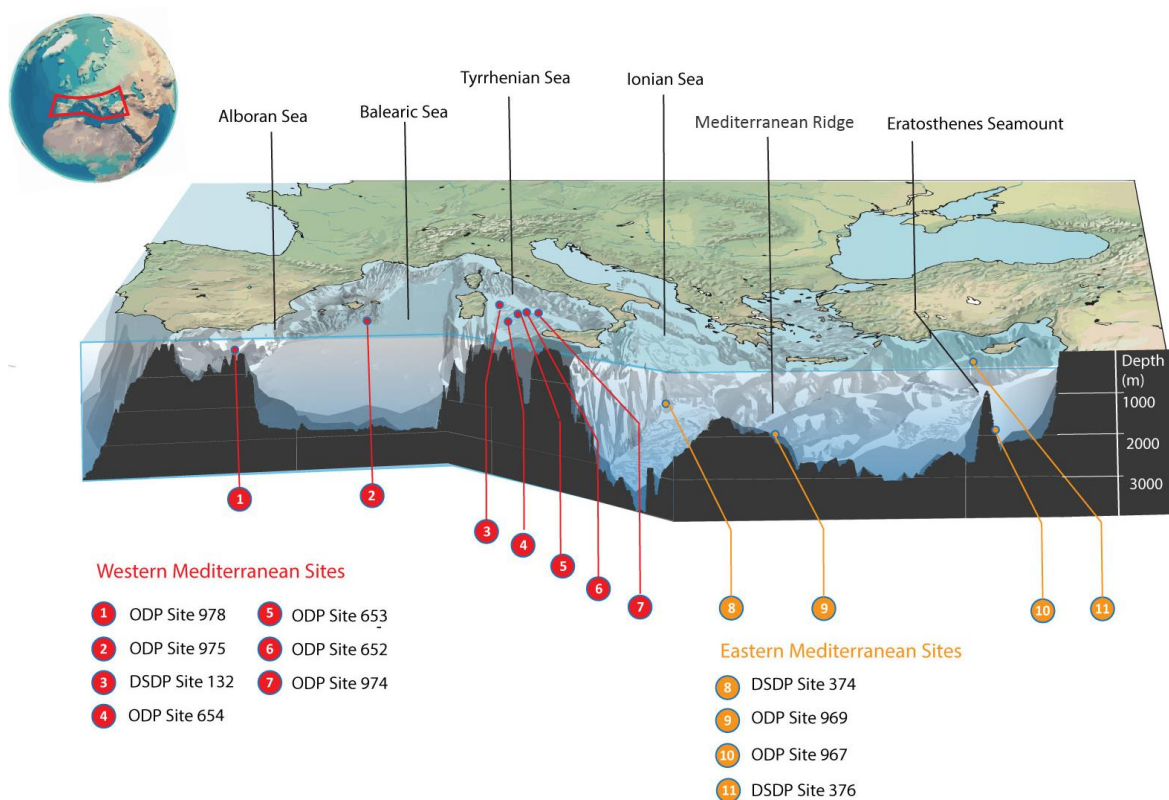
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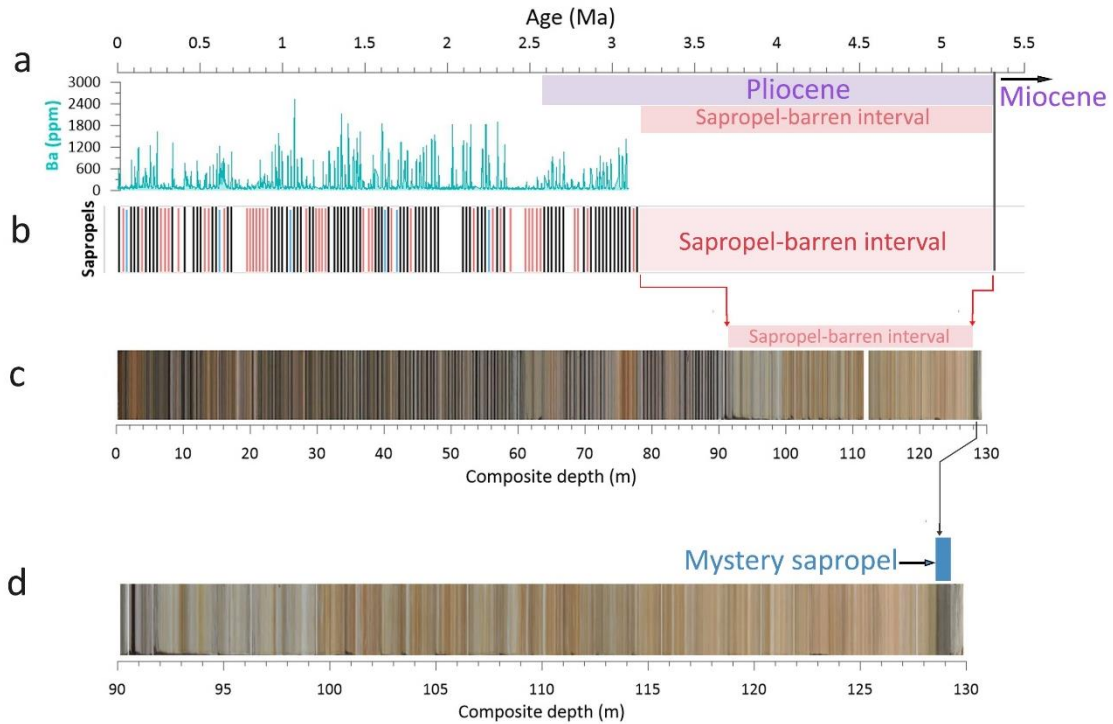
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Additional information

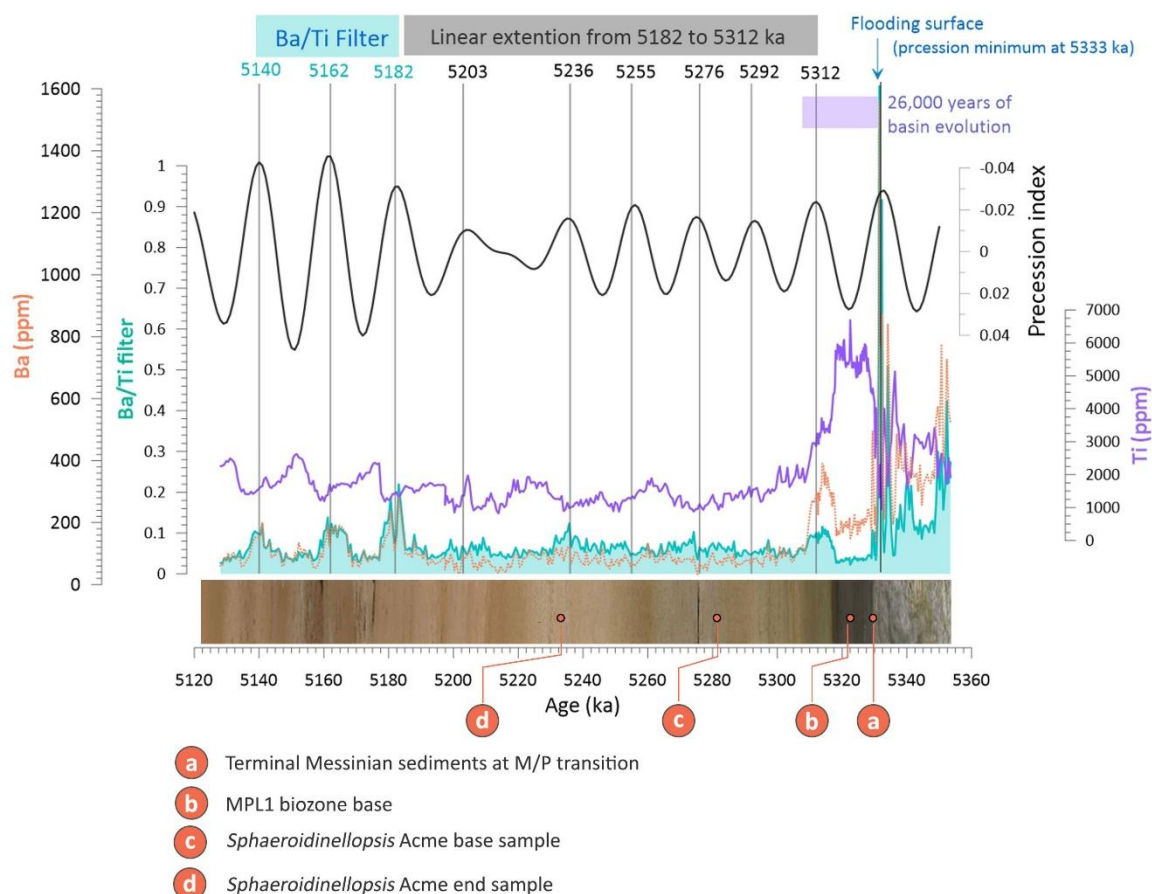
Supplementary information is available for this manuscript



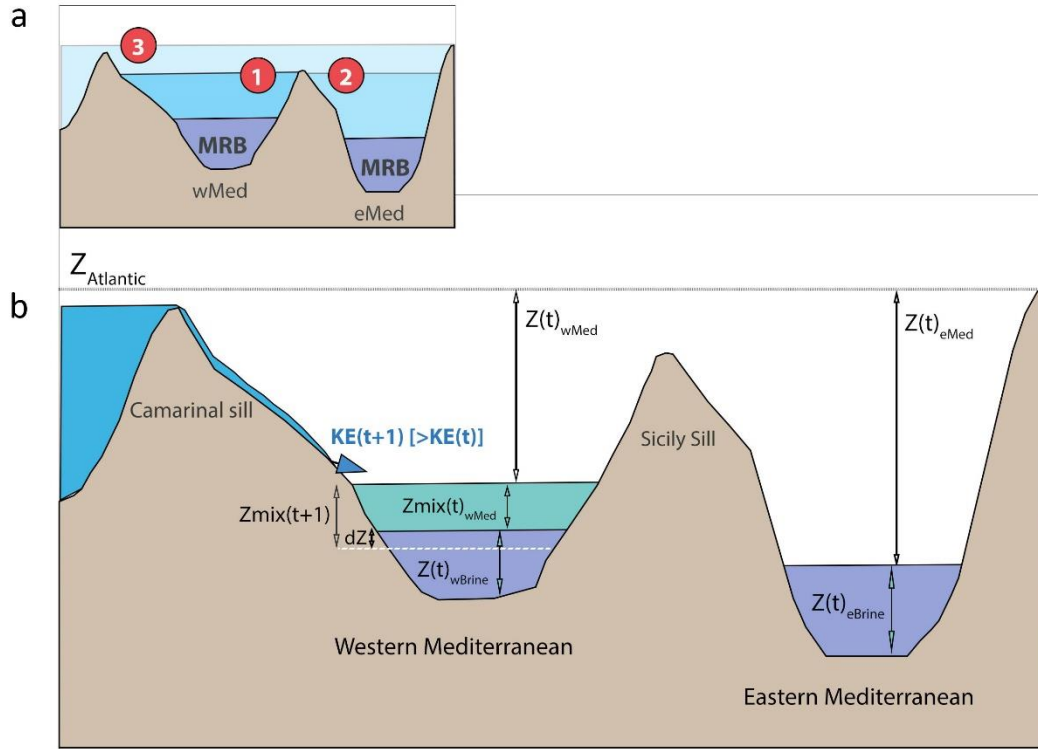
Extended Data Fig. 1 | Locations of DSDP and ODP sites with complete records across the Miocene-Pliocene transition. Illustration of the Mediterranean basin with locations of ODP and DSDP sites where complete records across the Miocene/Pliocene boundary have been retrieved (see Supplementary Table 1). XRF core scanning data for this study were obtained from ODP Site 967 (Eratosthenes Seamount northern flanks). The cross-section was drawn using Ocean Data View 5.3.0.



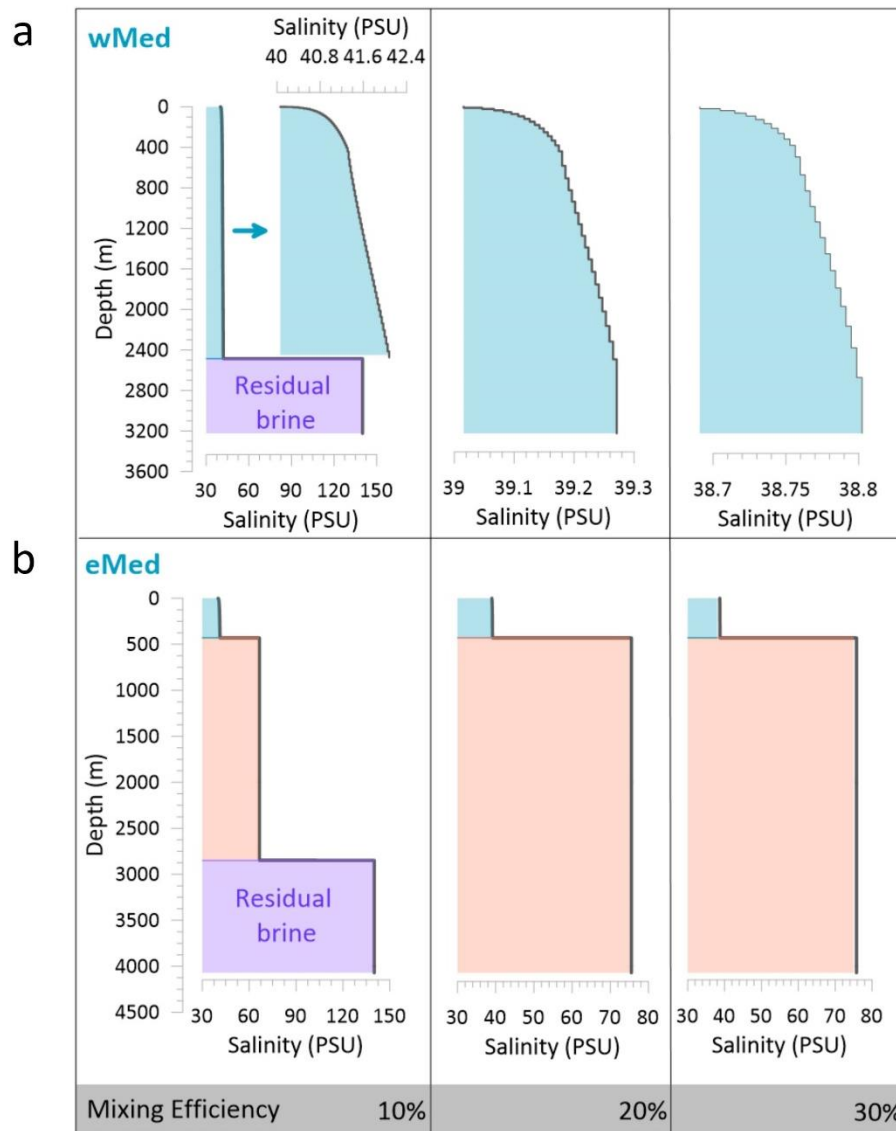
Extended Data Fig. 2 | Sapropel record for ODP Site 967. a, Ba record for ODP967 from scanning XRF data for the last 3 million years⁶². b, Sapropel stratigraphy for ODP Site 967. From 5.3 to 3.2 Ma²³, sediments are barren of sapropels (black = sapropels, red = red intervals, blue = ghost sapropels). c, Stack of core images for ODP967 arranged according to composite depth, with sapropel occurrence. Sapropel-barren interval is indicated by the section shaded in pink. d, Enlarged view of the sapropel-barren interval. Location of the ‘mystery sapropel’ is indicated by blue shading.



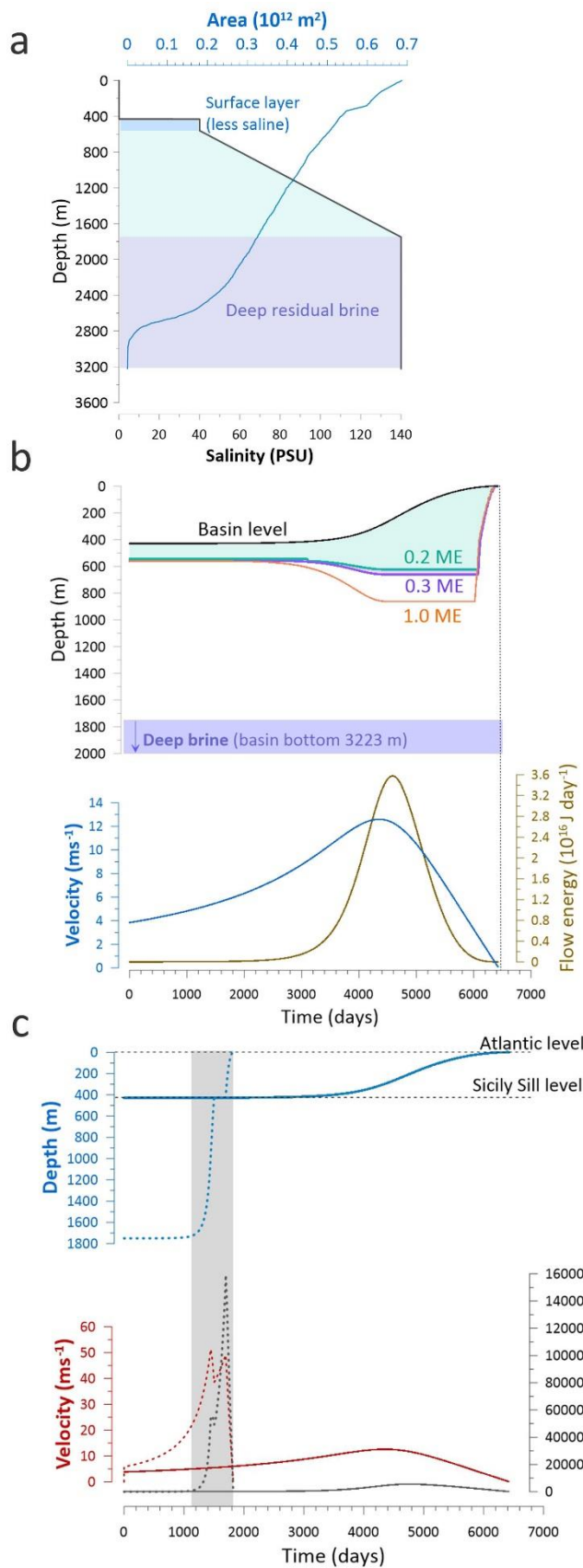
Extended Data Fig. 3 | Chronology. Three peaks in the Ba/Ti record were tuned to insolation maxima (precession minima, June 21, 65°N)⁶³ between 5140 and 5182 ka. Below this (splice depth 125.03–127.23 m), clear Ba/Ti peaks are absent, so ages were interpolated linearly assuming a sedimentation rate equivalent to that for 5162–5182 ka. This assumption is validated by the resulting insolation maximum alignment at 5312 ka (splice depth 127.23 m) with the next Ba/Ti peak. The succeeding Ba peak (at splice depth 128.35 m) is the largest, so the maximum of the smoothed curve was tuned to 5333 ka based on the timing of the Mediterranean reflooding event³. Available ODP 967 biostratigraphic datums²² (a, b, c, d) validate our chronology (see Supplementary Table 2 for details).



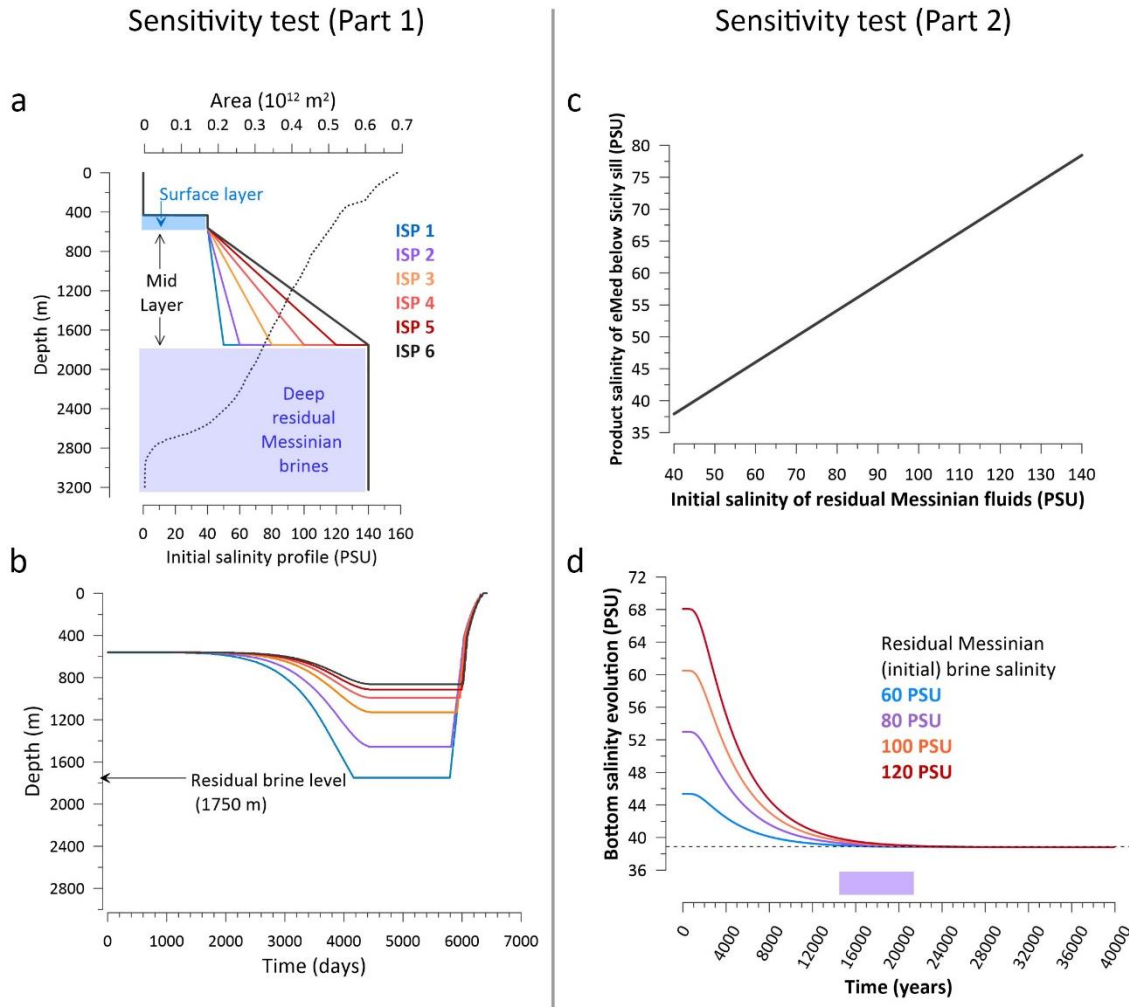
Extended Data Fig. 4 | Conceptual model for Mediterranean refilling. a, Sketch of main Zanclean flooding stages (ZFS). ZFS 1 ends as the wMed level reaches the Sicily Sill. ZFS 2 ends as the eMed level reaches Sicily Sill. In ZFS 3, both basins rise to the Atlantic level concurrently. MRB, Messinian Residual Brines; wMed, Western Mediterranean; eMed, Eastern Mediterranean. b, Sketch of basin evolution during the flooding phase. As flood waters flow into the basin, mixing with residual brines (purple) occurs. The mixing extent depends on the kinetic energy of flow entering the brine surface. For increased kinetic energy, a dz depth of brines will be added to the mixed layer (green). The mixed layer thickness increases accordingly. $KE(t+1)$, kinetic energy of flow entering the brine; $KE(t)$, kinetic energy of flow in the previous timestep; $Z(t)_{wMed}$, wMed level at a given time; $Z(t)_{eMed}$, eMed level at a given time; $Z_{mix}(t)_{wMed}$, wMed mixed layer extent at a given time; $Z(t)_{wBrine}$, wMed brine thickness at a given time; $Z(t)_{eBrine}$, eMed brine thickness at a given time; and $Z_{Atlantic}$, Atlantic level.



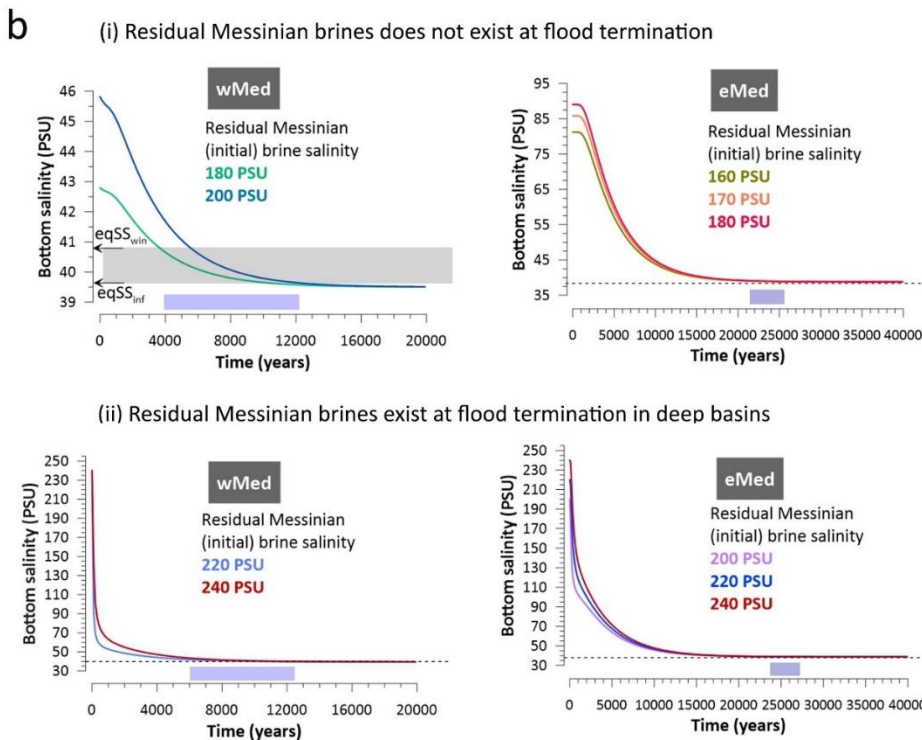
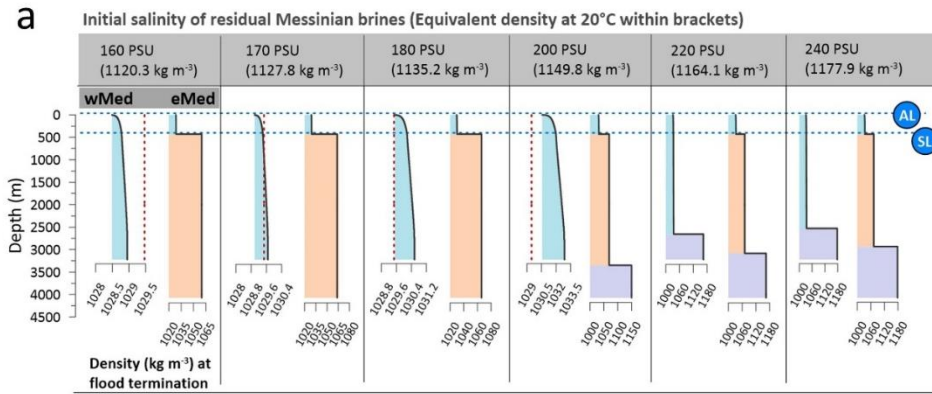
Extended Data Fig. 5 | Salinity profiles for wMed and eMed at the end of the Flooding Phase for different ME values. For our main model, we use $ME = 20\%$ (0.2), which is the widely accepted value for shear-driven mixing in stratified fluids^{55,56}. Here we test the effect of ME change on basin evolution, for the 10–30 % ME range. a, Salinity profiles (wMed) at the end of the Flooding Phase for different ME values. At 10% ME, a ~700-m-thick residual brine layer remains in the bottom of the wMed. The salinity profile above the pycnocline is enlarged in this case. For 20% and 30% ME, the wMed does not contain residual brine. b, Salinity profiles (eMed) at the end of the Flooding Phase for different ME values. For each ME value, strong stratification occurs at the Sicily Sill level, where dense fluids lie toward the bottom (salinity profile colours: blue-green = wMed mixed layer; orange = eMed mixed layer; purple = residual Messinian brines; during the final flood stage, mixing occurs only in the wMed, from which mixed waters overflow toward the eMed above Sicily Sill – indicated by an upper blue-green eMed layer).



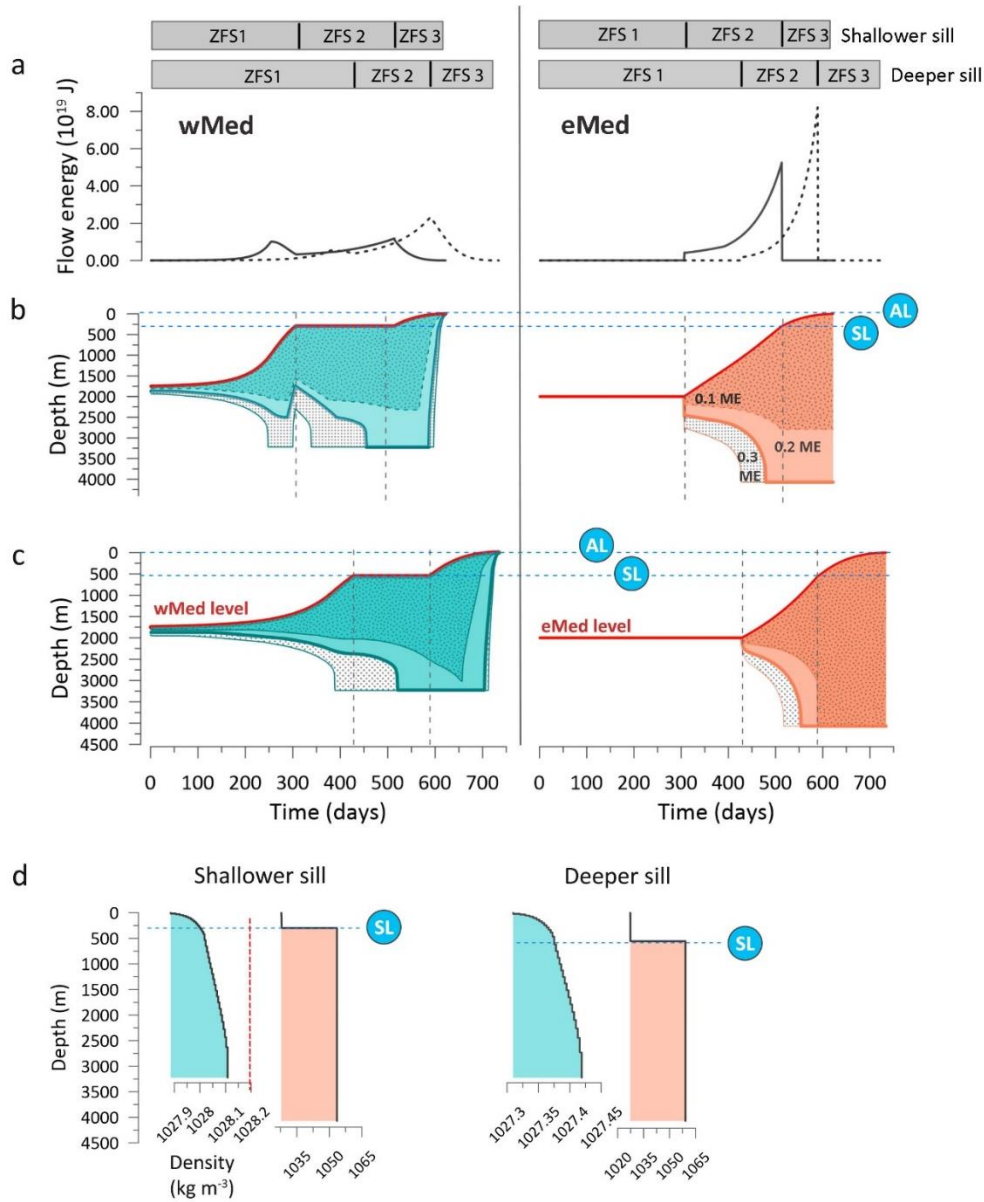
Extended Data Fig. 6 | Summary of sensitivity test (Part 1) results. a, wMed salinity profile (black) where the basin is filled to the Sicily Sill level. The thin surface layer is composed of evaporated Paratethyan waters. Blue line is wMed hypsometry. b, Evolution of the wMed level (black), mixing depth at different mixing efficiencies (0.2, 0.3 and 1 ME), velocity and flow kinetic energy with time, for the basin configuration in a. Even at 100% mixing efficiency (1 ME), flow energy fails to erode the deep brine layer. c, Comparison of refilling abruptness between a scenario where the basin is filled to the Sicily Sill level (thick lines), and a deeply desiccated basin before the catastrophic termination (dotted lines). The length of the flooding mode increases to 6400 days for a filled basin, while discharge and flow velocity are much less compared to a catastrophic termination. The shaded section demarcates the interval (dotted lines) used to compute basin evolution in the main text.



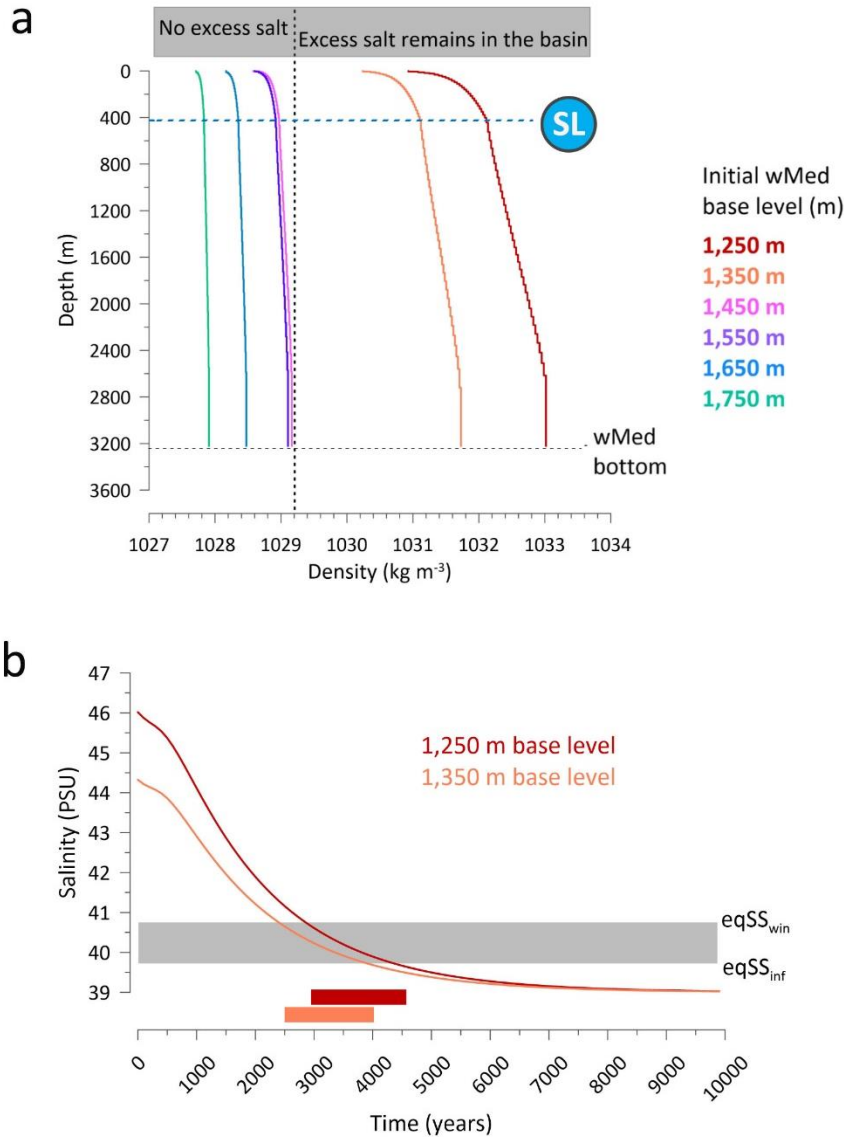
Extended Data Fig. 7 | Sensitivity test Part 1 and Part 2 results. (a,b; Sensitivity test Part 1 - Testing for different initial salinity profiles) a, Initial wMed salinity profiles used for the test; surface layer (430–560 m) and residual brine layer (below 1750 m) salinities were kept unchanged at 40 and 140 PSU, respectively. Mid-layer salinity was changed, as shown in the Figure (ISP 1 to ISP 6, ISP; initial salinity profile). For the mid-layer, salinity was increased linearly from 40 PSU at 560 m, to 50 PSU (ISP 1), 60 PSU (ISP 2), 80 PSU (ISP 3), 100 PSU (ISP 4), and 120 PSU (ISP 5), at the deep brine surface (1750 m). ISP 6 is the same as used in Extended Data Fig. 6. The black dotted line is wMed hypsometry. b, Evolution of the mixing depth at 100% mixing efficiency for different starting salinity profiles in a. For ISP 1, mixing depth reaches the brine surface, but the flood energy is insufficient to erode the brine layer. Maximum mixing depth does not extend below 1500 m for any other starting salinity profile, implying that the flood energy is insufficient to reach deep wMed brines below 1750 m. The same colours for ISPs are used for mixing depth evolution lines. The black dotted line indicates the wMed level rise as Atlantic waters fill the Mediterranean. (c,d; Sensitivity test Part 2) c, Approximation of the final eMed salinity below the Sicily Sill at the end of basin refilling (Zanclean flooding), as a function of initial Mediterranean residual fluid salinity. Residual fluid salinity in wMed and eMed are considered equal. Below 140 PSU, all wMed salt will be transferred to the eMed. d, eMed evolving phase when initial residual fluid salinity is set below 140 PSU (140 PSU was used for the main text model calculations - see Methods for reasoning). Duration of salt removal is tested at initial salinities of 60, 80, 100, and 120 PSU. The dotted line represents the maximum eMed surface salinity. The purple box above the time axis represents the expected salt removal duration for salinities between 60 and 120 PSU.



Extended Data Fig. 8 | Summary of sensitivity test (Part 3) results. a, Post-flood density profiles for the wMed and eMed for initial salinities > 140 PSU. Salinities between 160 and 240 PSU were chosen. The vertical dotted line (red) represents the winter density of wMed surface waters. Up to 170 PSU, the post-flood wMed density profile has lower than winter density values. This will result in rapid convective mixing and removal of remaining wMed salt. Above 180 PSU, greater than winter surface densities appear in the wMed. Above 220 PSU, flood energy is no longer sufficient to transfer deep wMed salt to the eMed. Strong eMed stratification is present in all cases (profile shading: blue-green, wMed mixed layer; orange, eMed mixed layer; purple, residual Messinian brines; AL, Atlantic level; SL, Sicily Sill level). b, Duration of wMed and eMed salt removal, where stratification exists. The Figure is separated into two parts due to the wide salinity range. For the wMed, model outputs indicate salt removal durations of ~4,000 years at an initial 180 PSU salinity, which can increase up to 12,000 years at 240 PSU. For the eMed, a range between ~21,500 to 27,500 years is expected between 160 and 240 PSU. The purple box above the time axis represents the expected salt removal duration (eqSS_{win}, equal surface salinity of winter surface water; eqSS_{inf}, equal salinity of inflow water – see Methods for explanation).



Extended Data Fig. 9 | Summary of sensitivity test (Part 4) results. a, Flow energy in the wMed and the eMed for a ~30% shallower (300 m) or deeper (560 m) than present Sicily sill. Thick and dotted lines correspond to energy evolution for shallow and deep sill depths, respectively. b, Sea-level and mixing depth evolution for the wMed and the eMed when the Sicily sill is shallower than present (300 m). c, Sea-level and mixing depth evolution for the wMed and the eMed when the Sicily sill is deeper than present (560 m). In b and c, red curves in each panel represent the rise of basin level. Green (for wMed) and orange (for eMed) curves indicate the mixing depth evolution with time, for different mixing efficiencies (ME). Dots in coloured background, 0.1 ME; coloured-only background, 0.2 ME; Dots in white background, 0.3 ME. For a, b and c, refer to the grey colour panels at the top of the figure for Zanclean flooding stages (ZFS 1–3) for shallower and deeper sill settings. d, Density profiles at the end of the flooding phase for shallow and deep sill settings. Vertical red-dotted line represents the present wMed surface density (Mediterranean Atlantic water density in the wMed²⁹). Green shading, wMed mixed layer; orange shading, eMed mixed layer; AL, Atlantic level; SL, Sicily sill level.



Extended Data Fig. 10 | Summary of sensitivity test (Part 5) results. a, Density profiles for the wMed at the flooding phase termination, for different starting base levels of the wMed and the eMed (eMed base level is 250 m lower than the mentioned wMed base level for each test). Vertical dotted line represents the winter wMed surface density. Beyond this line, excess salt remains in the wMed as a result of incomplete salt transfer to the eMed. b, Duration of post-flood salt diffusion for starting base levels which results in excess salt in the wMed (1,250 and 1,350 m wMed base levels below Atlantic level; correspond to 1,500 and 1,600 eMed levels, respectively). Coloured panels above the time axis represent the expected duration of salt removal from wMed to the Atlantic, for corresponding curves with same colour (eqSS_{win}, equal surface salinity of winter surface water; eqSS_{inf}, equal salinity of inflow water – see Methods for explanation). SL; Sicily sill level.

CHAPTER 3

Organic carbon burial in Mediterranean sapropels intensified during Green Sahara Periods since 3.2 Myr ago

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As revealed by ODP Site 967 sediment record, organic carbon burial in Mediterranean sapropels abruptly intensified at ~3.2 Myr, indicating another major oceanographic transformation of the Mediterranean basin. This chapter investigates the nature of 3.2 Myr transformation, using a multi-proxy reconstruction. It provides the first ever compilation of X-ray fluorescence, stable oxygen isotope and environmental magnetic records for a single eastern Mediterranean drilling site, that span past 5.2 Myr period.

Statement of Contribution

This thesis is submitted as a Thesis by Compilation in accordance with https://policies.anu.edu.au/ppl/document/ANUP_003405

I declare that the research presented in this Thesis represents original work that I carried out during my candidature at the Australian National University, except for contributions to multi-author papers incorporated in the Thesis where my contributions are specified in this Statement of Contribution.

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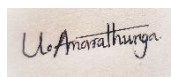
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Contribution to paper: I contributed to oxygen isotope and environmental magnetic data generation, and for the development of hypotheses (mainly on including the tectonic influence on Mediterranean ventilation)

K.M.G. designed and led the study and write-up; K.M.G., U.A., J.D.A., T.P., Y.Q. and L.R.-S. generated $\delta^{18}\text{O}$ and magnetism data; D.H., P.H. and X.Z. assisted with magnetism measurements; D.L. performed XRF core-scanning; D.L. and T.W. developed the ODP967 composite depth splice and chronology; K.M.G. and R.H. calibrated scanning XRF data; K.M.G. and S.G. performed WD-XRF analyses; L.J.L. contributed WD-XRF data; E.J.R., A.P.R. and all the above co-authors contributed to manuscript development.

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Organic carbon burial in Mediterranean sapropels intensified during Green Sahara Periods since 3.2 Myr ago

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Abstract

Dark organic-rich layers (sapropels) have accumulated in Mediterranean sediments since the Miocene due to deep-sea dysoxia and enhanced carbon burial at times of intensified North African run-off during Green Sahara Periods (GSPs). The existence of orbital precession-dominated Saharan aridity/humidity cycles is well known, but lack of long-term, high-resolution records hinders understanding of their relationship with environmental evolution. Here we present continuous, high-resolution geochemical and environmental magnetic records for the Eastern Mediterranean spanning the past 5.2 million years, which reveal that organic burial intensified 3.2 Myr ago. We deduce that fluvial terrigenous sediment inputs during GSPs doubled abruptly at this time, whereas monsoon run-off intensity remained relatively constant. We hypothesize that increased sediment mobilization resulted from an abrupt non-linear North African landscape response associated with a major increase in arid:humid contrasts between GSPs and intervening dry periods. The timing strongly suggests a link to the onset of intensified northern hemisphere glaciation.

Introduction

‘Green Sahara Periods’ (GSPs) have been a fundamental characteristic of North African climate change for more than 8 Ma^{ref.1}. Only the most recent GSP during the early-mid Holocene (~11 to 6 thousand years ago, ka; the ‘African Humid Period’) has been studied in detail at numerous locations²⁻⁴, and it extended to East Africa⁵⁻⁷. However, there are few continuous, well-dated GSP records that extend beyond 1.5 Ma (or even beyond the last 300 ka), and no high-resolution North African humidity reconstructions encompass the entire Plio-Pleistocene. Mediterranean sediments contain a particularly rich archive of past GSPs. Here, organic-rich layers (‘sapropels’) form in response to deep-sea anoxia and nutrient inputs when significantly increased run-off enters the basin via the Nile and wider North African margin⁸. These periods correspond to enhanced boreal summer insolation maxima and minima in Earth’s orbital precession cycle, resulting in a more northerly and intensified African rainbelt^{8,9}. Sapropels are a natural testbed for understanding deep-sea redox and carbon burial processes; however, their formation mechanisms are still debated⁸, and there is currently no continuous high-resolution proxy record of Plio-Pleistocene sapropels.

Ba/Al, Ti/Al, and planktic $\delta^{18}\text{O}$ in Eastern Mediterranean sediments are useful proxies of past GSPs and sapropels. Ba/Al reliably tracks sapropel intervals because it correlates with original organic carbon burial (C_{org}) in sapropels and is mostly unaffected by post-depositional redox reactions¹⁰, while surface water freshening due to monsoon run-off is recorded by strong negative $\delta^{18}\text{O}$ peaks^{11,12}. Ti/Al in the open Eastern Mediterranean reflects relative variations in North African aeolian vs riverine inputs to the basin¹³. Aeolian-sourced Ti/Al in the open Eastern Mediterranean is enhanced relative to fluvially-sourced Ti/Al because heavier (Ti-bearing) suspended particles preferentially settle near the Nile fan. Al normalization (for Ti and Ba) also removes closed-sum effects.

Here, we address the dual need for high-resolution records of North African humidity/aridity changes and sapropel deposition through the entire Plio-Pleistocene, by presenting the first continuous, astronomically dated GSP and sapropel proxy records back to 5.2 Ma from Eastern Mediterranean Ocean Drilling Program (ODP) Site 967 (Figures 1-2; Supplementary Figure S1). From the same site, we also present high-resolution records of Saharan dust and riverine inputs over the past 5.2 Ma. Our data reveal a fundamental change in sapropel development, provide much-needed climatic context for understanding hominin evolution and migrations out

of Africa, and are essential for modelling the mid-Pliocene—the most recent interval with CO₂ levels approximating modern levels¹⁴.

Results and Discussion

Green Sahara Periods. Ti/Al, Ba/Al, and planktic $\delta^{18}\text{O}$ record GSP timings over the Plio-Pleistocene (Fig. 3). The Ba/Al signal is consistent with a typical sapropel sequence^{10,15}, and lower Ti/Al values correspond to Ba/Al spikes, $\delta^{18}\text{O}$ minima, and precession minima. The $\delta^{18}\text{O}$ record reflects long-term global sea level/ice volume changes¹⁶, with superimposed negative $\delta^{18}\text{O}$ excursions that relate to African run-off into the Eastern Mediterranean and warming within fresher surface-water layers^{12,17,18}. African run-off reaching ODP967 would have derived primarily from the Nile^{18,19}, which is fed by East African precipitation influenced by both the Indian and African Monsoons and their moisture convergence at the Congo Air Boundary²⁰. African run-off also entered the Eastern Mediterranean from the wider North African margin when the African rainbelt migrated northward^{18,21,22}. This rainbelt is associated with the intertropical convergence zone (ITCZ), the West African monsoon, and East African precipitation^{20,23}. Thus, ODP967 $\delta^{18}\text{O}$ reflects both West and East African precipitation. While changes in local Eastern Mediterranean precipitation over the entire Plio-Pleistocene are not well-constrained, their impacts on ODP967 $\delta^{18}\text{O}$ are likely to be minimal compared to African run-off because Eastern Mediterranean surface waters are the evaporative source for local precipitation (with little excess $\delta^{18}\text{O}$ fractionation)^{8,12}. The similar range of $\delta^{18}\text{O}$ minima at precession minima throughout the record (-1 to -2 ‰ but reaching -3 ‰, Fig. 3; note by convention reversed $\delta^{18}\text{O}$ axis) suggests that maximum African (monsoon) run-off into the Eastern Mediterranean reached roughly similar intensities throughout the Plio-Pleistocene. Furthermore, the ODP967 Ba/Al, Ti/Al, and $\delta^{18}\text{O}$ records all attest to continuity of run-off maxima and ‘sapropel-like’ Pliocene C_{org} fluxes.

The longest continuous (albeit lower-resolution) time-series of Saharan/North African hydroclimate changes extend back to ~4-4.5 Ma and are based on terrigenous (= non-biogenic) sediment fluxes offshore of Northwest Africa and Arabia^{24,25}, where terrigenous components are primarily sourced from aeolian dust²⁵. At ODP967, an isothermal remanent magnetization (IRM) proxy for hematite (IRM_{900@120mT}; see Methods) reflects Saharan dust inputs to this site²⁶. IRM_{900@120mT} values remain relatively low until ~1.4 Ma, with notable increases at 1.2 and 0.9 Ma, coincident with the Mid-Pleistocene transition (MPT) (Fig. 4e). Increased dust fluxes at the MPT are also observed in a lower resolution ODP967 IRM record extending back

to 3 Ma^{ref.26,27}, and in dust records from ODP sites 664 (Fig. 4h) and 721/722 (Arabian Sea)²⁷. There are also discrepancies among these records, and among terrigenous (dust) records from other ODP sites off Northwest Africa^{25,27} (Fig. 1). For example, sites more proximal to the Sahara (e.g. ODP659) have high-amplitude dust fluxes throughout the Plio-Pleistocene²⁵, whereas more distal sites (e.g., ODP662/3 and 664) record higher-amplitude dust fluxes from ~3 Ma and 2.7 Ma (Fig. 4g, h). At ODP Site 959, Ti/Al values suggest increasing aeolian dust inputs from ~3.5 Ma, with potentially a slight increase at 3.2 Ma (Fig. 4i), although this might partly reflect Guinea Current changes²⁸. Lower dust inputs tend to coincide with GSPs, but not consistently (Supplementary Figure S3); instead, they likely relate to distance from dust source areas and prevailing dust trajectories^{25,27}, i.e., factors other than humidity/aridity changes.

The Plio-Pleistocene sapropel record. Intriguingly, there are no visibly preserved sapropels in most of the Pliocene portion of ODP967^{ref.29} (Fig. 2) □ visible sapropels appear from 3.2 Ma onward. However, not all Eastern Mediterranean ODP sites record the same lithological change at 3.2 Ma (Table 1): Sites 964 and 967 lack visible sapropels before this time, while Sites 966 and 969 contain a visible sapropel sequence down to the core base at 4.5 and 5.3 Ma, respectively²⁹. Western Mediterranean sapropels are mostly limited to the last 1.8 Ma and are, therefore, not considered here (Supplementary Table S1). The difference among Eastern Mediterranean sites remains unexplained. It is unlikely to relate to Pliocene sedimentation rates, which are similar among the four sites (Supplementary Figure S4), but may relate to water depth, because Pliocene sapropels are absent from the deepest sites²⁹. Spatial offsets in the timing, duration, and intensity of sapropel formation are expected^{8,30}, but such a dramatic contrast in Pliocene sapropel preservation among Eastern Mediterranean sites implies basin-wide changes in the balance of deep-water oxygen supply (ventilation) vs demand (C_{org} remineralization and, likely, export).

The ODP967 sapropel-sequence change coincides with a shift to larger amplitude Ba/Al and Ti/Al fluctuations (Fig. 4b-d), a two-to-threefold increase in terrigenous element concentrations (Supplementary Figure S5), and a shift in the mean and variance of Ti/Al based on change-point analysis (Fig. 4c). Change-points at ca 4.4 Ma and ca 1.9-1.2 Ma are fewer/more time-diffuse and do not coincide with major lithological (sapropel) changes, hence we do not focus on these changes. At ODP967, element fluxes reflect sediment density changes associated with sapropel lithology (Supplementary Figure S7); hence, relative variations in terrigenous vs biogenic element concentrations more accurately indicate terrigenous inputs. Run-off and terrigenous sediment inputs to the Levantine Basin are dominantly sourced from

North Africa^{19,22,31}, and elevated terrigenous element concentrations at ODP967 tend to be associated with insolation maxima, although not consistently (Supplementary Figure S6). Plio-Pleistocene Northern Mediterranean sediment sources to ODP967 are unconstrained and, hence, cannot be excluded, but are likely less significant than African sources^{19,22}. The 3.2 Ma geochemical shift and sapropel deposition/preservation change, thus, imply a major increase in monsoon run-off and/or suspended load, or a fundamental reorganization of Eastern Mediterranean deep-water circulation and sedimentation. We formulate four testable hypotheses (Table 2) that invoke: a) a marked change in North African climate/landscape (Hypotheses 1-2; $H_{1,2}$); and b) Sicily Sill uplift ($H_{3,4}$). We now consider our results in the context of these scenarios.

African climate/environment shift at 3.2 Ma. Considering H_1 (see Table 2), a marked freshwater run-off increase into the Eastern Mediterranean would be registered in ODP967 $\delta^{18}\text{O}$, irrespective of the freshwater source. However, ODP967 $\delta^{18}\text{O}$ reaches similar minima throughout the last 4.5 Ma (Fig. 3). H_1 also implies a shift to more rainfall after 3.2 Ma, which is inconsistent with pollen data³² (Fig. 4f) and modelling results³³⁻³⁵ that indicate a generally greener Pliocene Sahara (i.e., forests and wetlands). Leaf wax $\delta^{13}\text{C}_{31}$ at ODP Site 659 (Fig. 1) is generally more negative in the Pliocene compared with the last glacial cycle, which is consistent with elevated Pliocene North African humidity³⁶. Similarly, high-resolution pollen and tree index records from the Baringo Basin reveal a marked shift to drier conditions at 3.2 Ma^{ref.37} (Fig. 4j), which is consistent with leaf wax isotope data from DSDP Site 231 in the Gulf of Aden³⁸ (Fig. 4k). Leaf wax isotope records (δD , $\delta^{13}\text{C}$) in that study were interpreted in combination with other regional palaeoclimate records and suggest two main shifts to drier conditions: at 5-4.5 and 3.3-3.0 Ma. Hence, available evidence causes us to reject H_1 .

H_2 implies a more erodible North African landscape from ~3.2 Ma onward, which in turn suggests more arid or variable climate conditions, or the emergence of new—possibly seasonal—drainage pathways. Equally, a reduction in soil-stabilizing vegetation would facilitate sediment erosion through existing channels. Pollen records support a shift to increased aridity and climate variability after 3.2 Ma (see above), while dust records are more equivocal: only two ODP sites (662/3 and 664) record a shift to higher amplitude dust inputs at around 3 Ma (Fig. 4g, h). However, aeolian dust records can reflect other factors (e.g., wind patterns, distance to dust source), which could explain some offsets (Sites 662/3 and 664 are more distal from the Sahara than Site 659). Furthermore, if the amplitude increase in ODP967 Ti/Al variations (aeolian vs riverine proxy) at 3.2 Ma is African-climate driven, then the lack of a

coeval shift in ODP967 IRM_{900@120mT} (aeolian proxy) implies that the Ti/Al change primarily reflects a change in riverine rather than aeolian components. At ODP967, this component is sourced primarily from the Nile^{18,19}. While the Sahara has likely existed since the Miocene³⁹, the Nile evolved through the Plio-Pleistocene⁴⁰⁻⁴². The timings of its various development stages are not well constrained, but a recent synthesis⁴¹ proposes a Late Pliocene/early Pleistocene connection of the Blue Nile/Atbara-Tekeze rivers to the palaeo-Nile, and emergence of the modern Egyptian Nile flood plain and delta (the White Nile joined the main channel within the last 0.5 Ma^{ref.41}). Nile evolution could, therefore, account for a major mid/late Pliocene shift in drainage pathways and suspended sediment.

It is implicit to H_2 (and inferred from our ODP967 $\delta^{18}\text{O}$ record) that freshwater run-off fluxes during GSPs must have been decoupled from long-term changes in suspended sediment loads. Several lines of evidence suggest that this is plausible. First, factors determining river sediment loads over geological time reflect a complex interplay of tectonics (e.g., rock type, relief) and climate (e.g., precipitation, run-off). Peak suspended load does not always correspond to peak run-off, unlike typical annual cycles, so landscape changes driven by tectonic (and climate) evolution can result in more erodible surfaces, and thus increased sediment loads, without an attendant change in local rainfall⁴³. Second, ecological modelling and data suggest that African biomes are highly sensitive to small reductions in precipitation⁴⁴. Major biome changes in tropical Africa have been simulated without a total annual precipitation change, simply by altering rainfall seasonality⁴⁵. Moreover, inclusion of soil feedbacks in GSP simulations can reproduce pollen-inferred vegetation shifts at around 400 mm/yr mean precipitation, relative to ~600 mm/yr in the absence of soil feedbacks⁴⁶.

We also cannot ignore potential effects of large-scale global changes on African climate/landscape at ca 3.2 Ma. The first major Northern Hemisphere glaciation (based on global benthic $\delta^{18}\text{O}$) is in stages M2–MG2 at 3.295–3.340 Ma^{ref.47} (Fig. 2 and 4n), although the onset was spatially variable and as early as 3.6 Ma^{ref.48}. However, the average time-dependent standard deviation of benthic $\delta^{18}\text{O}$ from 25 high-resolution records starts to increase at 3.2 Ma^{ref.48}. Stronger high-latitude cooling and intra- and inter-hemispheric SST gradients are observed from ~3.3 Ma^{ref.49,50}, coeval with a tenfold IRD (ice-rafted debris) flux increase off East Antarctica⁵¹ (Fig. 4m). Central Asian aridification has also been dated to 3.3 Ma, based on halite content, grain size, and magnetic proxies from the Qaidam Basin⁵². All of these developments would have impacted atmospheric dynamics and latitudinal temperature gradients that drive seasonal North African climate variability, so they could relate to either H_1

or H_2 . We have rejected H_1 . Therefore, based on available evidence, we retain H_2 as a possibility.

Strait of Sicily reconfiguration. Considering H_3 and H_4 (Table 2), Mediterranean tectonics could alter basin and sill depths, which would in turn affect deep-water ventilation. Tectonics within the wider Eastern Mediterranean catchment could also affect terrigenous fluxes to the seafloor, by rerouting transportation pathways and/or increasing continental erosion. The Mediterranean Basin has been tectonically active since reaching its modern configuration in the Oligocene-Miocene⁵³. Detailed palaeomagnetic work in Sicily suggests a rapid (80,000-100,000 yr) differential clockwise rotation at 3.21 Ma, near the C2An.2n-C2An.2r boundary⁵⁴ (Fig. 4a). The rotation compressed the Sicilian fold-and-thrust belt and its foreland⁵⁴⁻⁵⁶ and accelerated Tyrrhenian Sea opening between 3.5 and 2 Ma^{ref.54}, and is consistent with evidence of middle Pliocene tectonics in the Sicilian Strait⁵⁶. The timing corresponds with the Trubi-Narbone Formation boundary and may correspond to a rotational phase in northern Italy and a tectonic event north of Crete⁵⁴.

The close timing between lithological changes at ODP967 (and likely also at Site 964^{ref.29}) and inferred tectonic adjustment of the Sicilian Strait is tantalizing. In the modern Mediterranean, Eastern Mediterranean deep-water flushing over the Sicily sill depends on Bernoulli aspiration (akin to ‘pulling’ waters out of the eastern basin) and Eastern Mediterranean deep-water formation ‘pushing’ deep waters out⁸. At the present sill depth (440 m), Bernoulli aspiration is limited to <800 m; deep Eastern Mediterranean ventilation therefore relies on the deep-water formation pump. During sapropel phases, this pump was effectively turned off, leading to anoxic deep waters⁸. Calculations suggest that a 200-400 m deeper Sicily Sill would only marginally affect deep Eastern Mediterranean ventilation (Methods); nevertheless, we retain H_3 and H_4 for further evaluation.

Deep-sea ventilation versus carbon export. Reduced deep Eastern Mediterranean ventilation during sapropel/monsoon periods is forced by surface buoyancy gain (i.e. freshening), yet the relationship between sapropel C_{org} content and degree of buoyancy forcing is complex⁸. Sapropel C_{org} is typically of marine origin, but the type, mechanism, and amount of primary/export production is uncertain; however, consensus suggests a well-developed deep chlorophyll maximum for most sapropels⁸. If increased terrigenous fluxes from 3.2 Ma onward (e.g. hypothesis H_2) brought more labile terrestrial C_{org} and nutrients to the Eastern Mediterranean, they may have fuelled higher primary productivity and C_{org} export rates relative

to the Pliocene, leading to more intensely developed sapropels. Evidence to support/refute this is equivocal or non-existent. Riverine nutrient inputs remain unquantified even for the most recent sapropel⁵⁷. Pliocene sapropels in astronomically dated sections from Sicily and Cyprus contain lower C_{org} concentrations than typical Pleistocene sapropels^{58,59}, but sapropels in outcrops typically contain less C_{org} and total N than sapropels in offshore cores⁶⁰. There is general consensus among earlier studies⁶⁰⁻⁶² that Pliocene and Pleistocene sapropels are similar, and that Pliocene sapropels can contain high C_{org} ($\leq 30\%$)^{ref.62}, but the down-core depth intervals studied in these examples correspond to ages younger than 3.1 Ma. Meanwhile, similar early/mid-Pliocene and Pleistocene abundances of *Florisphaera profunda*—indicative of a deep chlorophyll maximum—are observed in sapropels from outcrops in Cyprus⁵⁹ and at ODP967^{ref.63}, implying similarly elevated Pliocene and Pleistocene primary productivity during sapropel deposition.

Nonetheless, hypothesis H_2 cannot account for Eastern Mediterranean ventilation changes after 3.2 Ma, so improved sapropel preservation after 3.2 Ma must be solely due to increased C_{org} export. In contrast, Sicilian Strait shoaling (H_{3-4}) could, in principle, induce an increased tendency toward Eastern Mediterranean deep-water stagnation, but—as yet—evidence remains circumstantial and sparse. Major benthic foraminiferal turnovers are documented between 3.6 and 2.6 Ma in the Punta Piccola section⁶⁴ (Southern Italy) and deep ODP sites in the Western and Eastern Mediterranean basins⁶⁵, which indicate increasing instability in bottom-water conditions. However, the main change is focussed at ~2.7 Ma, some 500,000 years after the events discussed here. Coupled Mg/Ca- $\delta^{18}O$ and ϵNd trends suggest that Mediterranean Outflow Water (MOW) intensified between 3.5 and 3.3 Ma^{ref.66}, but this pre-dates our observed geochemical shift. Nevertheless, seismic data and core sediments from the Gulf of Cadiz (Fig. 1) indicate a hiatus at ca 3.2-3.0 Ma and subsequent contourite deposition, which is attributed to MOW intensification in response to Strait of Gibraltar tectonics⁶⁷. The timing is based on preliminary biostratigraphic results, and might be older (~3.4-3.3 Ma) according to a revised mid-late Pliocene chronology for Site U1387^{ref.68}. Regardless, deep-water exchange through the Sicilian Strait, rather than the Strait of Gibraltar, is the critical factor for deep ventilation of the Eastern basin⁸. Contributions to Pliocene buoyancy forcing from local precipitation/evaporation are unknown, but we assume that they were negligible relative to African run-off forcing. Likewise, elevated SSTs cannot solely account for buoyancy forcing, given that they only partially contribute to water-column stratification during Last Interglacial sapropel formation^{17,18}, and mostly in response to salinity-driven stratification.

Conclusions

We have evaluated different hypotheses (climatic vs tectonic) to explain a marked shift in Eastern Mediterranean sediments 3.2 Ma ago. We find that sill tectonics ($H_{3,4}$) could account for reduced ventilation after 3.2 Ma (which best explains subsequently increased ODP967 Ba and S concentrations) and may coincide with inferred tectonic activity in the Strait of Gibraltar. However, hypothesis H_3 cannot satisfactorily account for a doubling (or more) of terrigenous element concentrations at ODP967 after 3.2 Ma. Hypothesis H_4 might account for this if the terrigenous influx was locally sourced (i.e., Eastern Mediterranean borderlands), but circumstantial evidence is lacking, and—more importantly—Pleistocene terrigenous sediments at ODP967 predominantly originated from North Africa¹⁹. Conversely, a non-linear response of riverine terrigenous loads to African climate/landscape evolution (hypothesis H_2) better accounts for increased ODP967 terrigenous element concentrations and Ti/Al fluxes after 3.2 Ma. H_2 can also be directly linked to mid-late Pliocene global climate evolution. The 3.2 Ma shift could represent a critical North African landscape transition in response to a global climate state-shift to icehouse conditions⁶⁹. Increased geochemical signal variance is common prior to critical transitions in Eastern Mediterranean sediments⁷⁰, and the biggest systematic Ti/Al variance increase is from 3.4 to 3.2 Ma (Fig. 4d). African pollen evidence attests to a more arid Pleistocene compared to the Pliocene^{32,71}, and a significantly more erodible landscape must exist before a stepwise amplitude increase in fluvial suspended sediment can occur. Furthermore, North African desert-soil albedo and vegetation feedbacks strongly amplify rainfall variability^{46,72,73}. The 3.2 Ma increase in ODP967 Ti/Al and fluvial-sourced terrigenous elements might, therefore, signify the onset of modern-day North African aridity. Further quantitative studies (e.g., weathering proxies) are needed to confirm this. Nevertheless, we cannot (yet) fully reject H_4 . It is conceivable that both H_2 and H_4 are valid and were coupled to major global climatic and tectonic changes; future model-data comparisons should test this possibility.

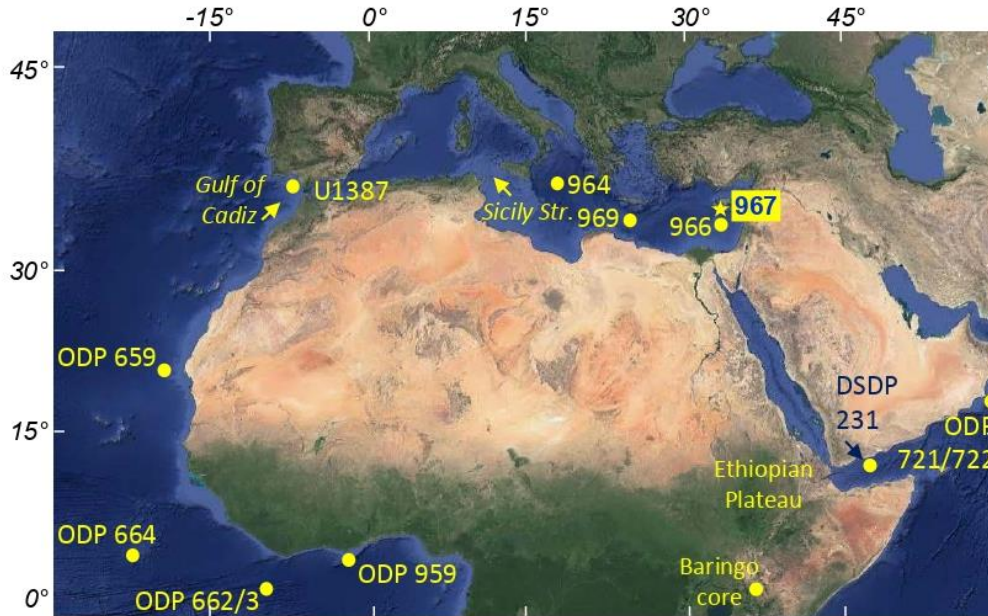


Fig. 1: Locations of sites discussed in this study. Eastern Mediterranean sites are from Ocean Drilling Program (ODP) Leg 160^{ref.29}. Base map ©2017 Google Earth, from Image Landsat ©2009 Geobasis-DE/BKG [Data: SIO, NOAA, US Navy, NGA, GEBCO].

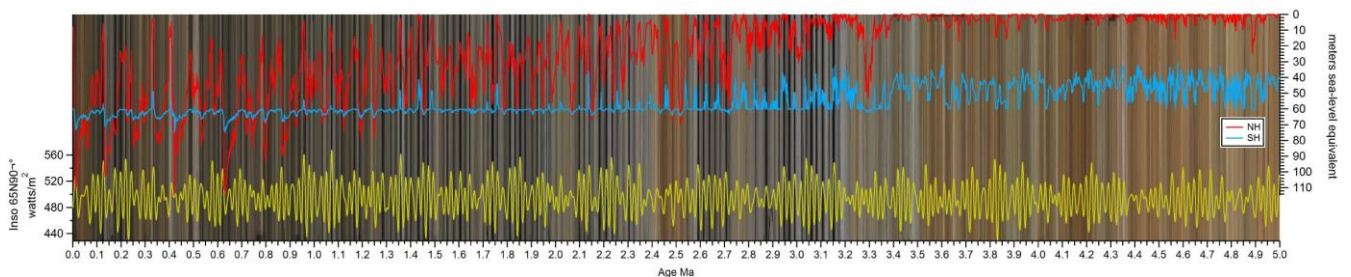


Fig. 2: ODP Site 967 composite core image. Northern and Southern Hemisphere ice-volume changes⁷⁴ (NH, red; SH, blue) in equivalent sea-level fall (the SH component includes -55 m equivalent sea level for the modern Antarctic ice sheet), and June 21 insolation at 65°N (yellow) illustrate timing relationships between climate forcing and lithology.

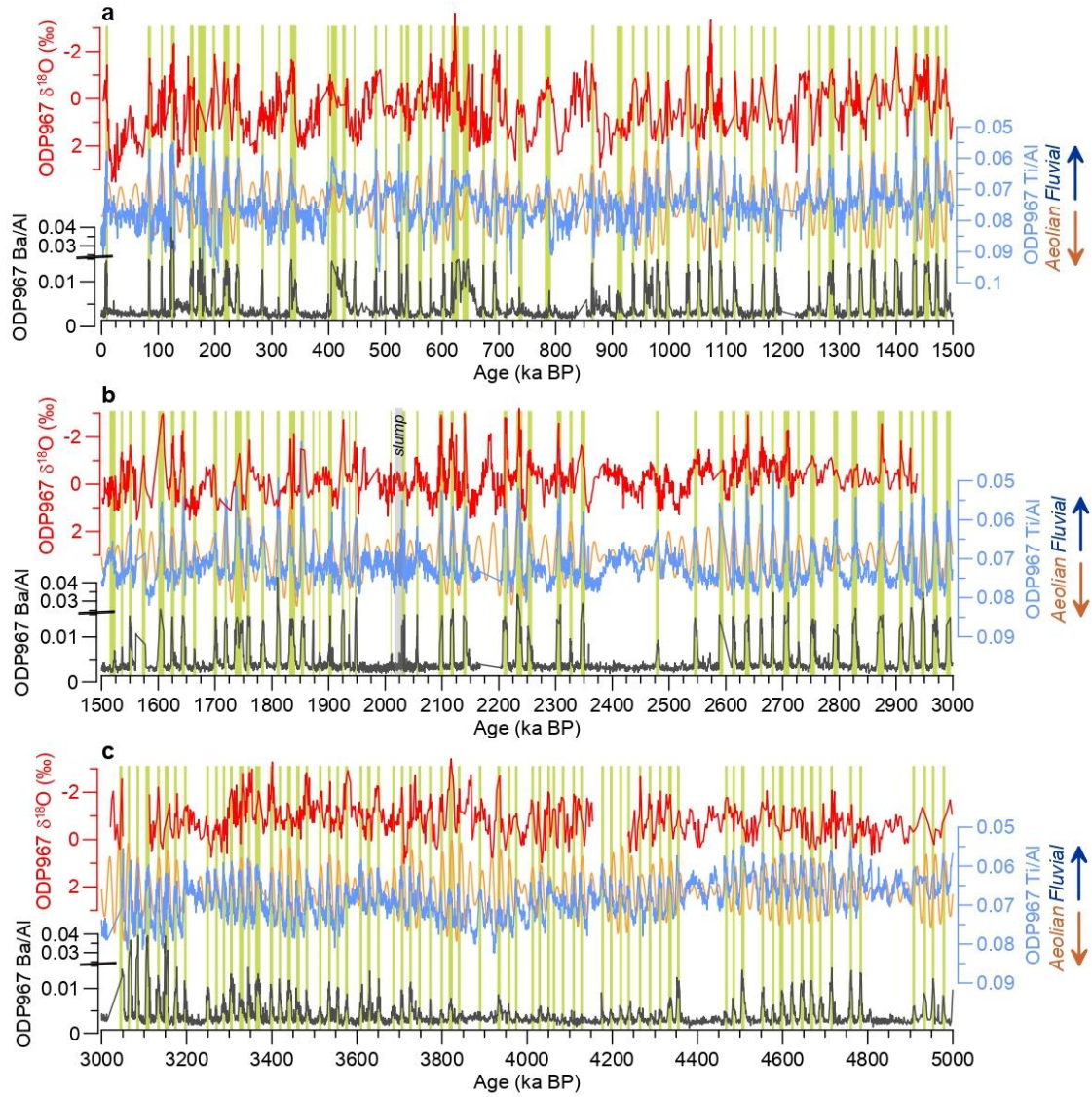


Fig. 3: Green Sahara Periods over the last 5 Myr. ODP Site 967 records of planktic foraminifera (*G. ruber*) $\delta^{18}\text{O}$ (red), Ti/Al (blue), and Ba/Al (grey) for time intervals 0-1.5 Myr ago (**a**), 1.5-3 Myr ago (**b**) and 3-5 Myr ago (**c**), with time in kiloyears before Present. Upward peaks correspond to precession minima (orange) and inferred Green Sahara Periods (green shading). (See Supplementary Figure S2 for detail over a selected interval).

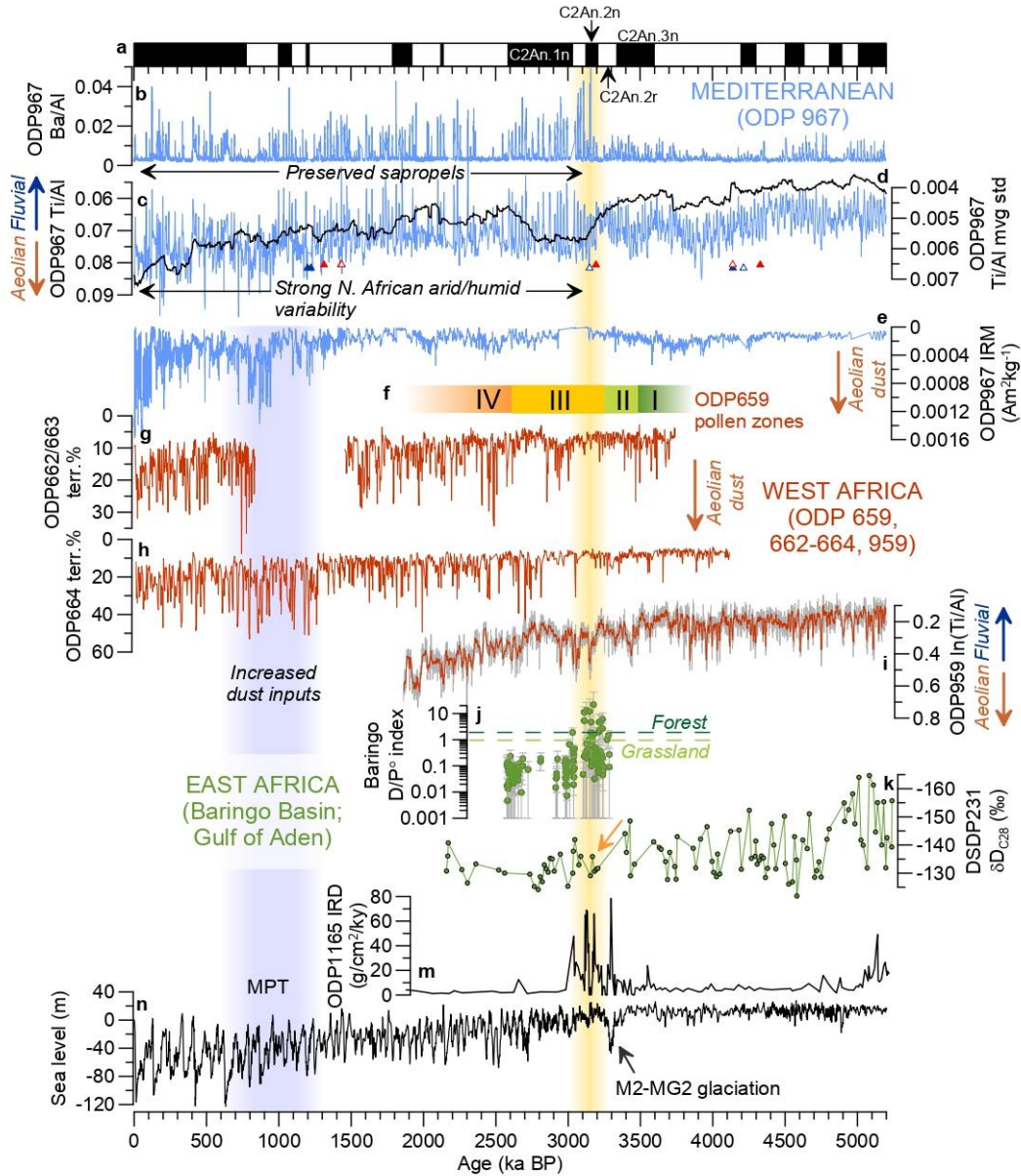


Fig. 4: Chronological and environmental context for the geochemical shift at ODP Site 967 at 3.2 Ma (see Fig. 1 for site locations, except ODP Site 1165 which is offshore Prydz Bay, Antarctica). **a)** Tectonic event around Sicily⁵⁴ in Chron 2An.2n; **b-e)** ODP967 Ba/Al, Ti/Al, 400-kyr moving standard deviation of Ti/Al (black), and magnetic dust proxy ($IRM_{900@120mT}$) (this study). Change-points in (c) are based on changes in the mean (red) and standard deviation (blue) of the Ti/Al time-series (closed triangles) and Ti/Al residuals (open triangles) after removing low-frequency (140-1200 kyr) variability; **f)** pollen zones from ODP Site 659^{ref.32} (green = more humid; yellow/orange = increasing aridity and humid/arid variability); **g-h)** aeolian dust records from offshore West Africa^{24,25}; **i)** ODP Site 959 Ti/Al (grey)²⁸ with 11-point running average (red); **j)** tree index based on pollen from Baringo Basin core BTB13, with 95% confidence intervals³⁷ (downward bars limited to y-axis); **k)** DSDP Site 231 leaf wax δD with inferred shift to more aridity at 3.3-3.0 Ma^{ref.38}; **m)** ODP Site 1165 ice-rafted debris (IRD) fluxes⁵¹; **n)** global sea-level reconstruction⁷⁴ based on benthic $\delta^{18}O$ (ref. 69). All records are plotted on their original chronology. Vertical shading denotes the Mid-Pleistocene Transition (MPT; grey) and geochemical shift at ODP967 (yellow).

Tables

Table 1: Sapropel preservation at Eastern Mediterranean ODP sites²⁹

Site	Water depth (m)	Location	Visible sapropel record
964	3665	Ionian Sea	≤ 3.2 Ma
967	2554	Levantine Basin	≤ 3.2 Ma
966	938	Levantine Basin	≤ 4.5 Ma*
969	2200	Mediterranean Ridge	≤ 5.3 Ma*

*Corresponds to basement of drilled site

Table 2: Working hypotheses

H_1	African freshwater run-off increased at 3.2 Ma; proportional sediment load increase
H_2	Sediment load in African run-off increased at 3.2 Ma; negligible change in freshwater flux
H_3	Sicily Sill uplift at 3.2 Ma; no major tectonic changes in wider Eastern Mediterranean
H_4	Sicily Sill uplift and major tectonic changes in wider Eastern Mediterranean at 3.2 Ma

Methods

Bulk element geochemistry. We combine published x-ray fluorescence (XRF) core-scanner data from ODP Site 967 spanning 0-3 Ma^{ref.15} with new XRF core-scanner data for the 3-5 Ma interval. Scanning was performed on archive core-sections at MARUM $\square\square\square$ University of Bremen, on an Avaatech XRF core scanner. Core sections were covered with 4 mm-thick Ultralene film and measured at 50 and 30 kV with 0.55 mA current and with a Cu and Pd-thick filter, respectively, and at 10 kV with 0.035 mA current (no filter); count time for all runs was 7 s. Element ‘counts’ for the entire 0-5 Ma interval were converted into element concentrations by multivariate log-ratio calibration⁷⁵, using published^{35,76} and new wavelength dispersive (WD)-XRF reference element concentrations (Supplementary Figure S8, S9). For these, 42 bulk sediment samples were chosen to cover a range of lithologies based on the XRF scan, then 1 cm³ dried ground sample was mixed with a lithium tetraborate/lithium metaborate flux and fused into 39 mm diameter beads. Major element abundances were analysed by WD-XRF using a Bruker S8 TigerTM spectrometer at Geoscience Australia. Loss on ignition (LOI) was measured by gravimetry after combustion at 1000°C. One in every ten samples was duplicated along with multiple analyses of 3 international standards (NCS DC70306, MAG-1, ML-2) and an internal basalt standard (WG1). Quantification limits for all major element oxides are <0.2% and reproducibility is within 1%.

The upper 40 m (0-1.3 Ma) of ODP967 contains cm-thick turbidites, which are not always visible, and which typically occur within sapropels⁷⁷. Sudden ‘extreme’ enrichments in Ti, Si, Zr, and to a lesser extent Fe and K, and corresponding Ca depletions, may therefore indicate a turbidite⁷⁶. Anomalous K spikes (relative to background values) are apparent at 2.3 and 2.9 Ma (Supplementary Figure S4), but elsewhere any potential turbidite signal is obfuscated by the dominant sapropel/marl signal.

ODP967 chronology. Published age-depth tie-points for the 0-3 Ma interval are based on tuning a principal-component derived sapropel proxy to precession¹⁵. Here, we extend the age model to 5 Ma by tuning the Ba/Ti record from XRF core-scanning to precession minima with zero phase lag (Supplementary Figure S1). Phase lags between a sapropel mid-point and nearest precession minimum/insolation maximum can be up to 3 ky but are not systematic and are likely limited to major deglaciations⁷⁸, hence (minor) lags would only be expected after the MPT.

Environmental magnetism. ODP967 U-channel samples were sliced at 1-cm intervals into non-magnetic plastic cubes and measured on a 2-G Enterprises cryogenic magnetometer at the Australian National University (ANU). IRM_{900@120mT} was obtained after imparting a 900 mT induction in a direct current field, followed by alternating field (AF) demagnetization in a peak 120 mT field.

Stable oxygen isotopes ($\delta^{18}\text{O}$). Bulk sediment samples were washed through 63 $\square\text{m}$ sieves with DI water and the residue was oven dried at 45°C for 24 hours. *Globigerinoides ruber* (white) specimens were picked from the >300 $\square\text{m}$ size fraction, adhering to ‘*sensu stricto*’ morphotypes and size range ($\pm 25 \square\text{m}$). Picked tests (typically 10-20, depending on abundance) were gently crushed and cleaned by briefly ultrasonicated in methanol, then air dried after decanting the fine suspended matter. Samples were analysed at ANU using a Thermo Fisher Scientific Delta Advantage mass spectrometer coupled to a Kiel IV carbonate device for sample digestion. Isotope data were normalized to the Vienna Pee Dee Belemnite (VPDB) scale using

NBS-19 or IAEA-603, and NBS-18. External reproducibility (1σ) was always better than 0.08‰.

Bernoulli aspiration depth (d). We use values from ref.8 in the equation of ref.79:

$$d = - \left(0.5h_2 + \left[0.25h_2^2 + \frac{u^2}{g \frac{\Delta\rho_v}{\rho_0 h_1}} \right]^{0.5} \right)$$

where h_1 approximates the depth of the open Eastern Mediterranean (~2000 m), h_2 is the Sicily Sill depth, u is the mean outflow velocity in the Sicilian Strait (0.2 m s^{-1}), $\Delta\rho_v$ is the vertical density gradient below the sill depth (0.03 kg m^{-3} today), ρ_0 is the density of the outflow layer at the sill ($\sim 1027 \text{ kg m}^{-3}$), and g is the acceleration due to gravity (9.81 m s^{-2}). For a 200 and 400 m deeper sill ($h_2 = 600$ and 800 m), d is -900 and -1000 m, respectively. Allowing a reduced density gradient below sill depth ($\Delta\rho_v = 0.02 \text{ kg m}^{-3}$, based on the modern Strait of Gibraltar), d is then -1010 and -1160 m, respectively. Thus, Eastern Mediterranean deep waters below ~1000 m would be poorly ventilated even if the Sicily Sill was 400 m deeper.

Data analysis

Change-points were estimated using the MATLAB built-in function “findchangepts”, following ref. 80. Change-points were determined based on the mean and standard deviation of the raw geochemical records, and a maximum of $n = 3$ change-points was stipulated as a parsimonious balance between constraining output to the most significant changes while allowing a >1 outcome. The moving standard deviation of the ODP967 Ti/Al record was calculated using the MATLAB built-in function “movstd”.

Data availability

ODP Site 967 data from this study are available online (see Supplementary Data)

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Author contributions

KMG designed and led the study and write-up; KMG, UA, JA, TP, YQ and LRS generated $\delta^{18}\text{O}$ and magnetism data; DH, PXH and XZ assisted with magnetism measurements; DL performed XRF core-scanning; DL and TW developed the ODP967 composite depth splice and chronology; KMG and RH calibrated scanning XRF data; KMG and SG performed WD-XRF analyses; LJL contributed WD-XRF data; all authors contributed to manuscript development.

Ethics declarations

The authors declare no competing interests.

CHAPTER 4

Estimating Plio-Pleistocene North African monsoon runoff into the Mediterranean Sea and temperature impacts

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Stable oxygen isotope values within Mediterranean sapropels are determined by the global ice volume, the oxygen isotope value and the quantity of North African monsoon runoff, and the magnitude of temperature concentration within the surface freshwater layer during sapropel formation. This chapter employs and further develops an existing Mediterranean box model, to isolate the strength of water column stratification (monsoon runoff and temperature concentration components) from ODP Site 967 $\delta^{18}\text{O}$ record which was presented in chapter 3. Thereby, we investigate the evolution of North African monsoon over the past 5 million-year.

Statement of Contribution

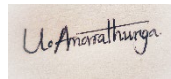
This thesis is submitted as a Thesis by Compilation in accordance with
https://policies.anu.edu.au/ppl/document/ANUP_003405

I declare that the research presented in this Thesis represents original work that I carried out during my candidature at the Australian National University, except for contributions to multi-author papers incorporated in the Thesis where my contributions are specified in this Statement of Contribution.

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Estimating Plio-Pleistocene North African monsoon runoff into the Mediterranean Sea and temperature impacts

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Key Points:

- We present quantitative estimates of Plio-Pleistocene North African monsoon activity based on deconvolution of planktonic foraminiferal $\delta^{18}\text{O}$
- Through the past 5 million years the North African monsoon was modulated by orbital eccentricity with remarkably stable amplitudes
- Apparent monsoon strengthening at ~2.6 Ma may instead be due to shifting runoff sources induced by Northern Hemisphere ice sheet initiation

Author contributions: This study was conceived by E.J.R. Analyses were designed and performed by D.H. using a version of the ODP Site 967 oxygen isotope reconstruction tuned to MedStack by U. A. All authors discussed the analyses and their interpretation. The manuscript was discussed and written by all authors.

Abstract

Sapropels are dark, organic-rich layers found in Mediterranean sediments that formed during periods of bottom water anoxia. While various mechanisms have been proposed to have caused anoxic conditions, a primary factor is considered to be water column stratification induced by freshwater runoff related to intensified North African monsoon precipitation during precession minima. Monsoon intensification also induced Green Sahara periods that may have impacted North African hominin dispersal. In this study, we present a novel regression-based deconvolution of a high-resolution planktonic foraminiferal oxygen isotope record to estimate the flux of freshwater runoff reaching the eastern Mediterranean over the past 5 million years. Sapropels are known to occur in clusters associated with periods of high orbital eccentricity. Our analysis reveals a persistent influence of orbital eccentricity in modulating the North African monsoon, and a possible shift in runoff source area induced by the initiation of Northern Hemisphere ice sheets. Our findings provide important insights into the role of the North African monsoon in shaping Mediterranean environmental changes over the past 5 million years.

Plain Language Summary

We investigate long-term changes in monsoon rains over North Africa, which annually result in freshwater flowing into the Mediterranean Sea. Over geological time, Earth's orbital variations have played a significant role in shaping the monsoon and, consequently, the quantity of freshwater entering the Mediterranean. Foraminifera, small marine organisms, record the oxygen isotope composition of their environment in their shells. Notably, the oxygen isotope balance in North African monsoon rains and the Mediterranean Sea differ, but eventually mix upon the freshwater entering into the Mediterranean. Our research combines a statistical analysis of oxygen isotope data preserved in foraminifera shells with a numerical model of the Mediterranean Sea, enabling us to estimate changes in monsoon freshwater input into the Mediterranean over the past 5 million years. This information not only enhances our understanding of monsoon evolution but also provides insights into the potential for hominin migrations in a more lush North African landscape characterized by higher rainfall than today.

1 Introduction

Intercalated marls and organic-rich sapropel layers in sedimentary sequences have provided crucial insights into the evolution of the Mediterranean Sea and the North African monsoon (see Cramp and O'Sullivan (1999), Emeis and Weissert (2009), Rohling (1994), and Rohling et al. (2015) for reviews). During orbital precession minima (Northern Hemisphere insolation maxima), the mean position of the North African monsoon front migrated northwards (Rossignol Strick, 1983; Rohling et al., 2002), resulting in so-called Green Sahara periods (GSPs) that supported increased vegetation and potentially a more hospitable environment for hominin populations (Larrasoana et al., 2013; Larrasoana, 2021). Furthermore, the northward shift of the monsoon rain belt increased freshwater runoff into the Mediterranean Sea via the Nile and paleoriver systems along the wider African margin (Rohling et al., 2015; Rossignol-Strick, 1985). High monsoon runoff increased the flux of nutrients into the Mediterranean Sea and induced water column stratification due to the formation of a buoyant low salinity surface layer. These conditions would induce deep-sea anoxia and the formation of organic-rich sapropels (Rohling et al., 2002, 2015; Rossignol-Strick et al., 1982). Furthermore, water column stratification resulted in preferential warming of the relatively fresh surface water layer, a process referred to as temperature concentration effect (Emeis et al., 2003). Not all precession minima resulted in sapropels, rather sapropels are found typically in clusters during periods when eccentricity modulation resulting in high amplitude precession cycles (Hilgen, 1991a, 1991b; Hilgen et al., 1993, 1995; Lourens et al., 1996, 2001; Rohling et al., 2015).

Monsoon runoff waters were characterized by strongly negative $\delta^{18}\text{O}$ values (Rohling et al. (2015), Amies et al. (2019), and references therein). Therefore, $\delta^{18}\text{O}$ of planktonic foraminifera tests ($\delta^{18}\text{O}_{\text{pf}}$) preserved in sapropels has the potential to provide information concerning runoff into the Mediterranean Sea and the long-term evolution of the North African monsoon (Emeis et al., 2003; Amies et al., 2019). For example, an ability to reconstruct changes in North African runoff reaching the Mediterranean Sea will enable inferences to be made concerning the strength of the monsoon and potential occurrence of GSPs during the Plio-Pleistocene, which was a key time interval for Hominin evolution (Larrasoana et al., 2013; Larrasoana, 2021).

We combine quantile regression (Koenker, 2005) and a Mediterranean Sea box model (Rohling, 1999; Rohling et al., 2004, 2014) to deconvolve an orbitally-tuned high-resolution $\delta^{18}\text{O}_{\text{pf}}$ record from eastern Mediterranean Ocean Drilling Program (ODP) Site 967 (Figure 1). Using box model derived sensitivities of $\delta^{18}\text{O}_{\text{pf}}$ to different forcing parameters, we estimate the flux of North African monsoon freshwater runoff reaching the Mediterranean Sea over the last 5 million years. These estimates are

used to infer long-term (e.g., 400-kyr eccentricity) orbitally-controlled changes in North African monsoon runoff.

2 Materials and Methods

Our approach is based on deconvolving long-term changes in $\delta^{18}\text{O}_{\text{pf}}$ to quantify the influence of North African monsoon runoff on the Mediterranean Sea. The deconvolution is underpinned by published records of Mediterranean $\delta^{18}\text{O}_{\text{pf}}$ and sea-level, and an established box model used to simulate changes in $\delta^{18}\text{O}_{\text{pf}}$ under different forcing scenarios. A flowchart provided in Figure 2 summarizes our proposed approach in a step-by-step fashion.

The ODP Site 967 *G. ruber* (w) $\delta^{18}\text{O}$ record of Grant et al. (2022) is adopted to represent $\delta^{18}\text{O}_{\text{pf}}$. Relative sea-level changes at Gibraltar (RSL_{Gib}) were estimated for the time interval of the ODP Site 967 $\delta^{18}\text{O}_{\text{pf}}$ record based on the eustatic sea-level (ESL) reconstruction of Rohling et al. (2021). Specifically, ESL driven change in RSL_{Gib} was obtained via the empirical relationship; $\text{RSL}_{\text{Gib}} = \text{ESL}/1.23$ estimated by Rohling et al. (2014) from an ensemble of glacial isostatic adjustment models relating ESL to depth of the Camarinal Sill (the critical location of water-exchange control for the Strait of Gibraltar). Importantly, the ESL to RSL_{Gib} conversion provides a representation of how RSL_{Gib} is expected to vary in response to ESL without associated changes in North African monsoon freshwater fluxes. Rohling et al. (2014) validated the RSL_{Gib} to ESL relationship by using it to deconvolve global deep-sea temperature since 5.3 Ma, and demonstrating that the resulting estimates were consistent with Mg/Ca-based temperatures. Following Rohling et al. (2014), we assume that $\text{RSL}_{\text{Gib}} = \text{ESL}/1.23$ provides a robust first-order approximation over the past 5 Myr.

The chronologies of the ODP Site 967 $\delta^{18}\text{O}_{\text{pf}}$ record of Grant et al. (2022) and the ESL record of Rohling et al. (2021) differ sufficiently that the intervals representing sapropel and marls are inconsistent. As will be shown, our deconvolution approach relies on separating records into sapropel and marl intervals and requires that the proxies involved have a consistent age model. The Medstack composite $\delta^{18}\text{O}_{\text{pf}}$ record of Wang et al. (2010) is selected as the basis for a common chronology. Importantly, sapropel and marl age intervals are provided within the Medstack framework, facilitating our deconvolution approach. The ESL chronology of Rohling et al. (2021) is consistent with Medstack and did not require modification. Retuning the ODP Site 967 $\delta^{18}\text{O}_{\text{pf}}$ of Grant et al. (2022) to Medstack requires age adjustments of less than ± 20 kyr. To estimate variability in the North African monsoon related to 100-kyr eccentricity cycles would require precession-scale accuracy when comparing $\delta^{18}\text{O}_{\text{pf}}$ and RSL_{Gib} . Because we cannot guarantee such age model accuracy, we focus on >400 -kyr eccentricity, which modulates both 100-kyr eccentricity and precession. Medstack is tuned

to the orbital solution of Laskar et al. (2004) and may differ slightly from more recently developed astronomical chronologies, such as CENOGRID (Westerhold et al., 2020), that are tuned to Laskar et al. (2010). However, our deconvolution is focused on long-term (>400-kyr) variability. Therefore, systematic differences in the Medstack and CENOGRID chronologies will be unimportant unless they are on the scale of hundreds of thousands of years. Importantly, systematic differences in the Laskar et al. (2004) and Laskar et al. (2010) orbital solutions on which the Medstack and CENOGRID chronologies are based, are minor for the age interval under consideration.

The Rohling et al. (2021) ESL values were converted to RSL_{Gib} via the empirical relationship: $RSL_{Gib} = ESL/1.23$ (Rohling et al., 2014). Importantly, the ODP Site 967 $\delta^{18}O_{pf}$ record was retuned to the stacked $\delta^{18}O_{pf}$ record of Wang et al. (2010) to place it on a chronology consistent with the RSL_{Gib} record.

2.1 Winter-Summer Box Model

Long-term average Mediterranean Sea $\delta^{18}O$ is controlled by a broad range of parameters, which include evaporation, precipitation and runoff, Atlantic inflow, water residence time in the basin, and global ice volume. To approximate the unknown relationship between $\delta^{18}O$ and different forcings, Rohling (1999) developed a Mediterranean basin box model that included summer and winter mixed-layer separation. This box model employed parameterizations for the key forcing processes. Rohling et al. (2014) reduced many aspects of the forcing, such as summer and winter sea surface temperatures (SST_s and SST_w , respectively) to functions of RSL_{Gib} . The parameterized seasonal differences in SST_s and SST_w were subsequently updated by Amies et al. (2019) based on a comparison of multiple SST proxies to:

$$SST_s = 22 + \frac{5.0RSL_{Gib}}{120} \quad (1)$$

and

$$SST_w = 17 + \frac{3.5RSL_{Gib}}{120} \quad (2)$$

where positive values of RSL_{Gib} correspond to sea-levels above modern. *G. ruber* (w) calcification is assumed to occur in summer, and yields a $\delta^{18}O_{pf}$ according to the relationship of O'Neal (1969) with adjustments for the difference between values versus Standard Mean Ocean Water for water and versus Pee Dee Belemnite for calcite (Rohling, 1999):

$$\delta^{18}O_{pf} = \frac{2.78 \times 10^3}{(SST_s + 273.15)^2} + \frac{\delta^{18}O_{sml} - 30.92}{1.03092} - 3.39 \quad (3)$$

where $\delta^{18}O_{sml}$ is the $\delta^{18}O$ of the model box representing the summer mixed layer. For compactness, we abbreviate the above expression to a more general form; $\delta^{18}O_{pf} = f_c(\delta^{18}O, SST)$.

2.2 Winter-Summer-Monsoon Box Model

Rohling et al. (2004) extended the Mediterranean basin model to include an intermittent surface “monsoon box” to represent the influence of freshwater runoff from the North African monsoon. Such freshwater fluxes (FWF) have been hypothesized to be the key drivers of water column stratification in the Mediterranean during precession minima, inducing increased productivity, sapropel formation, and negative $\delta^{18}O$ anomalies (Amies et al., 2019; Emeis et al., 2003; Rohling et al., 2015; Rossignol-Strick et al., 1982; Rossignol-Strick, 1985). Furthermore, water column stratification results in preferential warming of the relatively fresh surface layer, a process referred to as temperature concentration (ΔT , Emeis et al. (2003)). Based on a collection of numerical experiments aimed at stimulating observed $\delta^{18}O_{pf}$ anomalies across sapropel S5, Amies et al. (2019) parameterized the depth of the box representing the monsoon-induced upper summer mixed layer (USML) as; $-3.509 \Delta T + 30$. For planktonic foraminifera, such as *G. ruber* (w), expected to reside in the USML:

$$\delta^{18}O_{pf} = f_c(\delta^{18}O_{usml}(FWF), SST_s + \Delta T(FWF)), \quad (4)$$

where both $\delta^{18}O_{usml}$ and ΔT depend on FWF. While ΔT is related to monsoon FWF, the form of this relationship is unknown. Therefore, Equation 3 is part of an under-identified system and it is not feasible to estimate changes in FWF (ΔFWF) and ΔT separately without additional constraints.

2.3 Box Model Sensitivities

To estimate the influence of large-scale RSL_{Gib} changes on $\delta^{18}O_{pf}$, we employ the Winter-Summer box model of Rohling (1999), with the RSL_{Gib} -based forcing parameterizations of Rohling et al. (2014), including the seasonal SST adjustments of Amies et al. (2019). In addition to determining a continuous relationship between RSL_{Gib} and $\delta^{18}O_{pf}$, we consider the sensitivity of $\delta^{18}O_{pf}$ to changes in RSL_{Gib} by determining $\partial \delta^{18}O_{pf} / \partial RSL_{Gib}$ numerically using the Winter-Summer box model (Figure 2(a)). To estimate the influence of ΔFWF and ΔT , we employ the Winter-Summer-Monsoon box model with the USML depth parameterization of Amies et al. (2019). Sensitivities $\partial \delta^{18}O_{pf} / \partial \Delta FWF$ and $\partial \delta^{18}O_{pf} / \partial \Delta T$ were estimated numerically from this model also as a function of RSL_{Gib} (Figures

2(b) and 2(c), respectively). Changes in monsoon FWF represented by ΔFWF are scaled according to model estimates of the preindustrial annual Nile river runoff (Colleoni et al., 2015). Therefore, $\Delta\text{FWF} = 1$ represents a monsoon FWF equal to the preindustrial annual Nile river runoff, $\Delta\text{FWF} = 2$ corresponds to a monsoon FWF of twice the preindustrial annual Nile river runoff, etc.

2.4 Deconvolution of North African Freshwater Flux

As discussed, freshening of surface waters due to enhanced ΔFWF is hypothesized to have induced water column stratification. During these intervals, negative $\delta^{18}\text{O}_{\text{pf}}$ anomalies reflect both isotopically depleted surface waters and temperature concentration effects (Equation 4). Therefore, estimating the magnitude of the $\delta^{18}\text{O}_{\text{pf}}$ anomaly combined with box model estimates of $\delta^{18}\text{O}_{\text{pf}}$ sensitivities provides an approach to assess ΔFWF or ΔT . Our approach is described in detail below and is accompanied by a flowchart and list of terms to aid exposition (Appendix).

Estimation of $\delta^{18}\text{O}_{\text{pf}}$ anomalies in sapropel intervals requires interpolating non-sapropelic $\delta^{18}\text{O}_{\text{pf}}$ across the sapropel in a physically meaningful way. For example, within the sapropel interval $\delta^{18}\text{O}_{\text{pf}}$ may have been influenced by a number of factors, such as insolation driven changes in RSL_{Gib} and SST_s that are not related directly to ΔFWF and ΔT . Therefore, given the $\delta^{18}\text{O}_{\text{pf}}$ observations, it is necessary to estimate $\delta^{18}\text{O}_{\text{pf}}$ across the sapropel interval in a form consistent with ΔFWF and ΔT being zero. The difference between this estimate and the observations corresponds to the monsoon-related $\delta^{18}\text{O}_{\text{pf}}$ anomaly ($\Delta\delta^{18}\text{O}_{\text{pf}}$) resulting from FWF and temperature concentration effects. The required ΔFWF and ΔT to obtain such an anomaly can then be estimated via $\partial\delta^{18}\text{O}_{\text{pf}}/\partial\Delta\text{FWF}$ and $\partial\delta^{18}\text{O}_{\text{pf}}/\partial\Delta T$ obtained from the box models.

As explained above, our aim is to reconstruct long-term (e.g., 400-kyr eccentricity and longer) variations in ΔFWF and ΔT . Therefore, while not all sapropel intervals may conform purely with a North African monsoon FWF forcing scenario (Rohling et al., 2015), it is considered that this will be the primary process driving long-term changes in sapropel $\delta^{18}\text{O}_{\text{pf}}$ anomalies. To assess long-term trends in $\delta^{18}\text{O}_{\text{pf}}$, both within sapropel peaks and the portions of marls with low $\delta^{18}\text{O}_{\text{pf}}$ preceding and following sapropels, we employ quantile regression (Koenker, 2005). Quantile regression provides estimates of conditional quantiles, in contrast to traditional regression which estimates the conditional mean of a dependent variable. Quantile regression estimates are obtained by minimizing the difference between observed quantiles and those predicted using a parametric regression function. We utilize a smoothing cubic spline to obtain quantile regression estimates, with the degrees of freedom (dof) of

the spline controlling its smoothness. Quantile spline fits and their standard errors were obtained using the *statsmodel* package (Seabold & Perktold, 2010).

To represent the evolution of sapropel minima $\delta^{18}\text{O}_{\text{pf}}$ values, a smoothing cubic spline (dof = 50) was fit to the 0.1 quantile of ODP Site 967 observations within sapropel intervals ($Q_{0.1}^{\delta^{18}\text{O}_{\text{pf}}}(\text{S})$). Correspondingly, a second cubic spline (dof = 50) was fit to the 0.1 quantile of the $\delta^{18}\text{O}_{\text{pf}}$ in the marl intervals ($Q_{0.1}^{\delta^{18}\text{O}_{\text{pf}}}(\text{M})$, Figure 3(a)). The spline dof was selected based on its frequency response (Figure 4), which includes the 400-kyr eccentricity cycle that modulates the amplitude of precession. The fitted splines provide an estimate of the difference in $\delta^{18}\text{O}_{\text{pf}}$ minima between marls and sapropels; however, they do not consider the effect of non-monsoon dependent forcings, such as RSL_{Gib} , that influence $\delta^{18}\text{O}_{\text{pf}}$ in sapropels independently of ΔFWF and ΔT . To assess this influence, cubic splines (dof = 50) were fitted to the 0.9 quantiles of RSL_{Gib} for the sapropel and marl intervals ($Q_{0.9}^{\text{RSL}_{\text{Gib}}}(\text{S})$, and $Q_{0.9}^{\text{RSL}_{\text{Gib}}}(\text{M})$, respectively, Figure 3 (b)).

The mean ($\overline{\text{RSL}_{\text{Gib}}}$) and difference ($\Delta\text{RSL}_{\text{Gib}}$) in the RSL_{Gib} quantiles (Figure 5) can be expressed as:

$$\overline{\text{RSL}_{\text{Gib}}} = \frac{Q_{0.9}^{\text{RSL}}(\text{S}) + Q_{0.9}^{\text{RSL}}(\text{M})}{2} \quad (5)$$

and

$$\Delta\text{RSL}_{\text{Gib}} = Q_{0.9}^{\text{RSL}}(\text{S}) - Q_{0.9}^{\text{RSL}}(\text{M}) \quad (6)$$

As discussed in Section 2.1, the Winter-Summer box model parameterizes forcing as a function of RSL_{Gib} (Rohling et al., 2014). Therefore, box-model derived $\partial\delta^{18}\text{O}_{\text{pf}}/\partial\text{RSL}_{\text{Gib}}$ sensitivity provides an estimate of the $\delta^{18}\text{O}_{\text{pf}}$ contribution within sapropels that is not related to ΔFWF and ΔT (Figure 2(a)). Once this RSL_{Gib} -related contribution is accounted for, the difference in $\delta^{18}\text{O}_{\text{pf}}$ 0.1 quantiles between the sapropel and marl intervals yields an estimate of the sapropel anomaly; $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$ (Figure 6). Specifically, within a sapropel the anomaly due changes in forcing parameterized as a function of RSL_{Gib} is given by:

$$\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{RSL}_{\text{Gib}}} = \Delta\text{RSL}_{\text{Gib}} \frac{\partial\delta^{18}\text{O}_{\text{pf}}}{\partial\text{RSL}_{\text{Gib}}} \quad (7)$$

The final anomaly is then:

$$\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}} = Q_{0.1}^{\delta^{18}\text{O}_{\text{pf}}}(\text{S}) - Q_{0.1}^{\delta^{18}\text{O}_{\text{pf}}}(\text{M}) - \Delta\delta^{18}\text{O}_{\text{pf}}^{\text{RSL}_{\text{Gib}}} \quad (8)$$

Estimates of $\partial\delta^{18}\text{O}_{\text{pf}}/\partial\Delta\text{FWF}$ and $\partial\delta^{18}\text{O}_{\text{pf}}/\partial\Delta T$ enable estimation of ΔFWF and ΔT that could be responsible for the estimated $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$ sapropel anomalies. As shown in Figures 2(b) and 2(c), $\partial\delta^{18}\text{O}_{\text{pf}}/\partial\Delta\text{FWF}$ and $\partial\delta^{18}\text{O}_{\text{pf}}/\partial\Delta T$ are not independent of RSL_{Gib} . Therefore, $\partial\delta^{18}\text{O}_{\text{pf}}/\partial\Delta\text{FWF}$ and $\partial\delta^{18}\text{O}_{\text{pf}}/\partial\Delta T$ values are selected corresponding to modern RSL_{Gib} , which is a reasonable approximation for the majority of sapropels given that most developed during interglacials. Throughout the estimation process, uncertainties were assessed using standard error propagation techniques (Taylor, 1997).

3 Results and Discussion

Our approach provides an estimate of the $\Delta\delta^{18}\text{O}_{\text{pf}}$ anomaly due to monsoon-related freshwater runoff from the North African margin and Nile River (Figure 7(a)). Based on $\partial\delta^{18}\text{O}_{\text{pf}}/\partial\Delta\text{FWF}$ and $\partial\delta^{18}\text{O}_{\text{pf}}/\partial\Delta T$ sensitivities (Figures 2(b) and 2(c), respectively), estimated anomalies can be converted into ΔFWF and ΔT anomalies. As highlighted in Equation 4, because $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$ is based on a single species, it is not feasible to estimate ΔFWF and ΔT simultaneously without additional constraints. Therefore, the ΔFWF and ΔT anomalies are not independent of each other (the temperature concentration effect responsible for ΔT is a result of water column stratification induced by ΔFWF). The anomaly estimates, thus, represent the ΔFWF and ΔT required individually, not in combination, to explain $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$. For example, at 5 Ma $\Delta\delta^{18}\text{O}_{\text{pf}} \approx -0.7\text{‰}$, which corresponds to $\Delta\text{FWF} \approx 2.5$ or $\Delta T \approx 3^\circ\text{C}$. These anomalies must be interpreted as end-member scenarios, and the actual ΔFWF and ΔT anomalies will be some, potentially nonlinear, mixture of those end-members. Therefore, ΔFWF and ΔT should be interpreted as an indicative range of potential anomalies rather than a quantitative estimate of actual anomalies. Estimated $\Delta\delta^{18}\text{O}^{\text{mon}}$ ranges from $\sim 0\text{‰}$, corresponding to a minimal additional monsoon freshwater in the sapropel intervals, through to an extreme of $\sim -2\text{‰}$. Longer period variability in $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$ follows the 400-kyr cycle in eccentricity (Figure 7(b)).

This is to be expected given that the 400-kyr eccentricity cycle modulates the amplitude of the 100-kyr eccentricity cycle, which in-turn modulates precession and therefore insolation (Laskar et al., 2004). While such a pattern cannot be used to infer the existence of specific GSPs, it indicates that monsoon conditions conducive to GSPs occurred persistently over the last 5 Ma during peaks in the 400-kyr eccentricity cycle. Amies et al. (2019) employed a multi-species reconstruction to estimate that the *G. ruber* (w) $\delta^{18}\text{O}_{\text{pf}}$ anomaly associated with sapropel S5 (~128.3–121.5 ka, Grant et al. (2016)) was $\sim -2\text{‰}$ at ODP Site 967. Based on an inverse box model and data from a collection of Mediterranean sites, Amies et al. (2019) attributed the S5 $\delta^{18}\text{O}_{\text{pf}}$ anomaly to a ≤ 8.8 times increase in Nile FWF (relative to modern pre-Aswan discharge) and a temperature concentration effect of $\leq 5.7^\circ\text{C}$. These values are broadly consistent with our estimated $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$ if they are considered separately (i.e. an ≤ 8.8 times increase in Nile FWF, or a temperature concentration effect of $\leq 5.7^\circ\text{C}$), but not in combination. For example, based on the sensitivities in Figures 2(b) and 2(c), a ΔFWF of 8.8 and ΔT of 5.7°C would yield an anomaly of $\sim -3.5\text{‰}$. This demonstrates the challenges associated with making quantitative reconstructions of past monsoon activity when the physical relationship between ΔFWF and ΔT is poorly understood.

At ~ 2.6 Ma, there is a shift in $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$ of $\sim -0.3\text{‰}$ towards more negative values and larger amplitude cycles, implying potentially larger ΔFWF and ΔT that cannot be explained by eccentricity changes (Figure 7). Such a shift in the mean $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$ after ~ 2.6 Ma is opposite to previously hypothesized forcing mechanisms formulated from the analysis of proxy reconstructions and climate model simulations. For example, based on a suite of preindustrial and Pliocene simulations, Colleoni et al. (2015) inferred that freshwater flux into the Mediterranean Sea from the North African margin and Nile River was $\sim 40\%$ higher during the Pliocene. Their simulations did not consider monsoon anomalies in sapropels specifically, but their work indicates a more active hydrological system during the Pliocene. Based on high resolution elemental ratios and $\delta^{18}\text{O}_{\text{pf}}$ records, it has been hypothesized that at 3.2 Ma, when the gradual evolution to modern-day North African aridity commenced, monsoon-related freshwater flux remained relatively constant (Grant et al., 2022). Given these observational and modelling constraints it is apparent that the shift to more negative $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$ values and larger amplitude cycles at ~ 2.6 Ma, cannot be attributed to a larger and more variable freshwater flux.

Using the CLIMBER-2 Earth-system model, de Boer et al. (2021) modelled the impact of the African monsoon on the Mediterranean between 3.2 and 2.3 Ma. Based on simulated changes in the North African hydrological network combined with proxy records for continental runoff, they estimated that

prior to ~ 2.8 Ma the contribution of runoff originating from the Sahara region was dominant over runoff originating from the Sahel (Figure 1). After ~ 2.8 Ma and the onset of global cooling and inception of North Hemisphere glaciations, a scenario with approximately equal runoff contributions from the Sahara and Sahel regions is most consistent with proxy information. As highlighted by Rohling et al. (2015) and Amies et al. (2019), the $\delta^{18}\text{O}$ of freshwater in areas of North Africa that are currently covered by the Saharan desert is between -8 and -12‰. Therefore, the Winter-Summer-Monsoon box model was used to determine the sensitivity; $\partial\delta^{18}\text{O}_{\text{pf}}/\partial\delta^{18}\text{O}_{\text{mon}}$, where $\delta^{18}\text{O}_{\text{mon}}$ is the $\delta^{18}\text{O}$ composition of the monsoon FWF. Based on the $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$ anomalies in Figure 7a, $\partial\delta^{18}\text{O}_{\text{pf}}/\partial\delta^{18}\text{O}_{\text{mon}}$ was estimated for $\Delta\text{FWF} = 4$ (Figure 8). The sensitivity of $\delta^{18}\text{O}_{\text{pf}}$ to changes in $\delta^{18}\text{O}_{\text{mon}}$ implies that the observed change in $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$ can be explained readily by a shift in $\delta^{18}\text{O}$ of monsoon FWF of ~ -3.5 ‰ within the expected -8 and -12‰ interval. While this hypothesis will require more detailed investigation in future studies, it indicates the magnitude of the influence FWF $\delta^{18}\text{O}$ composition may have Mediterranean $\delta^{18}\text{O}_{\text{pf}}$.

4 Conclusions

Though a combination of a high-resolution proxy data, box model derived sensitivities, and quantile regression, we have estimated the $\delta^{18}\text{O}_{\text{pf}}$ associated with North African monsoon runoff into the Mediterranean Sea. Based on these anomalies, North African monsoon activity has followed a pattern of eccentricity modulation of precession over the last 5 Ma. During peaks in the 400-kyr eccentricity cycle, $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$ anomalies are consistent with a FWF increase corresponding to ~ 7 times the preindustrial annual output of the Nile river, or a temperature concentration effect of $\sim 8^\circ\text{C}$. Such a long-term pattern in monsoon FWF variability, and thus Mediterranean Sea stratification, is consistent with the occurrence of sapropels in the Mediterranean since the Miocene (Hilgen, 1995).

A negative shift in the background value of $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$ anomalies occurs around the time of the onset of Northern Hemisphere glaciation. Based on box model sensitivities, this shift corresponds to a change in $\delta^{18}\text{O}_{\text{mon}}$ of -3 to -4‰. Given uncertainties in $\delta^{18}\text{O}_{\text{mon}}$ through time (Rohling et al., 2015; Amies et al., 2019) and Earth-system model results indicating a change in monsoon freshwater source area coincident with the inception of Northern Hemisphere ice sheets (de Boer et al., 2021), we hypothesize that the reconstructed shift can be attributed to a change in the source area and/or composition of FWF entering the Mediterranean Sea.

Finally, based on the estimated monsoon FWF reaching the Mediterranean Sea over the last 5 Ma, the potential for conditions conducive to the occurrence of GSPs is clear. Given that monsoon FWF is modulated strongly by eccentricity, this provides an indication during which precession minima GSPs may occur.

5 Open Research

Jupyter notebooks and associated Python and Julia code to recreate the calculations presented in this work are available on GitHub at <https://github.com/dave-heslop74/ODP-Site-967-Models>. All materials will be archived on Zenodo with a permanent DOI on acceptance.

Acknowledgments

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Figures

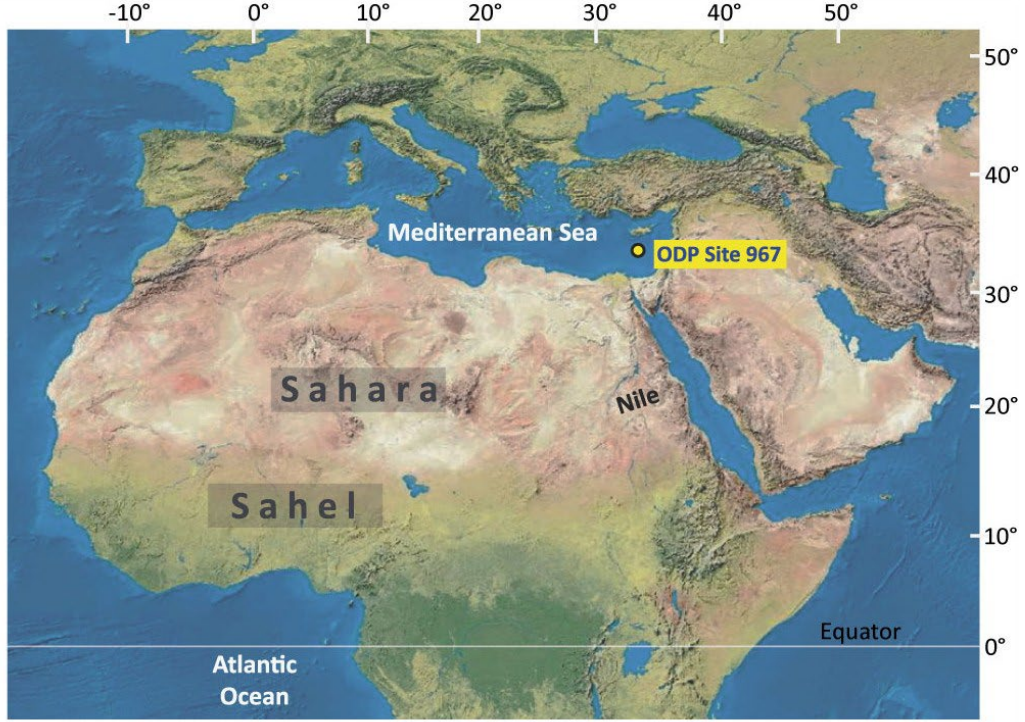


Figure 1. Map showing the Nile River and location of ODP Site 967 in the eastern Mediterranean Sea. Basemap colors indicate modern vegetated areas versus desert regions.

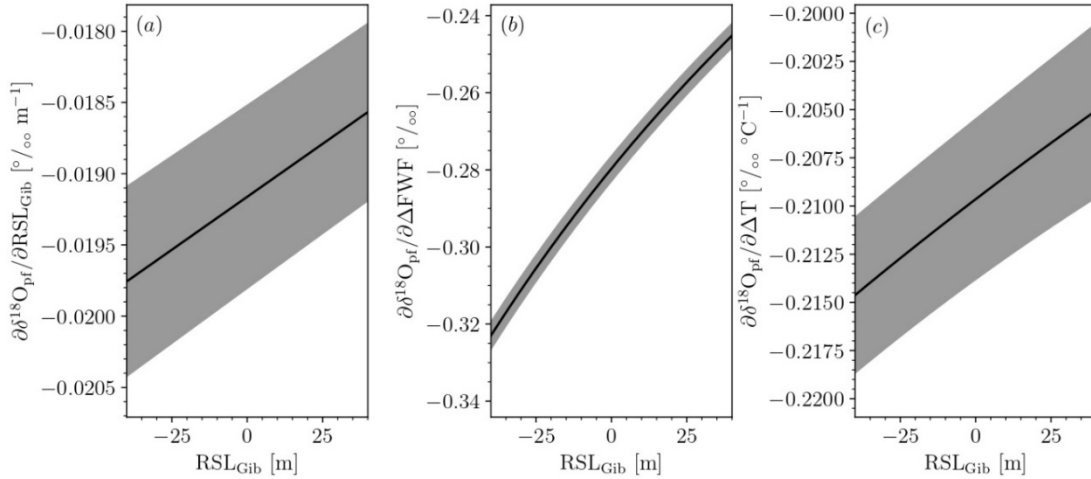


Figure 2. (a) Estimated sensitivity of $\delta^{18}\text{O}_{\text{pf}}$ to change in RSL_{Gib} as a function of RSL_{Gib} over an interval relevant for sapropel layers. Sensitivities were estimated numerically using the described Winter-Summer box model. Uncertainties were assessed via a Monte Carlo scheme, with the standard error on the sensitivity estimates shown by the shaded interval. (b) Same as (a) for Winter-Summer-Monsoon box model estimated sensitivity of $\delta^{18}\text{O}_{\text{pf}}$ to change in ΔFWF as a function of RSL_{Gib} . (c) Same as (b) for the estimated sensitivity of $\delta^{18}\text{O}_{\text{pf}}$ to change in ΔT as a function of RSL_{Gib} .

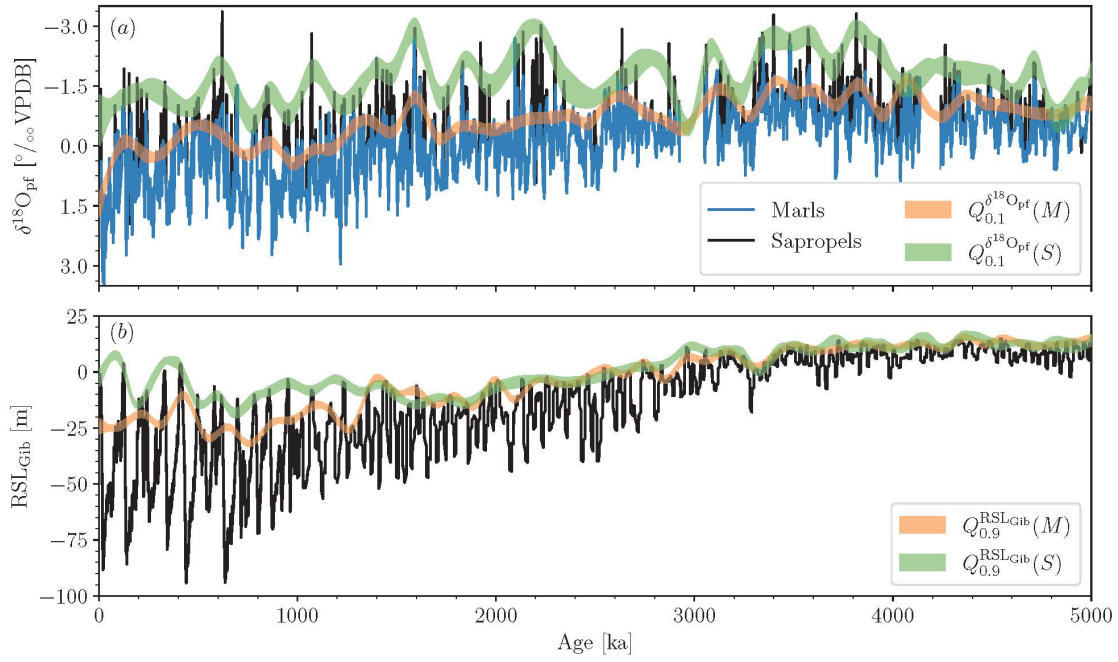


Figure 3. (a) Quantile regression of the ODP Site 967 $\delta^{18}\text{O}_{\text{pf}}$ record. Marl and sapropel samples are shown in blue and black, respectively. Orange and green represent the 0.1 quantiles for the marls ($Q_{0.1}^{\delta^{18}\text{O}_{\text{pf}}}(M)$) and sapropels ($Q_{0.1}^{\delta^{18}\text{O}_{\text{pf}}}(S)$), respectively, with the width of the bands corresponding to their 95% confidence intervals. (b) Quantile regression of the RSL_{Gib} sea-level reconstruction. Orange and green represent the 0.1 quantiles for the marls $Q_{0.1}^{\text{RSL}_{\text{Gib}}}(M)$ and sapropels $Q_{0.1}^{\text{RSL}_{\text{Gib}}}(S)$), respectively, with the width of the bands corresponding to their 95% confidence interval. Negative RSL_{Gib} values indicate sea-levels lower than today.

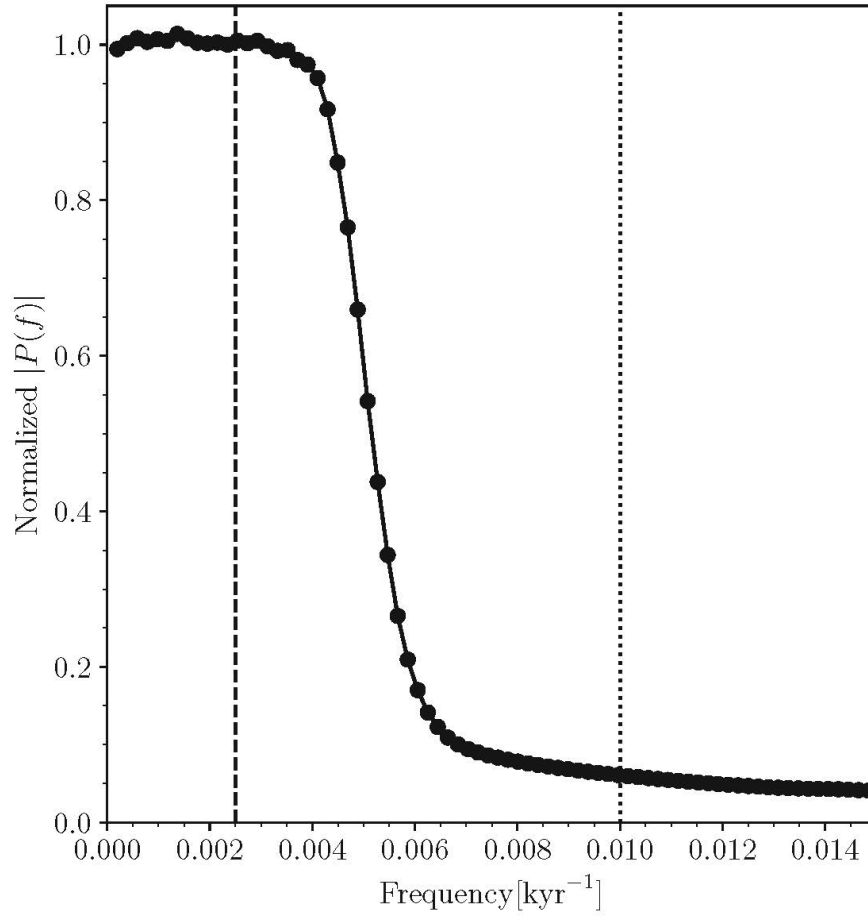


Figure 4. Frequency response, in terms of normalized amplitude, of a smoothing cubic spline with $\text{dof} = 50$ fitted to the 0.9 (or equivalently 0.1) quantile of a data series with the same length as the ODP Site 967 $\delta^{18}\text{O}_{\text{pf}}$ record. The frequency corresponding to the 400-kyr eccentricity cycle (dashed line) will not be attenuated by the spline. In contrast, the frequency corresponding to the 100-kyr eccentricity cycle (dotted line) will be attenuated strongly.

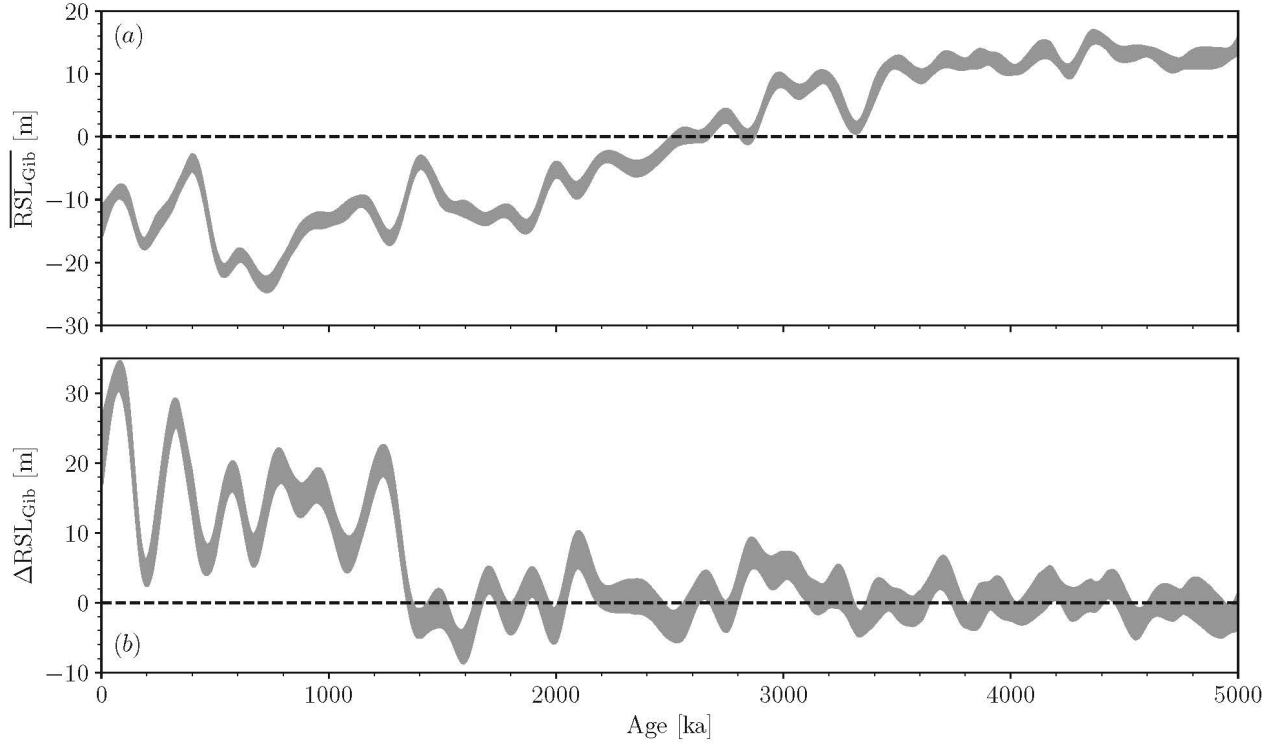


Figure 5. (a) Estimated mean RSL_{Gib} through sapropel intervals based on the average of the $Q_{0.9}^{RSL_{Gib}}(S)$ and $Q_{0.9}^{RSL_{Gib}}(M)$ quantile regressions. The width of the band corresponds to the 95% confidence interval. (b) Estimated difference in RSL_{Gib} between marl and sapropel intervals based on the difference of the $Q_{0.9}(S)$ and $Q_{0.9}(M)$ quantile regressions. The width of the band corresponds to the 95% confidence interval.

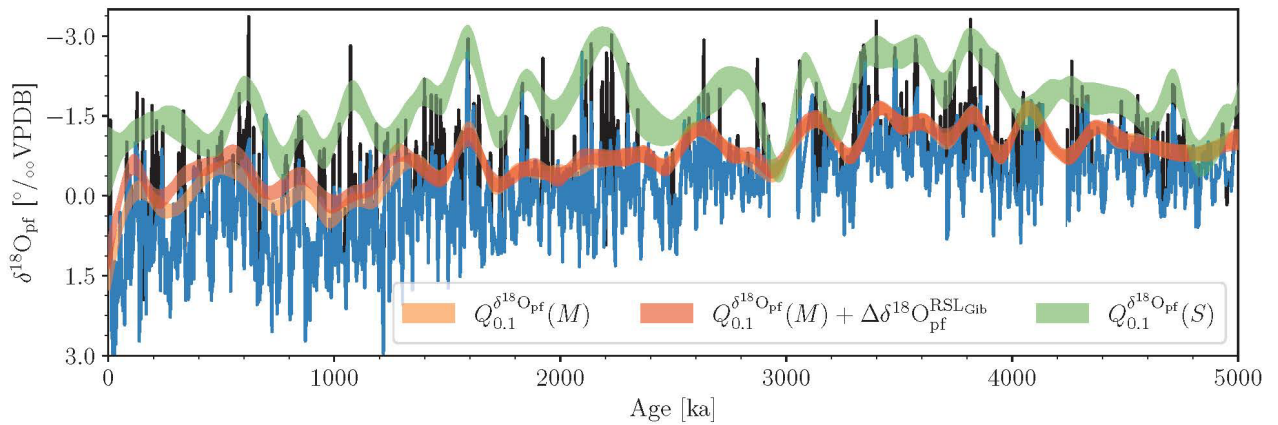


Figure 6. As in Figure 3(a), with the addition of the estimated RSL_{Gib} forced contribution to the marl 0.1 $\delta^{18}O_{pf}$ quantile (red).

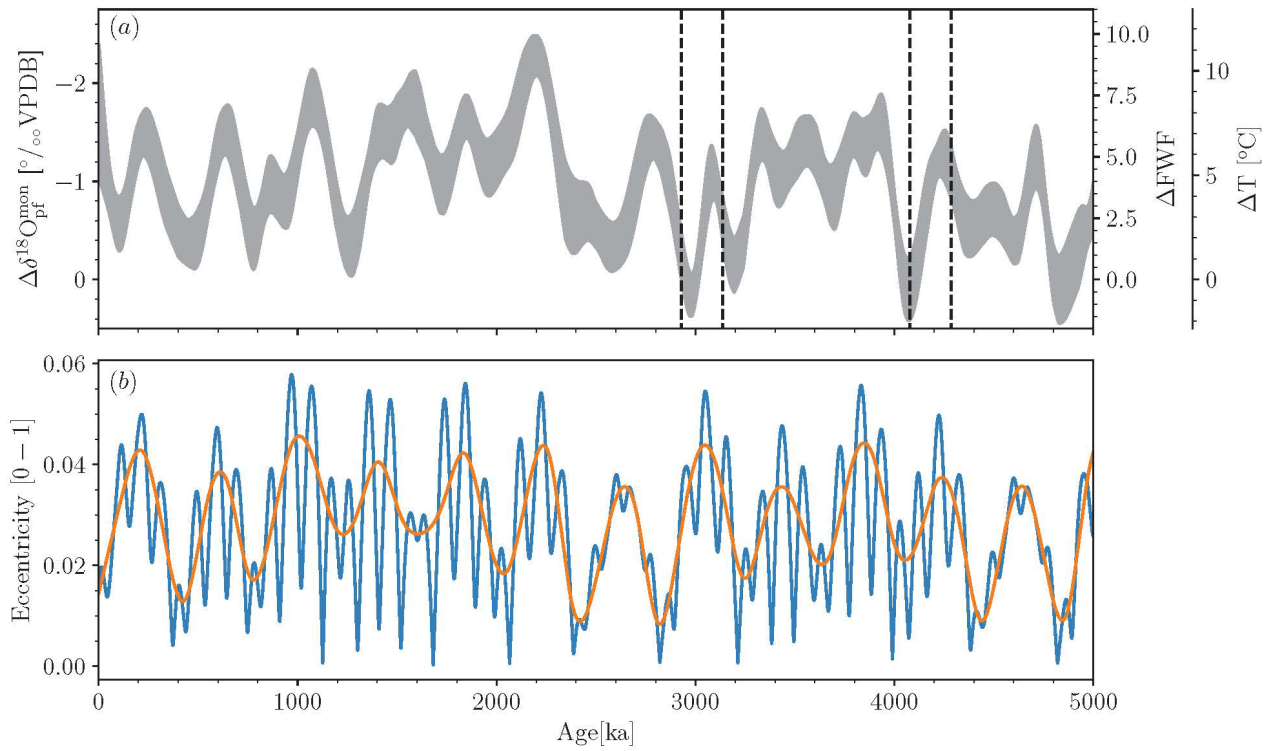


Figure 7. (a) Estimated $\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$ anomaly due to monsoon FWF and temperature concentration effects. Shading represents the 95% confidence interval. Dashed lines show the region of the reconstruction where the quantile regression cubic splines may have been unduly influenced by large gaps in the ODP Site 967 $\delta^{18}\text{O}_{\text{pf}}$ record (Figure 3 (a)). (b) Orbital eccentricity (blue) from the astronomical solution of Laskar et al. (2004). A 0.5 quantile regression with a dof = 50 smoothing cubic spline is shown in orange to emphasize the 400-kyr eccentricity cycle.

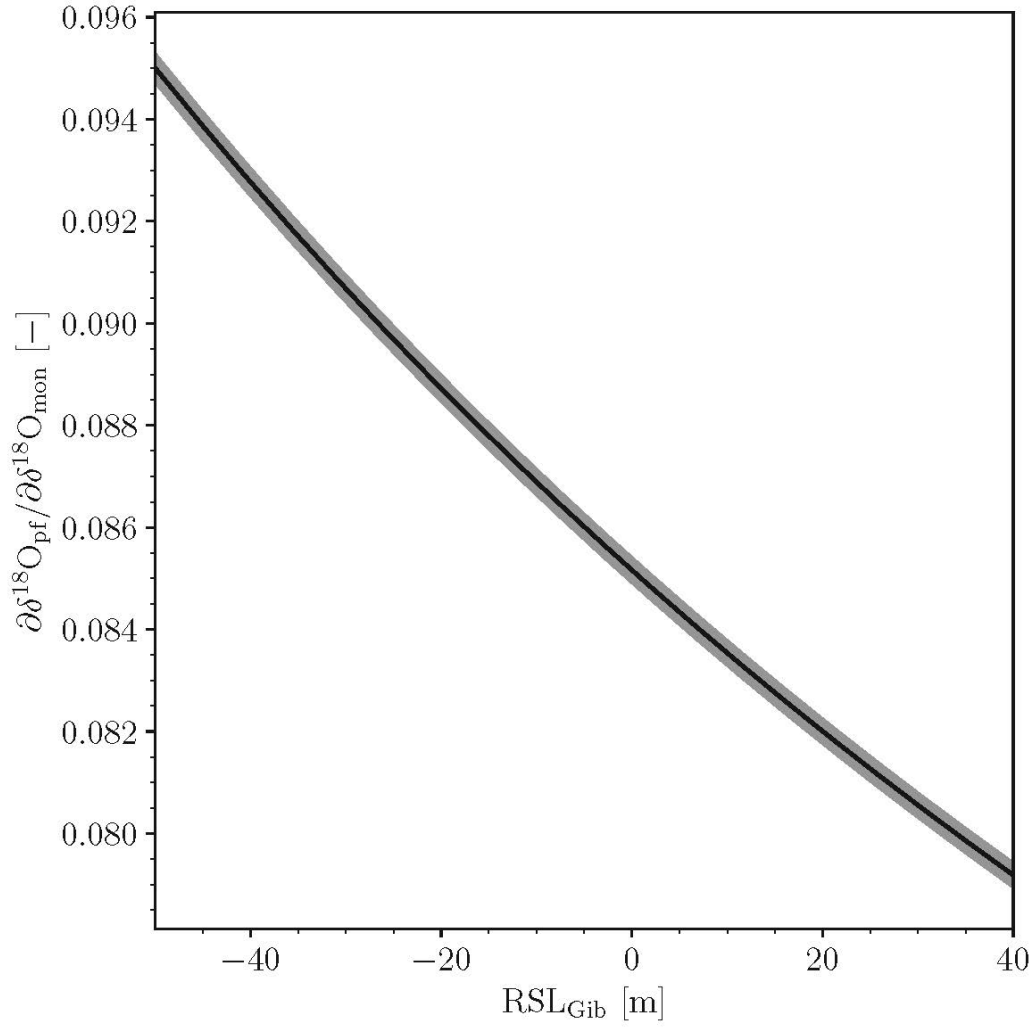


Figure 8. Estimated sensitivity of $\delta^{18}\text{O}_{\text{pf}}$ to changes in the $\delta^{18}\text{O}$ of monsoon fresh water runoff into the Mediterranean Sea. Sensitivities were estimated numerically using the described Winter-Summer-Monsoon box model. Uncertainties were assessed via a Monte Carlo scheme, with the standard error on the sensitivity estimates shown by the shaded interval.

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CHAPTER 5

A 0.5 million-year North African humid period within the Pliocene

This chapter is under review in Nature Geoscience

This chapter investigates an anomalously lengthy phase of sapropel absence in the eastern Mediterranean sediment record. Climate modelling combined with a proxy data compilation, reveals the existence of a half-million-year long Pan-North African humid period during the Pliocene, that facilitated the earliest known hominin migration to the Chad basin from East Africa.

Statement of Contribution

This thesis is submitted as a Thesis by Compilation in accordance with
https://policies.anu.edu.au/ppi/document/ANUP_003405

I declare that the research presented in this Thesis represents original work that I carried out during my candidature at the Australian National University, except for contributions to multi-author papers incorporated in the Thesis where my contributions are specified in this Statement of Contribution.

Title and authors: **Amarathunga, U.**, Rohling, E. J., Francke, A., Grant, K.M., Meijer, P.T., Hutchinson, D., Dosseto, A., Latimer, J. A Pan-North African humid period of the Pliocene

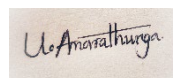
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Contribution to paper: U.A. designed and led the study, prepared samples for Li and Nd isotope analyses, analyzed the data and climate model outputs, developed the hypothesis, generated the figures and wrote the paper; A.F. and A.D. carried out Li and Nd isotope analyses; D.Hu. generated the climate model ice sheet configurations and performed the modelling experiments; D.He. advised on statistical analyses; K.M.G and J.L helped with sample selection and preparation; E.J.R. advised on data interpretation; all authors contributed to manuscript development.

Senior author or collaborating authors endorsement: _____



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1 May 2023

Chair of Supervisory Panel – Print Name

Signature

Date

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1 May 2023

Delegated Authority – Print Name

Signature

Date

A 0.5 million-year North African humid period within the Pliocene

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Past African humid periods resulted in expanded vegetation over the Sahara, due to northward tropical African rainbelt displacement, opening new migration pathways for hominins^{1–5}. Commonly, these precession-timed African humid periods ended within 15 thousand years due to rainbelt retreat^{6,7}. Eastern Mediterranean organic-rich layers (sapropels) reflect African humid periods, at least back to 8 Myr^{ref.5}. Here we combine climate modelling with new and published proxy data to show that weakened sapropel preservation during the warm 5.3–3.3 Myr period^{8,9} resulted from nutrient runoff limitation associated with enhanced North African vegetation cover due to a persistently more northward-located African monsoon front, relative to the mid-Pliocene (3.3–3.0 Myr, when glacial intensity increased). We find that sapropel absence between 3.8 and 3.3 Myr coincided with maximum long-term monsoon flooding and landscape stabilization by extension of humid, vegetated conditions throughout North Africa. Our model results indicate that this 0.5-Myr-long Pan-North African humid period (Pan-NAHP) ended at ~3.3 Myr because of southward African monsoon front displacement with the initiation of major Northern Hemisphere glaciations. The 3.8–3.3 Myr Pan-NAHP coincided with notable hominin diversity expansion over Eastern and central North Africa¹⁰. We posit that persistent green

corridors during the Pan-NAHP facilitated the earliest known hominin migration to the Chad basin¹¹, ~2,500 km to the west of their East African origin.

Main

North Africa (the present-day Sahara) has experienced astronomical precession controlled wet-dry cycles for at least the past 11 million years (Myr)¹². The wet episodes, known as Green Sahara Periods (GSPs) or African Humid Periods (AHPs), resulted from northward migration of the tropical African rainbelt during periods of increased boreal summer insolation^{2,13}. Periodic occurrence of AHPs modified North African hydrology, leading to establishment of vast fluvial systems consisting of interconnected lakes, rivers, and inland deltas^{2,3,14}. Consequently, savannah vegetation expanded over much of the currently hyper-arid landscape north of the Sahel^{5,6}. Expanded vegetation led to development of ‘green corridors’, that enabled migration of hominins and other animals northward of the Sahel, into the otherwise inhospitable desert landscape³⁻⁵. AHPs terminated within 8-15 thousand years as the African rainbelt retreated equatorward, progressively re-establishing hyper-arid conditions over the Sahara^{1,5-7}.

More recent AHPs (notably, the last AHP; 14.8-5.5 thousand years ago) have been studied using both terrestrial and marine geological records^{2,6,14}. However, onshore fossil and environmental evidence of AHPs is increasingly rare going back through time⁵. Occurrence of AHPs through the past few million years is best documented offshore in the eastern Mediterranean sedimentary record, in the form of organic-rich layers known as sapropels^{2,5}. Thus, the presence of Mediterranean sapropels is an important tracer of past AHPs back to the Late Miocene, which enables identification of over 230 humid episodes during the past ~8 Myrs⁵.

A 5.3-Myr eastern Mediterranean sapropel compilation indicates a phase of infrequent, irregular sapropel deposition from 5.3 to 3.3 Myr, with an absence of preserved sapropels between 3.7 and 3.3 Myr. This Early Pliocene phase of sporadic sapropel preservation terminated with initiation of Northern Hemispheric (NH) glacials at ~3.3 Myr (Fig. 1, Fig. 2, Extended Data Fig. 1). Here we investigate the nature and termination of this interval using new and compiled environmental proxy data that we interpret with targeted climate modelling scenarios. We then consider potential wider implications with respect to African landscape development, initiation of major northern hemisphere glaciation, and hominin evolution.

Eastern Mediterranean sapropel record

Sapropel formation during AHPs was driven by enhanced monsoon runoff to the Mediterranean via the Nile River and along the wider North African margin, during NH insolation maxima (precession minima)^{15,16}. Strong evidence for enhanced freshwater flux within sapropels is imprinted as distinct negative anomalies in stable oxygen isotope ($\delta^{18}\text{O}_{\text{Calcite}}$) measurements of surface-dwelling (planktonic) foraminiferal calcium carbonate shells^{16–18}. Enhanced monsoon runoff supplied nutrients that increased primary productivity, and curtailed deep water ventilation due to surface-water buoyancy increase, which together led to preservation of sinking organic matter^{16,19}. However, not every precession minimum resulted in sapropel formation¹⁶. Instead, sapropels commonly formed as clusters during intervals of high-amplitude precession minima¹⁶, related to orbital eccentricity maxima.

Eastern Mediterranean Ocean Drilling Program (ODP) sites provide a sapropel record back to the Miocene/Pliocene boundary^{8,9,20}. Here we compile the main deep basin sediment records (ODP sites 964, 966, 967, 969) to generate a stack of preserved sapropels through the past 5.3 Myr (Fig. 1, Extended Data Fig. 1). We observe that sapropels are significantly less frequently preserved before 3.3 Myr, than afterwards. This pattern corroborates a suggestion based on ODP Site 967 geochemical records alone⁸ (Fig. 1, Extended Data Fig. 1) that, after 3.2 Myr, an increase in the North African arid:humid contrast between AHPs and intervening dry intervals within each precession cycle gave rise to a more erodible landscape during arid periods⁸. Higher erosion rates during dry intervals would have resulted from minimized vegetation cover, leading to landscape instability and an increase in nutrient release. Increased nutrient discharge into the Mediterranean by monsoon runoff during subsequent humid intervals then resulted in enhanced productivity and, thus, increased organic carbon burial⁸. However, no mechanism was established to explain the inferred aridity increase during North African dry periods after ~3.2 Myr.

Climate modelling results: termination of Early Pliocene humid conditions

We find that eastern Mediterranean organic carbon burial intensification at 3.2 Myr followed initiation of NH glaciation across the 3.4–3.2 Myr interval (M2 glaciation at ~3.3 Myr)²¹. We observe increased mid-Pliocene (3.3–3.0 Myr) glacial ice volumes relative to the Early Pliocene, following a rapid ice volume increase during the M2 glaciation²¹ (Fig. 1, Extended Data Fig. 2). We hypothesize that the North African landscape changes that led to the observed change in

sapropel preservation around 3.3 Myr may have resulted from NH glacial intensification. To explore North African landscape/climate evolution before and after the M2 glaciation, we perform climate model simulations focussed on contrasting ice volumes (based on published ice volume reconstructions²¹) during the Early Pliocene (5.3-3.4 Myr), the M2 glaciation, and subsequent mid-Pliocene glacials (Methods, Extended Data Table 1).

Polar ice sheet growth strengthens lower atmospheric meridional temperature gradients, resulting in more vigorous meridional atmospheric circulation cells, and changing precipitation patterns^{22,23}. Accordingly, our climate model results indicate that NH meridional atmospheric circulation strengthened considerably, as polar ice sheets expanded during the M2 glaciation (Fig. 2, Methods). Over North Africa, stronger meridional circulation manifests during boreal summer in intensification of subsidence over the Mediterranean, and ascent over the Sahel. Importantly, we observe a 2°-3° southward shift of the 850 hPa easterly-westerly wind convergence zone over North Africa, which implies a southward displacement of the African monsoon front due to NH polar cooling^{23,24} (Extended Data Fig. 3). Our interpretation is supported by a notable decrease of 600 hPa ascent at ~20°N beyond the Sahel. Consequently, North African precipitation markedly decreases during the M2 glaciation, relative to the Early Pliocene (Fig. 2). Furthermore, we find that similar (albeit less intense) dry conditions occurred also during subsequent, less-intense mid-Pliocene glacials (Extended Data Fig. 4). We observe similar zonal wind and precipitation variability patterns, with less severity than during the M2 glacial. Thus, enhanced aridity and sediment erodibility during North African dry phases (insolation minima, which were largely contemporaneous to NH glacials) since 3.3 Myr may have increased nutrient discharge during subsequent humid phases, and thus favoured sapropel preservation. Conversely, more persistently humid conditions associated with reduced NH ice volumes before 3.3 Myr may have reduced North African erodibility during relatively arid phases, limiting the probability of sapropel preservation.

A notable shift to more positive long-term mean planktonic foraminiferal $\delta^{18}\text{O}_{\text{Calcite}}$ between 3.4 and 3.2 Myr at ODP Site 967 offers evidence for decreased long-term mean freshwater runoff to the Mediterranean. We observe generally more negative long-term mean $\delta^{18}\text{O}$ values through the Early Pliocene (before 3.4 Myr) compared to the period afterward. However, there is a clear long-term shift of ≥ 0.3 ‰ to even more negative $\delta^{18}\text{O}_{\text{Calcite}}$ values at ~3.8 Myr, which lasted until the

M2 glaciation (Fig. 3, Extended Data Fig. 2); the 3.8-3.3 Myr period contains the most negative long-term $\delta^{18}\text{O}_{\text{Calcite}}$ values since the Miocene. We do not observe a corresponding global ice volume shift, which suggests that the 3.8-3.3 Myr low $\delta^{18}\text{O}_{\text{Calcite}}$ values reflect a freshwater-borne anomaly for the Pliocene (i.e., freshwater amount and/or freshwater $\delta^{18}\text{O}$)^{17,18} (Fig. 1, Fig. 3, Extended Data Fig. 2). While individual $\delta^{18}\text{O}$ maxima (which indicate non-sapropel/arid intervals during precession maxima) reached similar values ($\sim 1\text{‰}$) during the 5.0-3.8 Myr and 3.3-3.0 Myr intervals, even individual $\delta^{18}\text{O}$ maxima were more negative ($\sim 0\text{‰}$) within the 3.8-3.3 Myr interval. To estimate a possible range of mean freshwater runoff increase that could have generated the observed $\geq 0.3\text{‰}$ shift to negative $\delta^{18}\text{O}$ at 3.8 Myr, we employed a Mediterranean box model (Methods). Our sensitivity tests indicate that an increase of up to 1.6 times the pre-Aswan Nile runoff can generate such a shift to generally more negative $\delta^{18}\text{O}$ values (Extended Data Fig. 2).

Observation-based Pan-North African humid period

We find that the longest period of preserved sapropel absence extends within the ~ 3.7 -3.3 Myr interval (with only two sapropels with low organic carbon contents at 3.8-3.7 Myr), even though a high-amplitude precession cluster exists within this period, centred at ~ 3.5 Myr (Fig. 3, Methods). This is a clear anomaly within an otherwise predictable sapropel preservation pattern in relation to insolation. Despite $\delta^{18}\text{O}$ values being more negative across the 3.8-3.3 Myr interval (indicative of elevated freshwater runoff), the absence of preserved sapropels suggests even lower eastern Mediterranean productivity (lower nutrient runoff due to further reduced North African erodibility) than during the rest of the Early Pliocene.

Core-scanning X-ray fluorescence (XRF) data corroborate our interpretations of enhanced freshwater runoff, and decreased erodibility over North Africa. In eastern Mediterranean sediments, the Ti/Al ratio is an established indicator of relative aeolian *versus* fluvial input^{8,16}. Low long-term earliest Pliocene mean Ti/Al values gradually increase to a maximum at ~ 3.9 Myr, followed by an abrupt return to lower values at ~ 3.8 Myr (Fig. 3). This supports our $\delta^{18}\text{O}_{\text{Calcite}}$ interpretation of a shift to higher relative fluvial input at ~ 3.8 Myr. Lower Ti/Al values are then maintained until ~ 3.3 Myr (M2 glaciation), where values increase again afterwards. Our data also indicate that the 3.9-3.8 Myr shift toward lower Ti/Al values occurred during both the alternating humid (sapropel) and dry (marl) intervals (Extended Data Fig. 5b), whereas the shift to higher

Ti/Al values at ~3.3 Myr mainly occurred due to increasing aridity in dry intervals (Extended Data Fig. 5).

The Nile River is the primary fluvial sediment source to the modern eastern Mediterranean^{25,26}. Sediment provenance analysis and end-member modelling of modern eastern Mediterranean sediments indicate that most Nile River terrigenous input originates from the Ethiopian Highlands in East Africa^{25–27}. The major aeolian dust input into the eastern Mediterranean originates from central Libya in North Africa²⁸. Nd isotope data for eastern Mediterranean sediment provenance indicate that terrigenous sediment sources were persistently in Northeast and East Africa across sapropel-marl cycles of the past 110,000 years (ϵNd within -1 to -8)²⁷. To evaluate if eastern Mediterranean sediment source regions changed considerably through the past 5 Myr, we present new Nd isotope values of the Site 967 sediment clay fraction (Fig. 3c). The ϵNd for sapropels ranges within a narrow window of -4.3 to -6.7, which implies little provenance change through time. This range also agrees with that found in Late Quaternary sapropels (approximately -3 to -7)²⁷, and likely represents sediments originating mainly from the Blue Nile (Ethiopian Highlands)²⁶ (Fig. 3, Extended Data Fig. 6). Within intercalated marls, ϵNd ranges between -4.0 and -8.4, where more negative values might indicate higher relative Central Sahara (-10 to -15) or White Nile (ϵNd ~-10) contributions^{26,27,29} (Fig. 3, Extended Data Fig. 6). Thus, our data indicate that eastern Mediterranean terrigenous sediment sources remained confined largely to North-central and Northeast-East African regions through the past 5 Myr.

Off the coast of Northwest Africa, ODP Site 659 provides the longest available Saharan aridity and dust export record, which demonstrates astronomically paced northwestern Saharan humid-dry oscillations over the past 11 Myr¹². ODP Site 659 is located underneath the main modern Sahara dust plume, where most of the aeolian input originates from the West and Central Sahara (North-West to North-Central Africa)¹² (Extended Data Fig. 6). For ODP Site 659, the $[\text{Al}+\text{Fe}]/[\text{Si}+\text{Ti}+\text{K}]$ ratio was used as an indicator of relative fluvial *versus* aeolian sediment input from Northwest Africa (higher values indicate more humid conditions with more intense chemical weathering). Intriguingly, there is a shift to increased fluvial input in ODP Site 659 at ~3.8 Myr, similar to that observed here at ODP Site 967. The $[\text{Al}+\text{Fe}]/[\text{Si}+\text{Ti}+\text{K}]$ ratio decreases rapidly at the M2 glaciation, which reflects termination of the enhanced humid conditions of the 3.8–3.3 Myr period (Fig. 3b, Extended Data Fig. 6). Moreover, our 2 lowest Pliocene ϵNd values appear within

the sapropel-barren interval, indicating likely increased terrigenous input from sustained central Saharan palaeoriver discharge during precession maxima (continuing humid conditions even during the relatively arid intervals), through the Northeast African margin to the Mediterranean (Fig. 3, Extended Data Fig. 6). Simultaneous emergence of enhanced humid conditions across Northwest, North-central and Northeast Africa implies the existence of a Pan-North African humid period (Pan-NAHP) between 3.8 and 3.3 Myr.

Our observation of enhanced humidity during the Pan-NAHP, relative to the entire Early Pliocene, is supported by additional East and Northcentral African geological records. East African rift system (EARS) lake clusters were coeval to eastern Mediterranean sapropel clusters during high amplitude precession minima^{5,30–33} (Fig. 4). Notably, deep EARS lake clusters existed in the Turkana and Afar basins between 3.7 and 3.4 Myr, indicating substantially increased humidity^{31–33} (Fig. 4b). Palaeoenvironmental reconstructions using fossil assemblages estimated ~doubled precipitation during deposition of the Lokochot member (3.6–3.4 Myr) of the Koobi Fora Formation, eastern Lake Turkana shores, relative to the Early Pliocene³⁴. In agreement, past woody cover reconstructions using fossil soils reveal maximum woody cover in the Omo-Turkana Basin and Awash Valley (Afar Basin) for the past 6 Myr at 3.6–3.4 Myr³⁵ (Fig. 4c). Moreover, megalake Chad in North-central Africa is the dominant hydrological feature recognized during past AHPs^{5,36}. Analysis of Chad basin environmental conditions using Be isotopes reveals that Plio-Pleistocene lacustrine sediment deposition centred at $\sim 2.31 \pm 0.21$ Myr, 3.00 ± 0.19 Myr, 3.60 ± 0.13 Myr and 4.20 ± 0.19 Myr³⁶, with maximum Pliocene sedimentation rates reached between 3.7 and 3.4 Myr, which has been attributed to enhanced runoff intensity under humid conditions³⁷ (Fig. 4b). In summary, North-central and East African lacustrine records indicate that the coevally wettest Pliocene phase of these regions occurred simultaneous to the Pan-NAHP identified here.

Wider implications and possible influence on early hominin dispersal

Our climate model results indicate that generally humid conditions over North Africa before 3.3 Myr resulted from a persistently more northerly monsoon front, relative to the mid-Pliocene, which enhanced precipitation over the Sahara and Ethiopian Highlands (Fig. 4e). Our results support previous suggestions of globally coherent humid subtropics through the warm Early Pliocene, due to decreased global meridional temperature gradients³⁸. Moreover, we find that the long-term North Atlantic meridional temperature gradient decreased stepwise since ~ 3.9 Myr, culminating

in lowest values at 3.6-3.4 Myr. North Atlantic warmth is reflected by reduced NH ice volumes and elevated global sea levels during the Pan-NAHP^{39,40} (Extended Data Fig. 7). We postulate that reduced meridional temperature gradients during the Pan-NAHP, compared to the rest of the Pliocene, may have optimized northward tropical African monsoon front displacement, yielding more humid conditions over North Africa^{13,41}.

Finally, our findings provide new insights into environmental changes associated with African early hominin evolution and dispersal. Multiple hominin species are thought to have coexisted during the 3.7-3.3 Myr period (within the Pan-NAHP identified here); the so-called ‘Pliocene hominin diversity conundrum’^{10,42} (Fig. 4, Extended Data Fig. 8). In addition to the East African species *Australopithecus afarensis*, different species were distinguished based on their locomotor adaptation and diet, from several fossil sites including the Turkana and Afar basins^{10,42,43}. *Australopithecus bahrelghazali* from the Chad Basin (3.58±0.27 Myr)^{10,11,36} was contemporaneous to the East African australopithecines (Fig. 4, Extended Data Fig. 8), although it remains ambiguous whether *A. bahrelghazali* was a geographical variant within the *A. afarensis* taxon, or a different species^{44,45}. While periods of enhanced humidity are associated with increasing hominin habitat suitability beyond the Sahel, hydrological modelling demonstrates that the probability of along-rift hominin dispersal increases under more humid conditions^{46,47}. Accordingly, it has been proposed that stable Pliocene climate periods (with major lake phases) provided vegetated corridors for early hominins to migrate out of east African refuge areas to the adjacent rift valleys and beyond³³. Our analysis here suggests that simultaneous major Central and East African Lake phases, together with maximum woody cover (reaching 60%) to the North of Turkana Basin³⁵, occurred only during the Pan-NAHP (Fig. 4). Therefore, we infer that the 3.8-3.3 Myr Pan-NAHP reconstructed here facilitated the earliest known hominin migration to the Chad basin, some 2,500 km west of their habitats in East Africa, likely via enduring green corridors connecting open East African habitats with North African Savannah³³ (Extended Data Fig. 8).

Methods

Eastern Mediterranean sapropel compilation

To generate the sapropel stack, we combine sapropel stratigraphies of all available deep eastern Mediterranean Ocean Drilling Program (ODP) sites, which were tuned to NH boreal insolation maxima and subsequently correlated with our ODP Site 967 stable oxygen isotope record. All available ODP sediment records are located at >900 m water depths^{8,20} (Extended Data Fig.1).

At shallower than ~400 m depth in the eastern Mediterranean, sapropels are unlikely to be preserved due to sufficiently ventilated conditions^{16,19,48}. Below this level, the organic matter quantity buried in sediment changes with water depth^{19,48}, and is determined by a) the degradation rate during settling through the water column and b) the degradation rate at the sediment-water interface⁴⁸. The organic matter import flux (amount of organic matter reaching the sediment-water interface at a certain depth) decreases with water depth^{19,48}. However, burial efficiency during sapropel formation (amount of organic matter amount buried in sediment, after water column and sediment-water interface degradation) increases with water depth, due to decreasing oxidant fluxes at the sediment-water interface.

Intensification of eastern Mediterranean organic carbon burial over time can be observed at the four ODP sites, which increased substantially the sapropel preservation frequency. At ODP sites 967 and 969, preserved sapropels are absent for 3.2-5.3 Myr and 3.2-4.3 Myr, respectively, which indicates complete post-depositional oxidation. Before 3.2 Myr, nutrient supply to the eastern Mediterranean was likely substantially reduced⁸. Therefore, we suggest that low organic carbon fluxes to the deep basin were insufficient to generate preserved sapropels during these intervals. Occasional sapropel preservation can be observed at Site 969, before 4.3 Myr. At ODP Site 966, the sediment record is tectonically disturbed within the 5.3-4.5 Myr interval⁴⁹. Between 4.5 and 3.8 Myr, Site 966 sapropel preservation is frequent, compared to Site 969²⁰. We interpret this to be a result of the organic carbon import decrease to deeper water depths at Site 969, which was insufficient for organic carbon burial. Between 3.70 and 3.82 Myr, there are only two preserved sapropels at Site 966, with low (~1%) organic carbon contents. Therefore, preserved sapropels are absent across the entire eastern Mediterranean ODP cores within the 3.3-3.7 Myr period (while only two low-organic carbon sapropels are observed between 3.7 and 3.82 Myr, only at Site 966)^{8,20,49}. We posit that organic matter imported to even the shallowest eastern Mediterranean site

(Site 966 at ~940 m water depth) was insufficient for sapropel preservation during the 3.3-3.7 Myr period, which indicates even more reduced surface productivity compared to the Early Pliocene.

Climate Model Experiments

We observe a considerable mean global ice volume increase during the M2 glaciation and subsequent Mid-Pliocene glacials, compared to the Early Pliocene. Pan-NAHP termination is coeval with the M2 glaciation (~3.34-3.27 Myr), and eastern Mediterranean organic carbon burial intensifies subsequently. We calculate mean ice volumes for Early Pliocene and Mid Pliocene glacials using a published ice volume reconstruction²¹ (Extended Data Table 1). Our calculations indicate that NH ice volume increased significantly more, compared to the Southern Hemisphere (SH), during the M2 glaciation. As explained in the text, we speculate that the ice volume increase disrupted stable humid conditions during the Pan-NAHP (and relatively humid conditions through the 5.3-3.3 Myr period). To evaluate the possible impact of increasing ice volumes on North African climate, we employed a coupled climate model, as described below.

Model components. Model experiments were carried out using the coupled climate model GFDL CM2.1, which consists of dynamic ocean, atmosphere, land and sea ice components⁵⁰. The ocean component is updated to incorporate Modular Ocean Model version 5.1.0 (MOM5), using a resolution of 1° latitude x 1° longitude x 50 vertical levels, with latitudinal refinement within ± 30° latitude down to 0.33° at the equator, as in ref.⁵⁰. The ocean and sea ice horizontal grid uses a tripolar configuration, consisting of a regular latitude-longitude grid from 85°S to 65°N, and a bipolar grid north of 65°N with poles over North America and Eurasia. The other model components are the same as in GFDL CM2.1, namely the GFDL Atmosphere Model 2, Land Model 2 and Sea Ice Simulator. The atmosphere resolution is 2° latitude x 2.5° longitude x 24 levels, as in the original GFDL CM2.1.

Boundary conditions. In this study, we use three experimental configurations, representing (i) the Early Pliocene (5.3-3.4 Ma), (ii) the M2 glaciation (~3.3 Ma) and (iii) Mid Pliocene glacials (3.27-3.0 Ma). A summary of these configurations is shown in Extended Data Table 1. The Early Pliocene simulation serves as a control experiment, where our intention is to compare results from glacial simulations with the Early Pliocene reference simulation.

Early Pliocene simulation. The early Pliocene simulation is set up using PRISM4 boundary conditions, as used in the Pliocene Model Intercomparison Project 2 (PlioMIP2)⁵¹. The palaeogeography, including topography and bathymetry, ice sheet extents, and vegetation types are all set according to the PRISM4 protocol.

The M2 glacial and Mid Pliocene glacial simulations use PRISM4 boundary conditions as a starting point, with modifications to the ice sheets to match the total ice volume from the compilation of ref.²¹. The chosen timeslices of published ice sheet reconstructions represent a physically realistic representation of a target ice volume, rather than an exact Pliocene ice sheet reconstruction. We note that a similar approach of reconstructing ice boundary conditions was used in the Pliocene modelling experiments of ref.⁵², where they used ice model reconstructions from different time periods to match their targeted ice volume for the Pliocene M2 scenario.

M2 glacial simulation. For the M2 glacial simulation, NH and SH ice sheets were derived from 12.5 kyr and 7.5 kyr timeslices of the ICE-7G_NA reconstruction⁵³, to match total ice volumes calculated for each hemisphere (NH = 52.13 m, SH = 62.16 m).

Mid Pliocene glacial simulation. For this case, we imposed NH ice sheets derived from the ice sheet reconstruction of ICE-7G_NA using their 8 ka timeslice⁵³, to achieve a total ice volume of 10.17 m sea level equivalent (SLE). For the SH, we used ref.⁵⁴, with their RCP4.5 scenario at year 5000 to achieve a total ice volume of 55.32 m SLE.

Initial conditions and spinup. Climate model runs were initiated using idealised ocean temperature and salinity initial conditions. Salinity was set to a uniform global value of 34.7 psu. Initial temperature was constructed using (i) surface sea surface temperature (SST) values from the PRISM4 dataset, (ii) a uniform deep ocean 6 °C value everywhere below 500 m depth, and (iii) linear interpolation between 0 and 500 m from the PRISM4 SST and deep ocean temperatures. The deep ocean value was chosen to be slightly warmer than the anticipated equilibrium to enable the start of deep ocean circulation that tends to initiate when the ocean is losing heat. Atmosphere and land components were initiated using a “cold start” condition. These components have a much lower heat capacity than the ocean, so they quickly reach quasi-equilibrium and the long-term spinup depends largely on ocean evolution. All three simulations were spun up from idealised initial conditions for 2000 years, using CO₂ forcing demarcated in Extended Data Table 1. The

analyses use the mean of the last 50 years of simulation to reduce the impact of short-term variability.

ODP Site 967 Nd isotopes

To evaluate sediment provenance at ODP Site 967 over the past 5 Myr, we measured Nd isotope values of the clay fraction of selected bulk sediment samples. Samples were chosen for consecutive sapropel-marl couplets covering the entire 0-5 Myr age range (Extended Data Fig. 6). Sample preparation was carried out at the Fenner School of Environment & Society, Australian National University. The procedure involved clay separation to separate aeolian silt, followed by ultrasonic leaching to remove non-detrital matter as outlined in ref.⁵⁵.

To separate the clay fraction from bulk sediment, ~1.5-2.5 g of each sample was gently crushed with an agate mortar and pestle. Each crushed sample was treated with a 5% NaPO₃ solution in a 50 ml centrifuge tube, and then kept on a mixing wheel overnight to prevent clay flocculation. The next day, the samples were centrifuged at 1,000 rpm for 360 seconds to separate the clay and silt fractions. The supernatant was decanted into a separate vial and centrifuged at 4,000 rpm to recover the clay fraction. This procedure was repeated 4-5 times for the remaining bulk sediments to extract as much clay as possible from each sample.

Sequential leaching involved initially mixing the separated clay fraction with ~8 ml of H₂O at room temperature to remove the water soluble fraction. Samples were then centrifuged at 4,000 rpm to remove the supernatant solution. All samples were subsequently treated with 0.5 M Mg(NO₃)₂ solutions at room temperature (to remove the exchangeable fraction, i.e. cations adsorbed to mineral surfaces), 1 M CH₃COONa at room temperature (to remove the acid-soluble fraction such as carbonate, with sonication at room temperature for 5 minutes, repeated 3 times), 0.1 M NH₂OH·HCl at 80 °C (to remove reducible fraction such as Fe and Mn oxides, with sonication at 80°C for 6 minutes, repeated 3 times), 15% H₂O₂-0.02 M HNO₃ at 80 °C (sonication at 80°C for 3 minutes, repeated 5 times) and 3.2 M CH₃COONH₄ in 20% HNO₃ at room temperature (centrifuged at 4000 rpm for 10 minutes, repeated three times, to remove oxidisable fraction such as organic matter and sulphides), successively. Sequential leaching was supported by sonication following the procedure elaborated in ref.⁵⁵.

Dried samples were analysed for Nd isotope values at the Mawson Analytical Spectrometry Services (MASS) at the University of Adelaide (UoA). Following grinding, complete HF sample dissolution, and column exchange chromatography to separate Nd from the sample matrix, Nd isotope analyses were carried out using an ISOTOPX Phoenix thermal ionisation mass spectrometer (TIMS). Nd concentrations in each sample, required to determine the amount of Nd loaded for column exchange chromatography, were analysed using an Agilent 8900x triple quad inductively coupled plasma mass spectrometer (QQQ-ICP-MS) at Adelaide Microscopy (UoA). All Nd isotope ratios were normalized to the JNdi-1 standard ($^{143}\text{Nd}/^{144}\text{Nd} = 0.512115 \pm 0.000007$), with independent measurements of JNdi-1 = 0.512121 ± 0.000006 (2σ , $n=2$). Isotopic signatures are expressed in epsilon notation, relative to the chondritic uniform reservoir value of 0.512638.

Mediterranean box model experiments

To estimate the freshwater input magnitude capable of generating a minimum shift of $\sim 0.45\text{‰}$ in ODP Site 967 $\delta^{18}\text{O}_{\text{calcite}}$ to more negative long-term $\delta^{18}\text{O}_{\text{calcite}}$ values, a Mediterranean Winter-Summer-Monsoon box model was employed (Extended Data Fig.2). The box model employed here is based on a family of models developed in refs.^{17,18}. The box model is coupled to an exchange transport model with the Atlantic via the Strait of Gibraltar and consists of a winter mixed-layer box, which is subsequently split into a summer-mixed box and a summer-subthermocline box. For two months in late summer a surface layer monsoon box is included into which monsoon freshwater runoff is added. At the end of summer, the summer-mixed, summer-subthermocline, and monsoon boxes are homogenized to form a new winter mixed box. This annual cycle can then be repeated until the model reaches equilibrium under a given fixed forcing scenario.

The Mediterranean box model in ref.¹⁸ employed a $\delta^{18}\text{O}_{\text{calcite}}$ forward modelling strategy to estimate relative sea level at Gibraltar (RSL_{Gib}). In our version of the model, RSL_{Gib} is a forcing parameter, which was estimated from the global mean eustatic sea-level (ESL) record of ref.²¹ based on the RSL_{Gib} to ESL conversion of ref.¹⁸. Thus, if the key properties of the model boxes, such as temperature, salinity, and $\delta^{18}\text{O}_{\text{calcite}}$, are fixed while RSL_{Gib} is allowed to change, the mean Mediterranean $\delta^{18}\text{O}_{\text{calcite}}$ change solely due to RSL_{Gib} changes can be separated from the initial

$\delta^{18}\text{O}_{\text{calcite}}$ record. This enables the model to be used in a sensitivity analysis to differentiate potential underlying causes of large-scale changes in ODP Site 967 $\delta^{18}\text{O}_{\text{calcite}}$.

Mediterranean surface freshening during times of sapropel formation lead to negative $\delta^{18}\text{O}_{\text{calcite}}$ anomalies due to both 1) isotopically depleted monsoon waters and 2) temperature concentration due to freshwater layer heating⁵⁶. It is not possible to determine the contribution from monsoon waters alone, without temperature measurements from surface-dwelling foraminifera⁵⁶. Therefore, to estimate the possible range of freshwater runoff and temperature concentration that would have generated the $\sim 0.45\text{‰}$ shift, we estimate 3 parameters:

$$\Delta\delta^{18}\text{O}_{\text{SST}} = \frac{\partial\delta^{18}\text{O}_{\text{Calcite}}}{\partial\text{SST}}, \quad (1)$$

where $\Delta\delta^{18}\text{O}_{\text{SST}}$ is the $\delta^{18}\text{O}_{\text{calcite}}$ change per 1°C of mean annual sea surface temperature change, at a given RSL_{Gib} , and

$$\Delta\delta^{18}\text{O}_{\text{T}_C} = \frac{\partial\delta^{18}\text{O}_{\text{Calcite}}}{\partial\text{T}_C}, \quad (2)$$

where $\Delta\delta^{18}\text{O}_{\text{T}_C}$ is the $\delta^{18}\text{O}_{\text{calcite}}$ change per 1°C of surface layer temperature concentration, at a given RSL_{Gib} , and

$$\Delta\delta^{18}\text{O}_{\text{FWF}} = \frac{\partial\delta^{18}\text{O}_{\text{Calcite}}}{\partial\Delta\text{R}}, \quad (3)$$

where $\Delta\delta^{18}\text{O}_{\text{FWF}}$ is the $\delta^{18}\text{O}_{\text{calcite}}$ change for a freshwater runoff increment equivalent to pre-Aswan Nile runoff at a given RSL_{Gib} (Extended Data Fig. 2).

Statistical analysis of palaeoclimate proxy records

To detect regime shifts in ODP Sites 967 and 659 geochemical and stable oxygen isotope records, change points were estimated using the MATLAB built-in function ‘findchangepts’, following ref.⁸. Change-points were determined based on ice volume mean and standard deviation; a maximum of three change-points was stipulated as a parsimonious balance between constraining outputs to the most significant changes while allowing a >1 outcome.

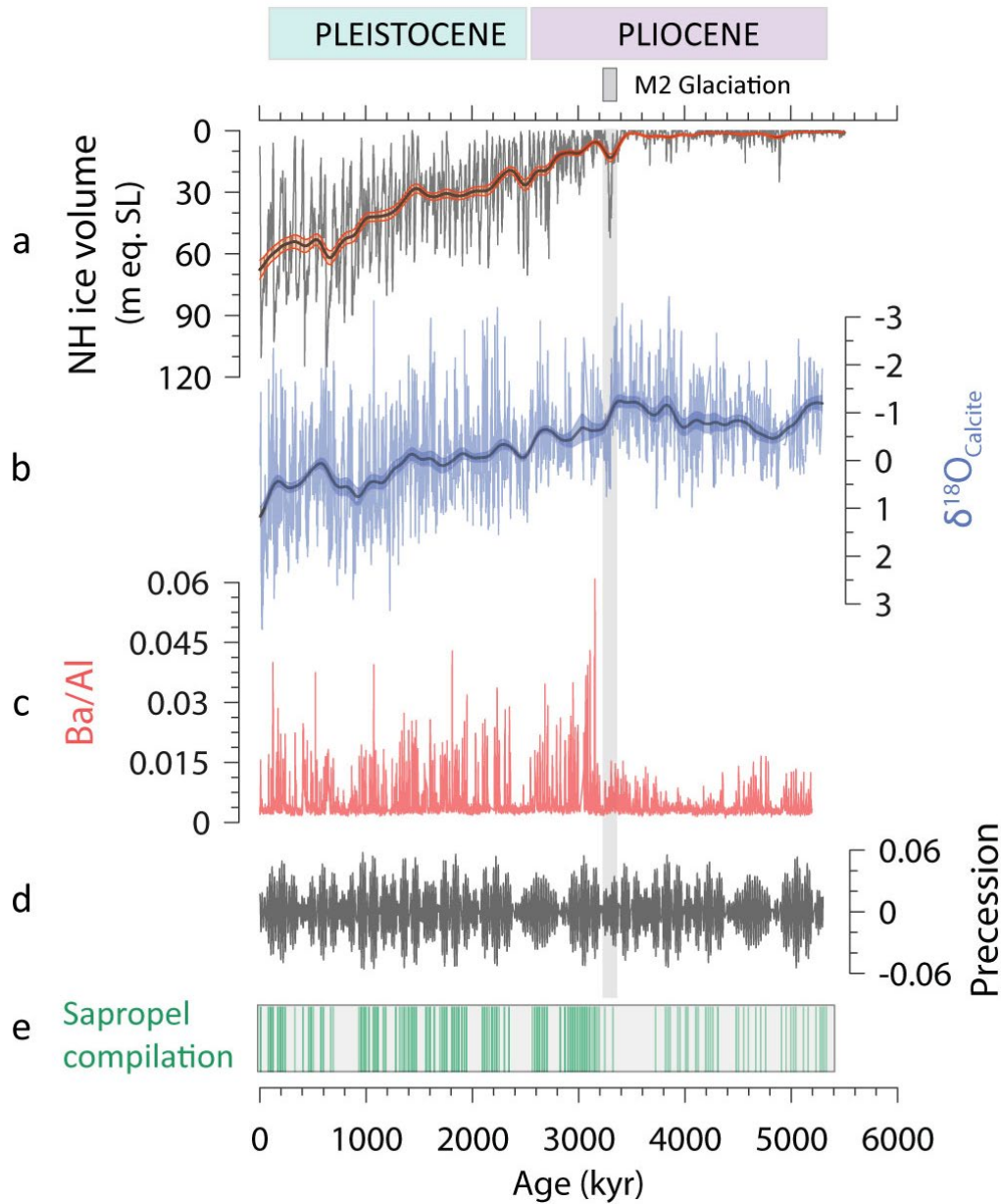


Figure 1| Eastern Mediterranean sapropels across the past 5 Myr **a**, NH ice volume evolution through the Plio-Pleistocene²¹. A rapid ice volume increase during glaciation M2 (~3.3 Myr) is indicated. Mean NH ice volume increases across the shaded transition (3.4-3.2 Myr) **b**, ODP Site 967 stable oxygen isotope record⁸. For **a** and **b**, thick black lines represent a 60-kyr moving average, where upper and lower lobes indicate 95% upper and lower confidence intervals. **c**, ODP Site 967 Ba/Al record, in which enhanced organic carbon burial is evident after 3.2 Myr⁸. **d**, Orbital precession variability through the Plio-Pleistocene. **e**, Eastern Mediterranean sapropel stack (see Methods). Sapropel occurrence is sporadic between 5.3 and 3.3 Myr. No sapropels are preserved within the 3.7-3.3 Myr period, with only two low-organic carbon sapropels existing within the 3.8-3.72 Myr period.

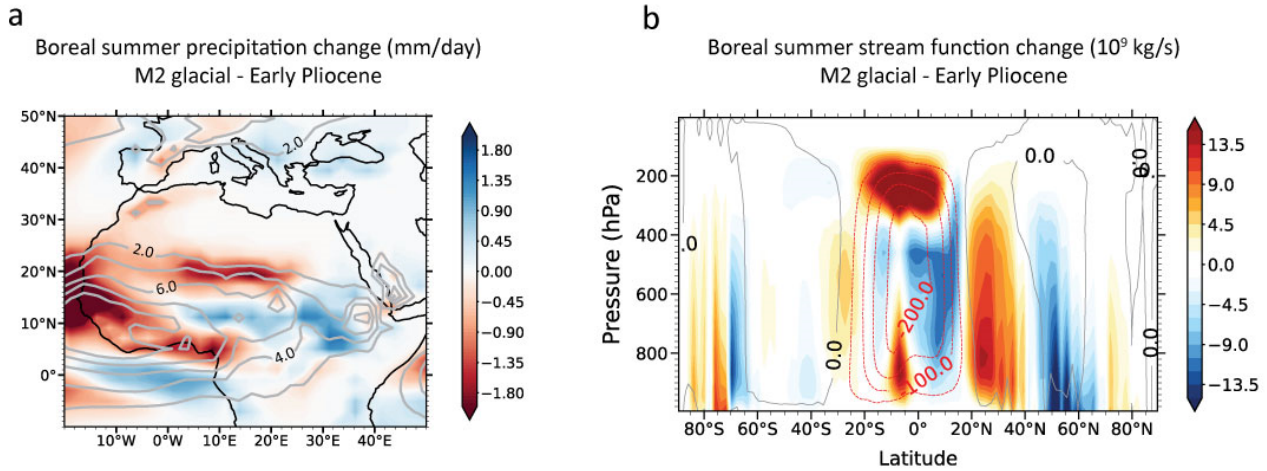


Figure 2| North Africa drying during the M2 glaciation **a**, Boreal summer precipitation change (M2 glacial-Early Pliocene), with strong drying over North Africa. Contours indicate Early Pliocene isohyets. **b**, Zonal mean meridional stream function change for boreal summer. Contours represent Early Pliocene wind velocities. Positive (grey) contour values indicate clockwise overturning circulation; negative (red) contour values indicate anti-clockwise overturning circulation. The Southern Hemisphere Hadley cell strengthens and contracts (with a tropopause height decrease), while all NH meridional cells are strengthened during the boreal summer.

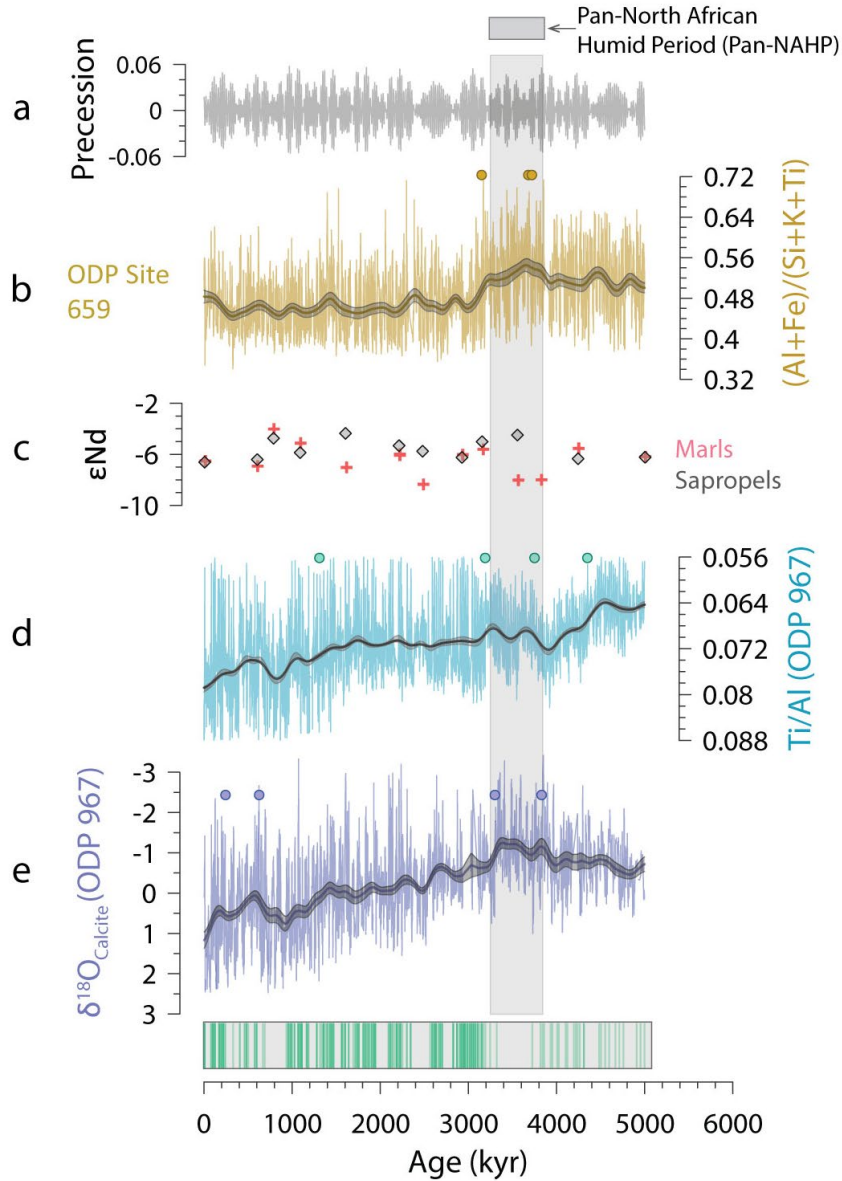


Figure 3| Evidence for enhanced humid conditions across North Africa during the 3.3-3.8 Myr interval. **a**, Orbital precession variability through the Plio-Pleistocene. **b**, West African ODP Site 659 $[Al+Fe]/[Si+K+Ti]$ ratio, where higher values indicate more alluvial sediment input under more humid conditions. **c**, ODP Site 967 ϵNd values for sapropel and marl sediments back to the Miocene-Pliocene boundary (see Extended Data Fig. 6 for provenance). **d**, Eastern Mediterranean ODP Site 967 Ti/Al ratio, where lower values indicate more alluvial sediment input. **e**, ODP Site 967 stable oxygen isotope record, indicating considerably negative mean values across the Pan-NAHP (highlighted in grey). Coloured dots for **b**, **d** and **e** represent linear change points for each record (Methods). Eastern Mediterranean sapropel stack is shown above the age axis. More extreme individual data points are not shown. See Extended Data Fig. 5 for complete range of data for each record.

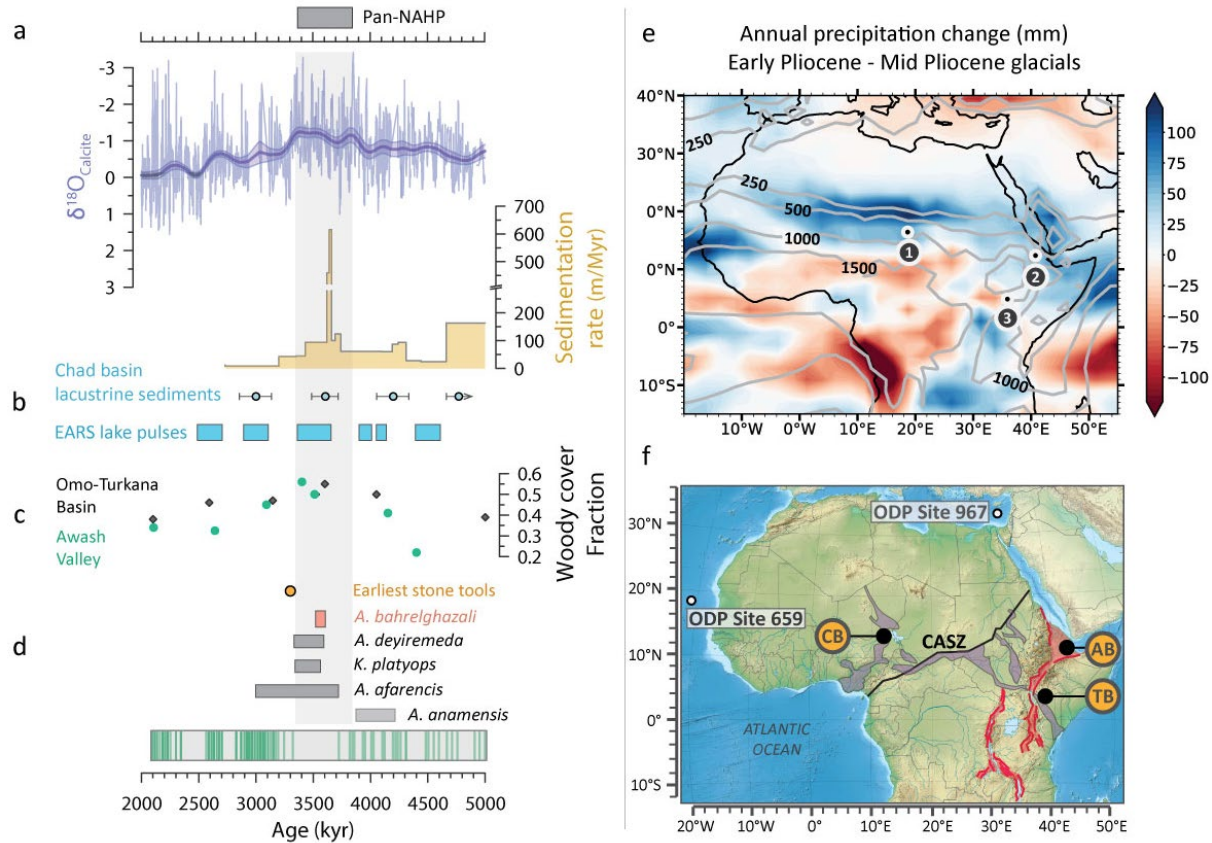
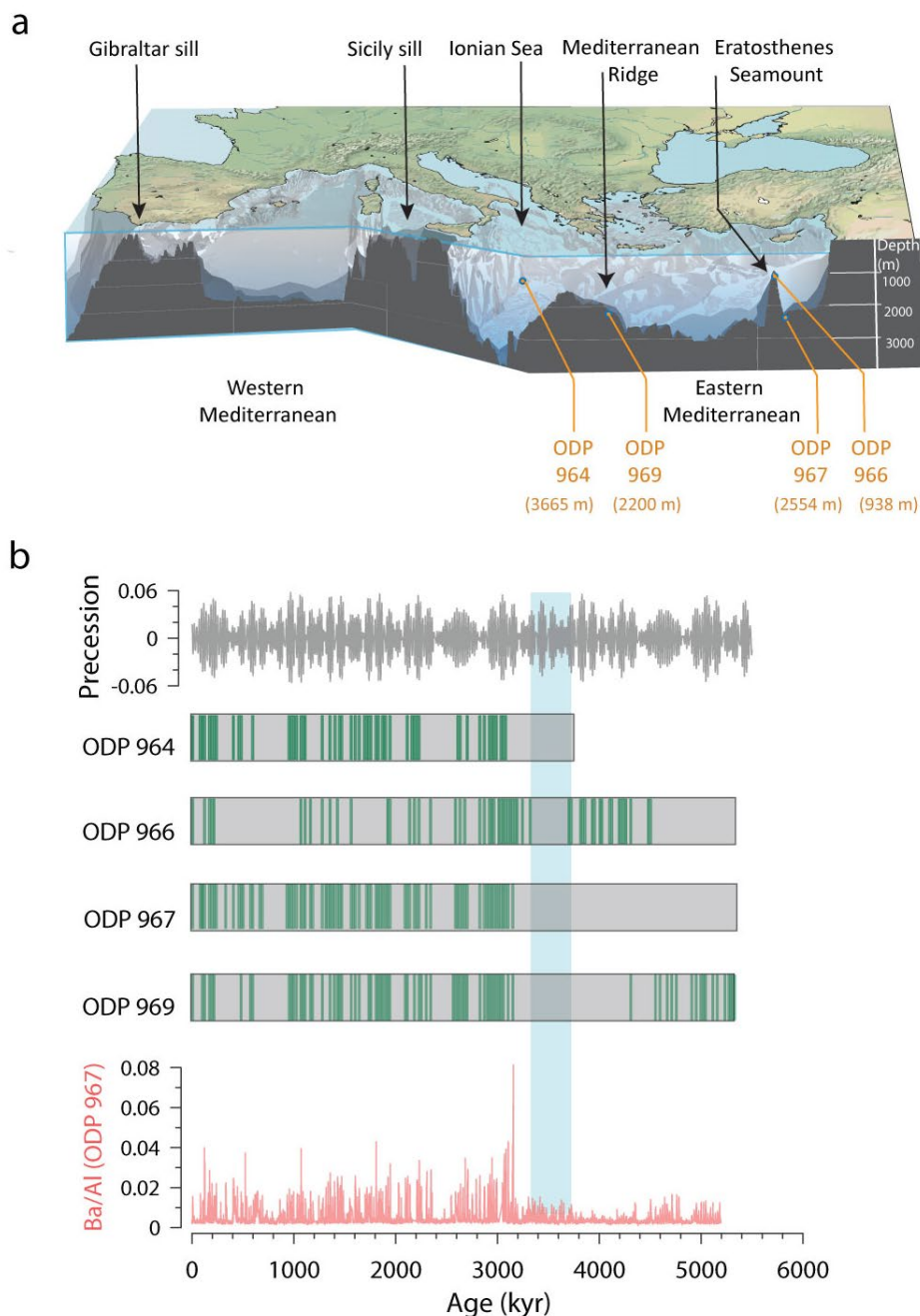
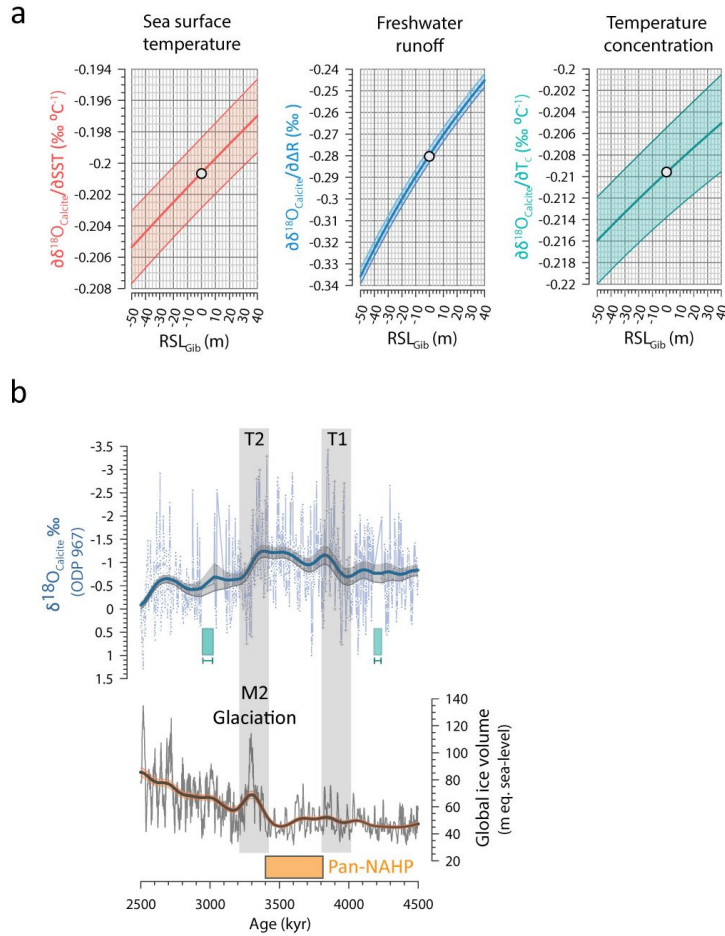


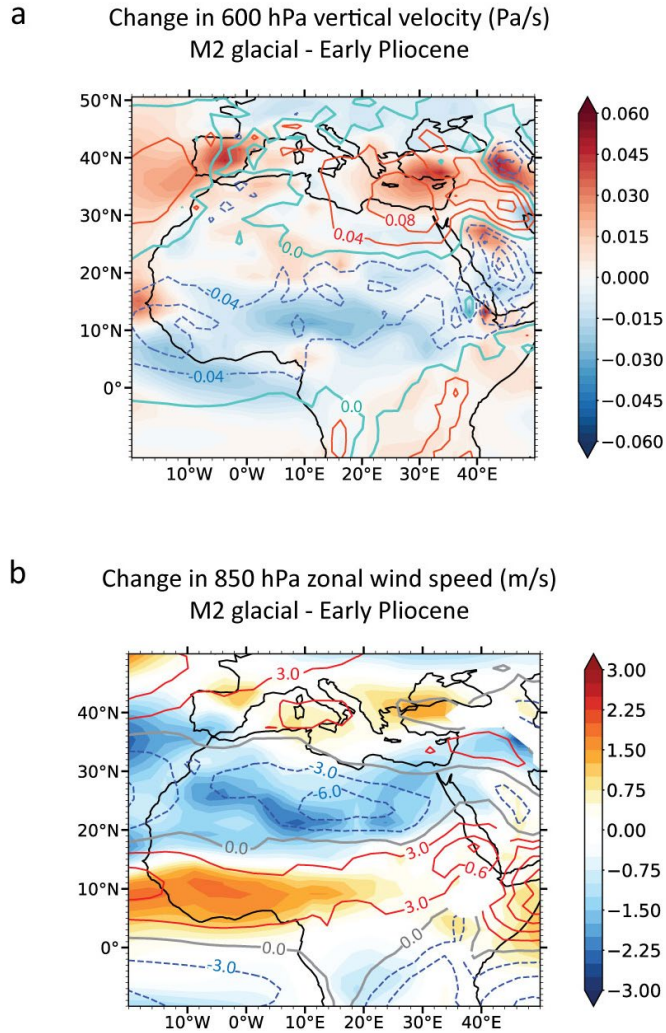
Figure 4| The Pan-NAHP and hominin evolution. **a**, ODP Site 967 stable oxygen isotope record for the 2-5 Myr period. **b**, Calculated Chad basin sedimentation rates³⁶, with a significant increase within the Pan-NAHP. Occurrence of Chad basin lacustrine sediments and East African lake pulses over the Pliocene are shown^{29-31,36}. **c**, Reconstructed woody cover fraction for Omo-Turkana Basin and Awash Valley (Afar Basin)³⁵, with a maximum within the Pan-NAHP **d**, Estimated time spans for multiple hominin species discovered within the Pan-NAHP (see Extended Data Fig. 8). The oldest known stone tools follow the Pan-NAHP termination⁴³. Eastern Mediterranean sapropel stack is shown below. **e**, Climate model results with annual precipitation change from Early Pliocene to Mid-Pliocene glacials, indicating enhanced Early Pliocene North African precipitation. Circled numbers 1, 2 and 3 represent fossil discovery sites for *A. bahrelgazali* (Koro Toro, Chad Basin)¹¹, and other East African australopithecines from Woranso-Mille, central Afar and Lake Turkana, Kenya^{42,45} (see Extended Data Fig. 8). Contours indicate isohyets for Mid Pliocene glacial climate. **f**, Map with the East and Central African rift systems, which have been suggested as a possible migration path for East African hominins to the Chad Basin³³ (see Extended Data Fig. 8). Miocene-Holocene East African rift system and Early-Late Cretaceous Central African rift system are highlighted in red and purple, respectively³³. ODP Sites 659 and 967 are indicated by white dots. CASZ, Central African shear zone (thick black line); CB, Chad Basin; AB, Afar Basin; TB, Turkana Basin.



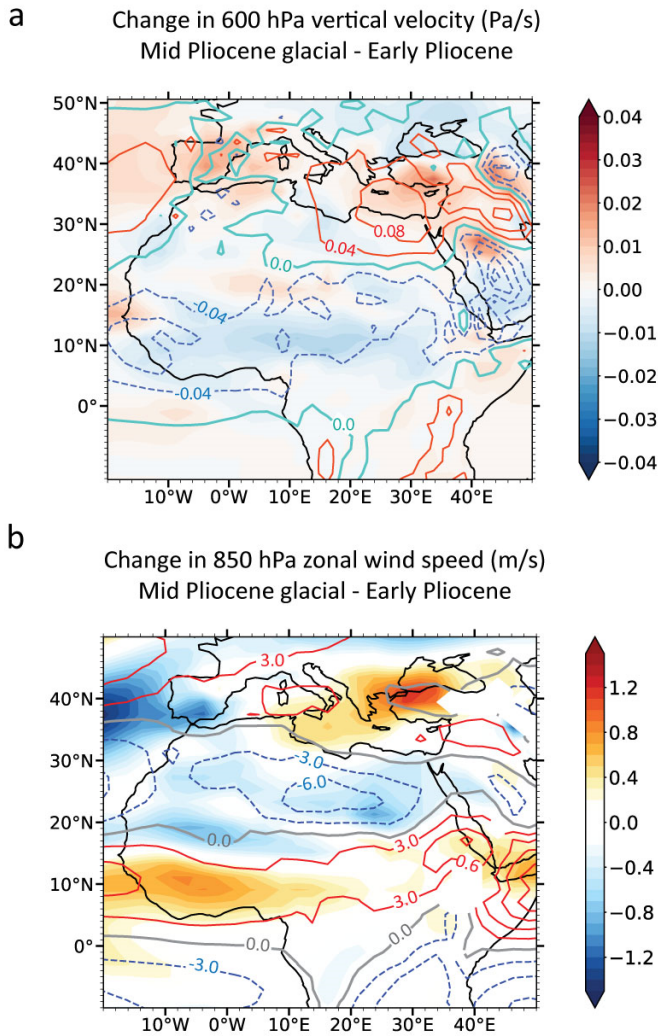
Extended Data Fig. 1 | The Eastern Mediterranean preserved sapropel record. a, Conceptual diagram with modern locations of eastern Mediterranean ODP sites. The present water depth at each site is indicated. **b,** Preserved sapropels at each site. The ODP Site 964 sediment record only goes back to ~3.8 Myr. At Site 966, sediments beyond 4.5 Myr are tectonically deformed^{20,49}. Prolonged sapropel absence during a period of high-amplitude precession minima (centred at ~3.5 Myr) over the entire Mediterranean is marked by vertical blue shading. The ODP Site 967 Ba record indicates enhanced organic carbon burial after 3.2 Myr, which is observed at all sites. The cross-section was drawn using Ocean Data View version 5.6.3.



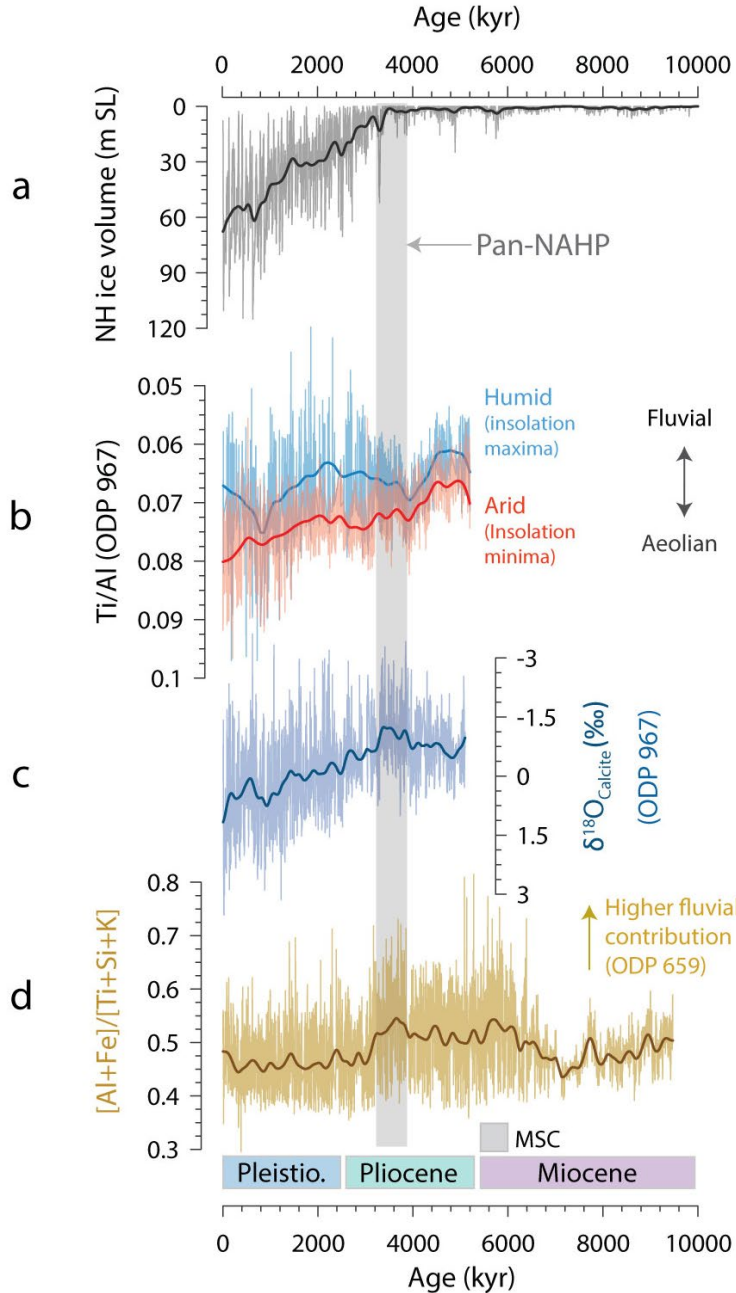
Extended Data Fig. 2 | Evidence for enhanced freshwater flux to the eastern Mediterranean during the Pan-NAHP. a, Mediterranean $\delta^{18}\text{O}_{\text{Calcite}}$ sensitivity to sea surface temperature (SST), monsoon runoff and surface water temperature concentration changes (see Methods). For unchanging Gibraltar sill relative sea-level (RSL_{Gib}), 1°C SST increase can cause a $\sim 0.2 \text{‰}$ $\delta^{18}\text{O}$ drop. A freshwater runoff increase equivalent to pre-Aswan Nile runoff can cause a $\sim 0.28 \text{‰}$ $\delta^{18}\text{O}$ drop. A 1°C surface freshwater layer temperature increase can cause a $\sim 0.21 \text{‰}$ $\delta^{18}\text{O}$ drop. For example, with unchanging SST and T_c across T1, the observed 0.45‰ shift to negative $\delta^{18}\text{O}$ can be generated with a runoff increase of 1.6 times modern Nile runoff equivalents. Shaded intervals indicate the standard error associated with sensitivity estimates. **b**, ODP 967 $\delta^{18}\text{O}$ and global ice volume change²¹ across the 2.5–4.5 Myr period. The blue dotted line (upper diagram) comprises all $\delta^{18}\text{O}$ data points across the interval. The thick grey line (lower diagram) indicates global ice volume evolution. Thick blue and black lines represent the 60-kyr moving average for the $\delta^{18}\text{O}$ and ice volume curves, respectively. The shading for each curve represents 90% confidence intervals. The shifts to more negative $\delta^{18}\text{O}$ values at T1 (transition 1) and more positive values at T2 (transition 2) are highlighted in grey vertical bars. While T2 was caused mainly by the global ice volume increase (a minimum of 0.3‰ , see Methods), T1 was largely caused by a mean freshwater runoff increase to the eastern Mediterranean (no relative global ice volume change across T1, see Methods). Green boxes indicate data gaps.



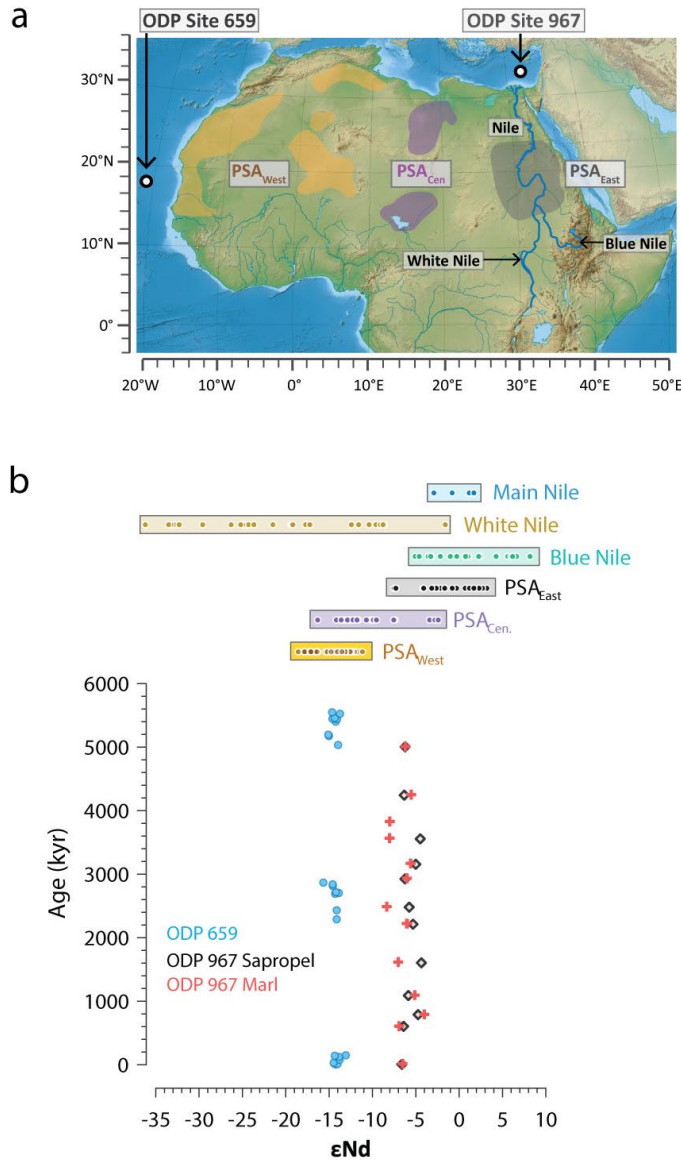
Extended Data Fig. 3 | Climate model result comparison between the Early Pliocene and the M2 glacial. **a**, Boreal summer 600 hPa vertical velocity change (M2 glacial-Early Pliocene), with decreased ascending motion over North Africa at $\sim 20^{\circ}$ - 25° N during the M2 glacial. Contours represent Early Pliocene climatology; continuous red lines indicate descending motion (positive) and dashed blue lines indicate ascending motion (negative). Decreased northward ascending motion indicates a more southward monsoon front during the M2 glaciation, resulting in the observed precipitation decrease centred at $\sim 20^{\circ}$ N. **b**, Change in 850 hPa zonal wind field (M2 glacial-Early Pliocene), which indicates southward displacement of the easterly (negative/dashed blue contours) -westerly (positive/ solid red contours) convergence zone (solid grey contour) centred at $\sim 18^{\circ}$ N over North Africa. Contours indicate Early Pliocene climatology, whereas shading indicates the change from Early Pliocene to the M2 glacial.



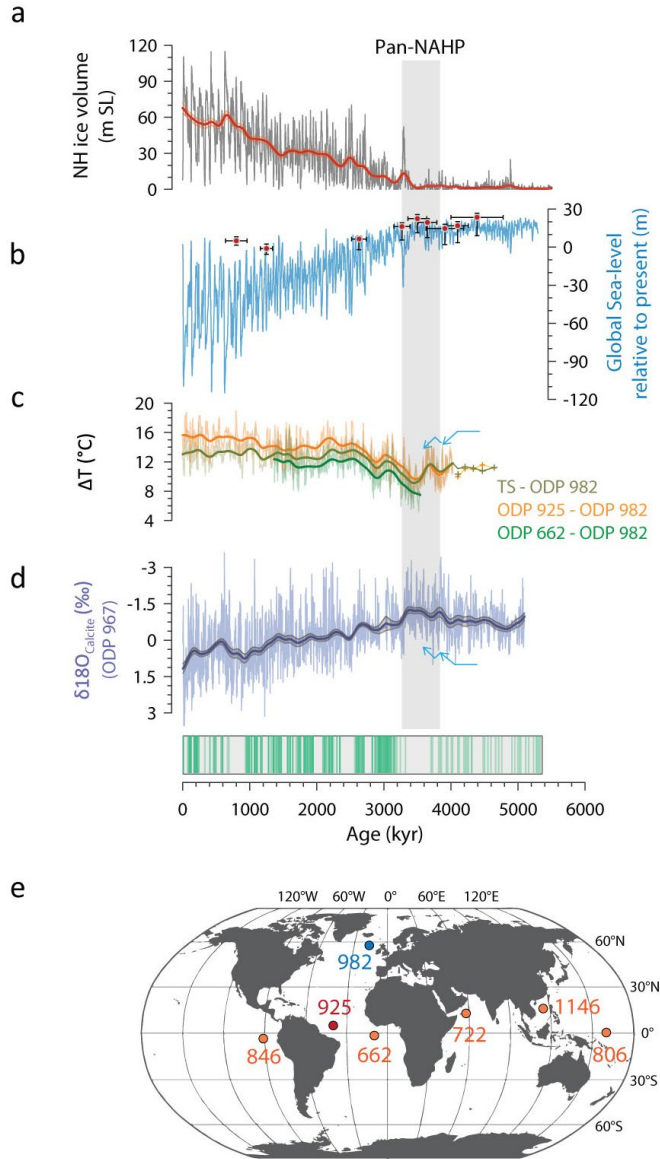
Extended Data Fig. 4 | Climate model result comparison between the Early Pliocene and Mid Pliocene glacials. **a**, Boreal summer 600 hPa vertical velocity change (Mid Pliocene glacial mean-Early Pliocene mean), with decreased ascending motion over North Africa centred at $\sim 20^\circ\text{N}$ compared to the Early Pliocene. Contours represent Early Pliocene climatology; continuous red lines indicate descending motion (positive) and dashed blue lines indicate ascending motion (negative). **b**, Change in 850 hPa zonal wind field (Mid Pliocene glacial mean-Early Pliocene mean), indicating a southward displacement of the easterly -westerly convergence zone centred at $\sim 18^\circ\text{N}$ over North Africa. Contour arrangement (type and color) is similar to Extended Data Fig. 3. Vertical and horizontal wind vigour is smaller during the Mid Pliocene glacials compared to the M2 glaciation (see Extended Data Fig. 3).



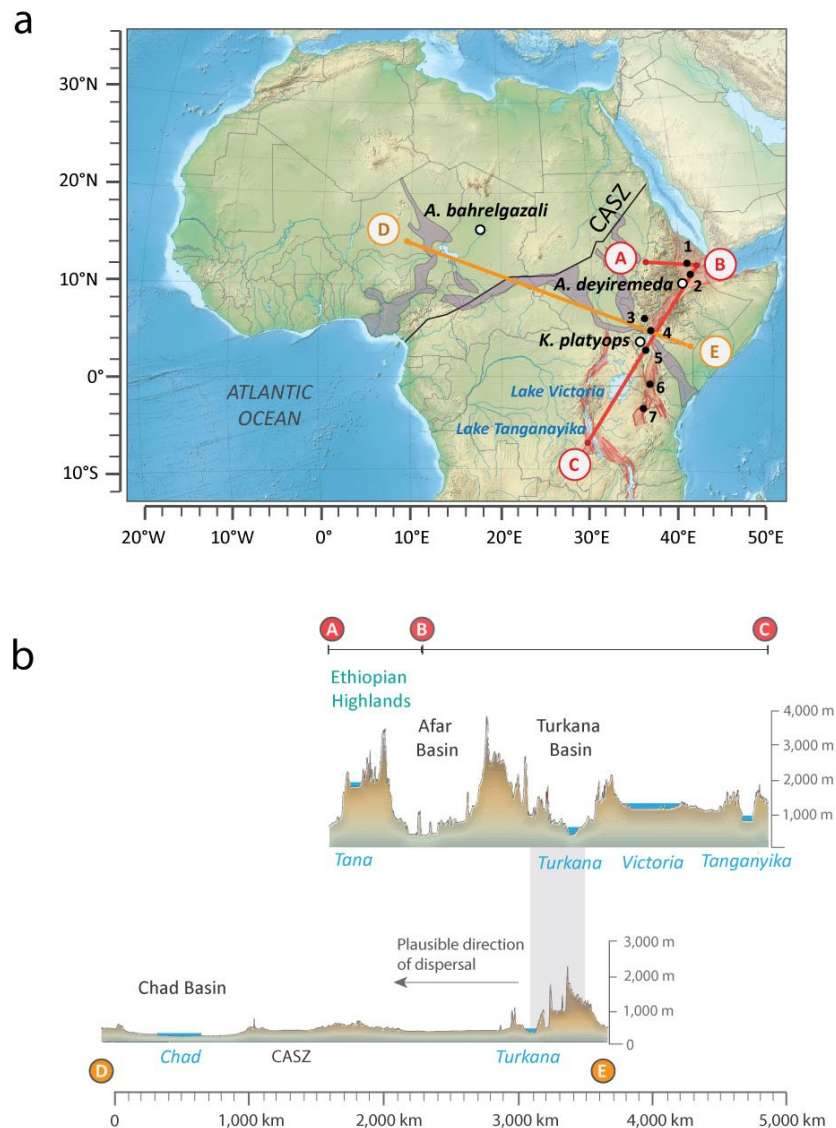
Extended Data Fig. 5 | Data for ODP sites 967 and 659. **a**, Northern Hemispheric ice volume evolution through the past 10 Myr. **b**, ODP 967 Ti/Al data, plotted separately for periods of sapropel (blue) and marl (orange) deposition. Thick blue and orange lines represent the 60-kyr moving average for sapropel and marl intervals. Both sapropelic and marl Ti/Al values indicate an abrupt slope change to higher relative fluvial sediment inputs at 3.8 Myr. At 3.4 Myr, only the marl Ti/Al values indicate the return of increased aeolian input to the eastern Mediterranean. **c**, ODP 967 $\delta^{18}\text{O}$ record back to the Miocene-Pliocene boundary. The thick blue line represents the 60-kyr moving average. **d**, ODP 659 $[\text{Al}+\text{Fe}]/[\text{Ti}+\text{Si}+\text{K}]$ record back to 10 Myr^{ref.12}. The thick brown line represents the 60-kyr moving average. MSC, Messinian salinity crisis.



Extended Data Fig. 6 | Nd isotope data for ODP Sites 967 and 659, compared with North African sediment source regions. a, Map of the main aeolian and fluvial sediment source areas for the eastern Mediterranean (ODP Site 967) and west Africa (ODP Site 659). Land areas highlighted in yellow, purple and grey indicate preferential dust source areas (PSAs) for western, central and eastern North African regions (PSA_{West}, PSA_{Cen.} and PSA_{East}, respectively). Main modern fluvial sediment contributors to the eastern Mediterranean (Main, Blue and White Nile) are shown. **b,** Comparison of data for sites 967 and 659, with modern ϵNd values from each sediment source region shown in **a**. Shaded horizontal bars indicate the range of values observed from each source region. Dots within the bars represent ϵNd values for individual samples, retrieved from published databases. ODP Site 659 values mostly correspond to ϵNd values from PSA_{West} and PSA_{Cen.}, as interpreted in ref.¹². ODP Site 967 ϵNd data from the present study indicate a largely constant sediment origin through the past 5 Myr.



Extended Data Fig. 7 | North Atlantic meridional temperature gradient evolution. **a**, Northern Hemisphere ice volume evolution through the past 5 Myr²¹. **b**, Global sea level relative to present²¹. Red circles with error bars represent global mean sea level (GMSL) benchmarks from Mallorca. Error bars indicate age uncertainties (horizontal) and 16th and 84th percentile sea-level ranges (vertical). **c**, Meridional temperature gradient (ΔT) evolution between North Atlantic ODP Site 982 and available tropical Atlantic temperature records^{39,40}. Thick lines represent the 60-kyr moving average for each record. Relatively stable Early Pliocene ΔT drops to the lowest values at 3.6-3.4 Myr. TS, Tropical stack. **d**, ODP 967 $\delta^{18}\text{O}$ record back to the Miocene-Pliocene boundary. Thick black line represents the 60-kyr moving average. Blue arrows in **c** and **d** demarcate the stepwise ΔT drop and simultaneous $\delta^{18}\text{O}$ decrease. The eastern Mediterranean sapropel stack is shown above the time axis. **e**, Map of locations of ODP sites used for the North Atlantic meridional temperature gradient evaluation. Orange labels indicate sites considered for the tropical stack (ODP sites 662, 722, 846, 1146 = alkenone-based temperature reconstructions; ODP Site 806 = Mg/Ca-based temperature reconstruction)^{39,40}.



Extended Data Fig. 8 | Pan-NAHP hominin sites and a possible migration pathway. **a**, Map of major hominin fossil sites for species coexisting during the Pliocene Pan-NAHP. White dots indicate discovery sites^{10,39,40,41,57} of *A. bahrelgazali* (Koro Toro, Chad Basin), *A. deyiremeda* (Woranso-Mille, central Afar) and *K. platyops* (Lake Turkana, Kenya). Numbered black dots indicate *A. afarensis* discovery sites (1, Woranso-Mille; 2, Hadar; 3, Omo basin; 4, Koobi Fora; 5, Lomekwi; 6, Kantis; 7, Laetoli). East and Central African rift systems⁵⁸⁻⁶⁰ are highlighted in red and purple, respectively. **b**, Cross-sections drawn to scale, along A-B-C and D-E lines on the map in **a**. The two sections have contrasting geographies along the East African rift valley and the Central African rift system. Lake names are in blue. Vertical grey shading indicates the intersection of two rift systems, where the Turkana depression is located³¹. The rift intersection was proposed as a bottleneck, where a possible hominin migration path toward the Chad Basin was proposed³³ across the CASZ. CASZ, Central African shear zone.

Extended Data Table 1: Ice sheet boundary conditions used for the early Pliocene, M2 glacial and Mid Pliocene glacial simulations.

Experiment	NH ice volume (m SLE)	NH ice boundary conditions	SH ice volume (m SLE)	SH ice boundary conditions	CO ₂ forcing (ppm)
Early Pliocene (3.312 – 5.3 Myr)	1.8	PRISM4 ^{ref.51}	42.5	PRISM4 ^{ref.51}	415
M2 glacial (3.264 – 3.312 Myr)	52.13	ICE-7G_NA: 12.5 kyr timeslice from ref. ⁵³	62.16	ICE_7G_NA: 7.5 ka timeslice from ref. ⁵³	250
Mid-Pliocene glacials (3.0 – 3.264 Myr)	10.17	ICE-7G_NA: 8 kyr timeslice from ref. ⁵³	55.32	RCP4.5 scenario, year 5000 from ref. ⁵⁴	375

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Data availability

The authors declare that all the data supporting the findings of this study are available with the manuscript, uploaded as additional files.

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Author contributions

U.A. designed and led the study, prepared samples for Nd isotope analyses, analyzed the data and climate model outputs, developed the hypothesis, generated the figures and wrote the paper; A.F. advised on Nd isotope analysis and data interpretation; R.M.K carried out Nd isotope analyses; D.K.H. generated the climate model ice sheet configurations and performed modelling experiments; D.H. advised on statistical analyses and performed the box model experiments; K.M.G. and J.L. helped with sample selection and preparation; E.J.R. advised on data interpretation; all authors contributed to manuscript development.

Competing interests

The authors declare no competing interests.

CHAPTER 6

Global cooling and atmospheric responses at the Early-Mid Pliocene transition

A modified version of this chapter is in preparation for Nature

This chapter recognizes global-scale environmental transformations that occurred during the initiation of Northern Hemispheric glacials, across the Early-Mid Pliocene transition (3.4-3.2 Myr), using a proxy data compilation and climate modelling. These widespread environmental shifts are coeval to the North African landscape changes explained in Chapter 2 and 3. The findings in this chapter convey the importance of focussing climate modelling experiments on the Early-Mid Pliocene transition, rather than focusing on Early and mid-Pliocene warm periods separately.

Statement of Contribution

This thesis is submitted as a Thesis by Compilation in accordance with https://policies.anu.edu.au/ppl/document/ANUP_003405

I declare that the research presented in this Thesis represents original work that I carried out during my candidature at the Australian National University, except for contributions to multi-author papers incorporated in the Thesis where my contributions are specified in this Statement of Contribution.

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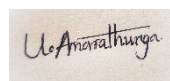
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Global cooling and atmospheric responses at the Early-Mid Pliocene transition

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During the Early Pliocene (5.3-3.4 Myr), Earth was 2-3 °C warmer than today, with major ice sheets essentially restricted to Antarctica¹⁻⁵. Gradual global cooling initiated Northern Hemisphere ice sheet expansion across the Early-Mid Pliocene (EMP) transition (3.5-3.2 Myr), marking the descent into bipolar glaciation^{4,5}. Even though warm Early Pliocene and mid-Pliocene interglacials have been studied as potential future climate analogues^{1,6-8}, the EMP transition has received insignificant attention. Here we use proxy data and climate modelling to show that EMP cooling caused weakened, expanded upper-tropospheric jet streams and intensified tropical (Hadley) circulations in both hemispheres. Consequent change in Northern Hemispheric westerly winds caused dry northern and central European winters, while Mediterranean winter precipitation was enhanced. Intensified subtropical atmospheric subsidence increased Mediterranean summer evaporation, strengthening the region's seasonal climate gradient. Furthermore, we find that upper-tropospheric jet stream behaviour predominantly depends on the final atmospheric thermal configuration, irrespective of the forcing mechanism (ice volume or CO₂ changes). Hence, our results provide useful opposite equivalents to trends suggested for the late 21st century under greenhouse warming⁹⁻¹¹, indicating a high likelihood of stronger, narrower upper-tropospheric jet streams in a warmer world, in addition to a weaker, latitudinally expanded tropical circulation.

Main

Earth's climate experienced a dramatic transformation through the past 5 million years (Ma), evolving from warmer than present conditions of the Early-Mid Pliocene (5.3-3.0 Ma)^{1,2} to the Late Pliocene amplification of glacial-interglacial cycles around 2.7 Ma^{ref.12}. During the warm Early Pliocene, continental ice sheets were largely constrained to Antarctica, whereas the Northern Hemisphere (NH) lacked major ice sheets^{4,5}. The Late Pliocene onset of bipolar glaciation resulted from gradual atmospheric cooling since ~3.6 Ma^{ref.13}, followed by several failed attempts at expanded NH glaciation in the mid-Pliocene (3.3-3.0 Ma)^{4,12}. Therefore, the Early-Mid Pliocene (EMP) transition (3.5-3.2 Ma) marks the onset of Earth's transition from unipolar to bipolar glaciation⁴.

The Early Pliocene (5.3-3.4 Ma) and mid-Pliocene warm periods have separately gained significant attraction as potential analogues for future global warming, leading to numerous modelling and proxy-based evaluations and interpretations^{1,6-8}. Due to reduced meridional and zonal temperature gradients¹⁴, atmospheric circulation was significantly less vigorous in the warm Pliocene^{15,16}. Subsequent polar cooling and ice sheet growth were associated with strengthening and shifting atmospheric circulation patterns, which initiated gradual modifications in global climate state and vegetation patterns^{8,17}. Yet, the importance and the impact on global climate of the increasing ice volume across the EMP transition have received little attention.

Coeval to gradual EMP cooling, geological records from NH mid-latitudes (the Mediterranean and continental Europe) and off West Africa reveal a series of environmental transformations¹⁸⁻²¹ (**Figure 1, Extended Data Fig. 1, Supplementary Table 1**), which relate to major modifications in atmosphere-ocean-land systems. North-central Europe experienced increasing aridity across the interval, while the Mediterranean seasonal contrast intensified^{18,19}. Trade winds strengthened over North-West Africa, simultaneous to the onset of glacial drying over North Africa^{20,21}. Separated by distance and with minor temporal discrepancies (likely due to timescale uncertainties), the relationship between these events has remained elusive. Here we merge paleoclimate data with climate modelling to propose a mechanism that explains the role of EMP global cooling on these widespread environmental transformations. We also evaluate potential implications for mid-latitude climate evolution under future greenhouse warming.

Synthesis of previous palaeodata

During the Early Pliocene, year-long precipitation prevailed in the northern Mediterranean borderlands^{18,19,22}. Then followed a notable climatic transformation, recognized in Gulf of Lion pollen records (**Fig 1h, Supplementary Table 1**); all species requiring year-long moisture disappeared while drought-resistant plants endured, which marks the onset of the modern-like Mediterranean seasonal rhythm of dry, warm summers and humid, cool winters¹⁸. A detailed high-resolution pollen record from Deep Sea Drilling Program (DSDP) Site 380 allowed precise dating of this Mediterranean environmental transition to 3.37 Ma¹⁹ (**Fig. 1i**). At around the same time, a Europe-wide palynological synthesis indicates the emergence of stronger continental climatic conditions (drying and cooling) in northern and central Europe^{19,22} (**Fig. 1i, Supplementary Table 1**); plant taxa indicative of humid conditions were replaced by increased abundances of herbaceous plants indicative of drier and colder conditions¹⁹.

The marine eastern Mediterranean record of Ocean Drilling Program (ODP) Site 967 documents a marked step in basin conditions toward the Late Pliocene²⁰. Preserved sapropels appear at 3.2 Ma^{20,23}, along with a two-fold increase in terrigenous input into the eastern Mediterranean²⁰ (**Fig. 1e, f**). In agreement with ODP 967 observations, other deep Mediterranean sediment records (ODP 969, ODP 964) demonstrate consistent preservation of sapropels only after 3.2 Ma, following an Early Pliocene interval with intermittent sapropel deposition and extensive sapropel oxidation^{20,23}. Initiation of sapropel preservation from ~3.2 Ma has been attributed to increased nutrient input and productivity, driven by a major increase in arid-humid contrasts between alternating precession-timed cycles of North African humid and dry conditions²⁰. Furthermore, ODP site 658 pollen data (west of Cap Blanc, NW Africa), indicate the establishment at ~3.2 Ma of northwest African aridity along with Trade wind strengthening²¹.

New observations

We extend the recently developed 0-5.0 Ma ODP site 967 $\delta^{18}\text{O}_{\text{calcite}}$ record²⁰ (eastern Mediterranean) to 5.3 Ma (**Fig. 1d**). The complete record reveals long-term gradual background change to lower $\delta^{18}\text{O}$ values through the Early Pliocene that terminates in a distinct shift to higher $\delta^{18}\text{O}$ values (≥ 0.5 ‰) from 3.38 Ma to 3.22 Ma (**Fig. 1d**). Such a shift to higher $\delta^{18}\text{O}$ in part reflects the increasing mean global ice volume influence on Mediterranean $\delta^{18}\text{O}_{\text{calcite}}$ ^{5,24}, and in part a substantial superimposed influence of eastern Mediterranean hydroclimate change; i.e., shifts in freshwater runoff and excess evaporation^{5,20,25} (**Extended**

Data Fig. 2). In addition, we note a shift to higher glacial aeolian dust input subsequent to ~3.2 Ma based on a recently published XRF record²⁶ for ODP Site 659, which supports the previous hypothesis²⁰ of increasing glacial North African aridity (**Fig 1g**).

We here propose a hypothesis that large-scale environmental changes across Europe and North Africa reflect a reorganization of major regional climatic drivers in response to EMP global ice volume increase and associated atmospheric cooling. The slow cooling trend initiated during the warm Pliocene culminated in 2 major glaciations during the EMP transition; marine isotope stages MG2 (3.37-3.32 Ma) and M2 (3.31-3.27)¹³. The M2 glaciation was more pronounced than the MG2 glaciation, reaching a global sea-level drop of ~60 m, with contributions from both NH and Antarctic ice sheets^{13,24,27,28}. Thereafter, the world entered the mid-Pliocene warm period (3.27-3.03 Ma)²⁷. Even though the mid-Pliocene warm period soon followed the M2 glaciation²⁷, we observe clearly increased NH and Antarctic glacial ice volumes after the M2 glaciation, relative to the warm Early Pliocene (**Fig. 1b**), with a ~12.5 m mean global ice volume increase across the EMP transition⁵ (Methods). Along with the NH ice volume increase, Atlantic sea surface temperature reconstructions^{29,30} reveal a continuous increase in the NH latitudinal temperature gradient (LTG) (**Fig. 1c**). Supported by these observations, we test our hypothesis with a coupled atmosphere-ocean climate model (Methods).

Climate modelling

Modern climate across a Europe-North Africa transect is dominated by seasonal changes in the meridional atmospheric circulation (**Extended Data Fig. 1, Supplementary Table 2**). The majority of North European precipitation is received via North Atlantic winter and summer storm tracks associated with the mid-latitude jet stream and westerly winds³¹. The Mediterranean winter climate is dominated by the westerlies, which bring instabilities that generate most of the region's annual precipitation (**Supplementary Table 2**). Conversely, Mediterranean summers are dry, due to the influence of subtropical tropospheric subsidence partly driven by regional Hadley cell (HC)³² (see **Supplementary Table 1 for choice of proxy locations and interpretations**). Combined, these processes generate the region's characteristic seasonal contrast (**Supplementary Table 2**). To the south of the Mediterranean, most of northern Africa beyond 20°N remains arid throughout the year, under the influence of dry easterly winds associated with subtropical subsidence and the Saharan heat low³³ (**Extended Data Fig. 1, Supplementary Table 2**).

Climate modelling and proxy-based reconstructions have been used to suggest that the Pliocene warmth resulted in more poleward westerlies, relative to their pre-industrial location⁸. Moreover, reduced surface LTGs during the warm Pliocene likely resulted in poleward-displaced and weakened Hadley circulation, which caused more precipitation in the subtropics¹⁶. Poleward expansion of the meridional and zonal tropospheric components is recognized to be a globally synchronous phenomenon during the warm Pliocene^{8,16}. To test the impact of ice volume changes on the environmental transformations registered in palaeodata (above), we adjusted polar ice volumes for the Early Pliocene (5.3-3.4 Ma), mid-Pliocene glacials and mid-Pliocene interglacials (3.3-3.0 Ma) in a coupled climate model (Methods). We use published NH and Antarctic ice volume reconstructions⁵, which indicate that both mid-Pliocene glacial and interglacial mean ice volumes were increased in both hemispheres, relative to mean Early Pliocene ice volumes (Methods, **Extended Data Fig. 3**).

Increasing polar ice volumes can generate thermal perturbations that affect atmospheric stability, baroclinicity and moist processes, which in turn modify strength and position of the jet streams, storm tracks, and subtropical HC descending limbs^{31,34}. The mid-Pliocene zonal mean atmospheric thermal structure shows consistent changes during both glacials and interglacials, relative to the Early Pliocene. We observe three major features: 1) a cooler tropical upper troposphere (TUT) relative to the tropical lower troposphere; 2) a lower-troposphere high-latitude cooling over both hemispheres; and 3) lower stratospheric warming (**Fig. 2a**). Importantly, these trends for EMP cooling are opposite to those found in future global warming experiments^{9,35,36}.

We find that mid-Pliocene jet streams, mid-latitude zonal winds, and precipitation patterns show similar trends over the NH in both glacials and interglacials, relative to the warm Early Pliocene (**Extended Data Fig. 4**), with changes (as expected) most pronounced during glacials. There is strengthening of the upper tropospheric NH winter jet stream at its poleward and equatorward flanks, while the jet core weakens (**Fig. 2b**). Jet stream expansion and core weakening is driven by reduced upper tropospheric and increased lower tropospheric LTGs³⁵, which result in equatorward and poleward shifts in the jet stream flanks, respectively. The weakening of the jet core appears in the lower troposphere with a weakening of the 850 hPa North Atlantic westerly winds (**Fig. 2c**). Consequently, European winter precipitation strongly decreases (**Fig. 2d**), in agreement with proxy data, due to weakening of the storm tracks. Meanwhile, strengthening of the NH winter jet stream occurs at its equatorward flank, with 850 hPa zonal winds over Northern Africa indicating stronger westerlies, relative to the Early

Pliocene (**Fig. 2c**). This results in increased storm activity and winter precipitation over the Mediterranean (**Fig. 2d**). Conversely, we observe an increase in excess evaporation over the Mediterranean during boreal summer, driven by strengthened tropospheric subsidence over the region (**Fig. 2f, g**). Mediterranean summer subsidence is governed by combined influences of the North African summer HC, and the stationary wave circulation driven by ascent associated with Southeast Asian monsoon^{ref.32}. Our model results indicate that enhanced subsidence over the Mediterranean is mainly driven by North African HC strengthening, as the Southeast Asian monsoon ascent seems to weaken due to equatorward contraction of the meridional atmospheric circulation (**Extended Data Fig. 5**). The increased mid-Pliocene winter-to-summer contrast in the Mediterranean freshwater budget relative to the Early Pliocene (**Fig. 2e, f**) agrees with Pliocene pollen records, which imply a stronger seasonal contrast after the M2-MG2 event (above).

Over a majority of North Africa (mainly over the Sahel up to 25°N), we observe a clear contrast in mid-Pliocene glacial versus interglacial boreal summer precipitation, which agrees with the previously proposed enhanced arid: humid contrast after 3.2 Ma²⁰. Our model results indicate that during glacial boreal summer, the southern hemispheric HC (zonal mean) was strengthened and contracted, simultaneous to a strengthening of the Northern HC (**Fig. 3c**). North African mid-Pliocene glacial HC strengthening (relative to the Early Pliocene) is evident from intensified 500 hPa vertical velocity over the Sahel and the Mediterranean (**Fig. 2g, Extended Data Fig. 5**). Our results agree with previous studies that indicate HC strengthening due to increasing surface LTGs during polar cooling events¹⁷. Glacial summer drying of North Africa during the mid-Pliocene may have been driven by a contraction of the tropical ascent, and an intensification of dry advection over the Sahel (**Fig. 2h**). The shift to higher ODP 967 $\delta^{18}\text{O}$ values may indicate a glacial drying-driven reduction of freshwater runoff to the Mediterranean. In contrast, North African precipitation increased during interglacials, relative to the Early Pliocene (**Extended Data Fig. 6**), likely driven by a more northward position of the intertropical convergence zone (ITCZ) in response to interglacial cooling over Antarctica relative to warmer conditions over the North Atlantic^{33,37}. Such a glacial-interglacial precipitation contrast agrees with observed organic carbon burial intensification from 3.2 Ma in the eastern Mediterranean²⁰, given that intensified glacial drying over North Africa would increase landscape erodibility, which would have facilitated the supply of increased amounts of nutrients to the Mediterranean during subsequent humid (interglacial) intervals, boosting primary production in the basin²⁰.

Finally, our model results also demonstrate the Pliocene global cooling influence on Southern Hemisphere (SH) atmospheric circulation, due to Antarctic and TUT cooling (**Fig. 3a**). Similar to changes in the NH, we observe SH strengthening of the upper tropospheric jet stream at its poleward and equatorward edges, while the jet core weakens (**Fig. 3b**). The austral winter HC strengthens and contracts, similar to the boreal winter HC (**Fig. 3c, d**), which is consistent with increased LTGs in both hemispheres¹⁷. Our observations are supported by evidence for substantial Antarctic ice sheet expansions since 3.3 Ma, following the EMP transition²⁸ (**Extended Data Fig. 7**). Antarctic ice sheet growth was associated with wind-driven strengthening of the Benguela upwelling system (indicated by a 10°C SST drop since 3.3 Ma)^{28,38}, and with stronger SH mid-latitude westerlies that drove enhanced dust inputs into the Southern Ocean during subsequent glacials^{28,39}. Overall, our results, supported by existing proxy records, imply that the onset of major global climate-environmental transformations occurred across the EMP transition, some ~0.5 My before the initiation of major glacial-interglacial cycles at ~2.7 Ma⁵.

Wider implications

Most global warming-related modelling studies indicate a poleward expansion of tropical circulation^{10,34,40}. However, the upper tropospheric jet stream response to anthropogenic warming is uncertain, due to a ‘tug of war’ driven by opposing influences of amplified TUT warming and Arctic lower tropospheric warming (Arctic Amplification; AA)^{35,41}. While TUT warming acts to shift the mid-latitude circulation system (including the jet streams and HC descending limbs) poleward, AA is expected to weaken the eddy-driven jet stream and shift North Atlantic storm tracks and equatorward, opposing the TUT-warming influence on NH mid-latitude climate^{35,42}.

More recent studies investigating the overall behaviour of the jet streams have revealed that the meridional extensions of the North Atlantic and SH jet streams are expected to decrease under global warming (contraction by reduced jet stream wobble), with an increase of the jet core speed^{43–45}. The contraction is suggested to be driven by the tug of war; opposite forcing of TUT and polar warming on the jet stream^{43–45}. Such changes are especially expected under high CO₂ emission scenarios, where SH high-latitude warming is expected to substantially reduce the Antarctic ice volume by the end of the 21st century, alongside the already existing Arctic warming^{11,45}.

We find that the EMP transition shows similar changes, albeit in the opposite sense because it was a cooling. Our sensitivity tests with fixed CO₂ concentrations across the EMP suggest that TUT and polar cooling alone are capable of generating the observed jet stream changes (**Extended Data Fig. 8**). Therefore, we posit that, despite the possible differences in climate forcing, the environmental responses during the EMP cooling transition offer critical insights and an important testbed for understanding and quantifying (in an opposite sense) the likely future warming-related atmospheric structure change and its influence on mid latitude climate and environmental conditions. From this perspective, we propose that, under high emission scenarios, subtropical tropospheric descent will continue to expand poleward, while the jet streams will become narrower and stronger. The Mediterranean region will then experience reduced winter precipitation, while continental Europe may expect a reduction in extreme winter weather events.

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Author contributions

U.A. designed and led the study, analysed the data and climate model outputs, developed the hypothesis, generated the figures and wrote the paper; D.Hu. generated the climate model ice sheet configurations and performed the modelling experiments; J.-P.S. compiled the pollen data, derived the climate indices, and contributed to the supplement; D.He. carried out statistical analyses and developed the Mediterranean box model; G.Z. advised on climate model interpretations; L.R.-S., S.F. and S.-M.P. contributed to data generation; E.J.R., K.M.G., A.M.H. and A.P.R. advised on data interpretation; all authors contributed to manuscript development.

Competing interests

The authors declare no competing interests.

METHODS

Stable oxygen isotopes ($\delta^{18}\text{O}_{\text{calcite}}$)

For ODP Site 967, new $\delta^{18}\text{O}_{\text{calcite}}$ data were generated for the 5.2-5.35 Ma period, which were added to the existing 0-5.2 Ma ODP 967 $\delta^{18}\text{O}_{\text{calcite}}$ record²⁰. To verify the magnitude of $\delta^{18}\text{O}_{\text{calcite}}$ shift at 3.2 Ma, previous measurements were duplicated across 3.0 – 3.8 Ma interval. Bulk sediment samples were washed through 63 μm sieves with DI water and the residue was oven dried at 45°C for 24 hours. *Globigerinoides ruber* (white) specimens were picked from the >300 μm size fraction, adhering to ‘*sensu stricto*’ morphotypes and size range ($\pm 25 \mu\text{m}$). Picked tests (typically 10-20, depending on abundance) were gently crushed and cleaned by briefly ultrasonicing in methanol, then air dried after decanting the fine suspended matter. Samples were analysed at ANU using a Thermo Fisher Scientific Delta Advantage mass spectrometer coupled to a Kiel IV carbonate device for sample digestion. Isotope data were normalized to the Vienna Peedee Belemnite (VPDB) scale using NBS-19 or IAEA-603, and NBS-18. External reproducibility (1σ) was always better than 0.08‰.

Analysis of ice-volume changes and $\delta^{18}\text{O}_{\text{calcite}}$ across the Early-Mid Pliocene transition

To detect regime shifts in NH and SH ice volume evolution, change points were estimated using the MATLAB built-in function ‘findchangepts’, following ref.⁴⁶. Change-points were determined based on the mean and standard deviation of the ice volume records, and a maximum of 3 change-points was stipulated as a parsimonious balance between constraining output to the most significant changes while allowing a >1 outcome. Mean ice volumes from the Early Pliocene (5.3-3.4 Ma) to the mid-Pliocene (3.26-3.0 Ma) glacials and interglacials were calculated based on the ice volume reconstructions in ref.⁵ (Supplementary information). To estimate the magnitude of the $\delta^{18}\text{O}_{\text{calcite}}$ shift at 3.4-3.2 Ma, a Gaussian kernel smoother was employed. The frequency response was modified to remove short eccentricity, obliquity and precession components from the mean background variability.

To evaluate the effect of Mediterranean relative sea-level (RSL) change on the observed $\delta^{18}\text{O}_{\text{calcite}}$ shift, a Mediterranean box model was employed^{24,25}. The box model is coupled to a model of exchange transport with the Atlantic via the Strait of Gibraltar and consists of a winter mixed-layer box, which is subsequently split into a summer-mixed layer and a summer-subthermocline layer. At the end of summer, these two layers are homogenized to form a new winter mixed-layer. This annual cycle can then be repeated until the model achieves

equilibrium under a given fixed forcing scenario. Importantly, the model structure and parameterizations follow those of ref.²⁴ and as such, do not include the additional of the surface monsoon box described in ref.²⁵.

The Mediterranean box model in ref.²⁴ employed a $\delta^{18}\text{O}_{\text{calcite}}$ forward modelling strategy to estimate relative sea level at Gibraltar (RSL_{Gib}). In our version of the model, RSL_{Gib} is a forcing parameter, which was estimated from the global mean eustatic sea-level (ESL) record of ref.⁵ based on the RSL_{Gib} to ESL conversion of ref.²⁴. Thus, if the key properties of the model boxes, such as temperature, salinity, and $\delta^{18}\text{O}_{\text{calcite}}$, are kept fixed while RSL_{Gib} is allowed to change, the mean Mediterranean $\delta^{18}\text{O}_{\text{calcite}}$ change solely due to RSL_{Gib} changes can be separated from the initial $\delta^{18}\text{O}_{\text{calcite}}$ record. This enabled the model to be used in a sensitivity analysis to differentiate potential underlying causes of large-scale changes in the ODP Site 967 $\delta^{18}\text{O}_{\text{calcite}}$ record.

Development of pollen-derived climate indices

To evaluate the precipitation and vegetation variations from the Early Pliocene to the Early Pleistocene, three reliable long pollen records were considered (Main Fig. 1). Garraf 1 borehole includes several marine bioevents resulting in a robust chronostratigraphy. The biostratigraphically calibrated DSDP Site 380 pollen record was correlated with a reference global oxygen isotope curve, to develop a reliable chronology¹⁹. Other pollen records were climatostratigraphically subdivided with reference to Site 380, and correlated with the reference global oxygen isotope curve, which illustrates in all three records the effect of the M2-MG2 event on the vegetation¹⁹. In the present study, linear sedimentation rates between data points were used to generate the chronologies for each site.

To interpret the nature of climate/vegetation transformations, a well-established method of calculating the ratios between climatically contrasted pollen taxa (or groups of taxa) was used^{19,22}. For each pollen record, most representative taxa of humid conditions ('Humidity indicators', HI), and dry conditions ('Dryness indicators', DI) were considered. The ratio between these two groups was used to establish a 'Humidity Index' (HI/DI) or its reverse as a 'Dryness Index' (DI/HI) for the chosen pollen records. Despite some regional differences, these groups (HI and DI) are on the whole composed of:

HI: the subtropical plants (*Engelhardia*, *Platycarya*, *Sequoia*-type, *Taxodium*-type, Sapotaceae, *Distylium*, *Nyssa*, *Myrica*, etc.) plus some warm-temperate plants (*Carya*, *Pterocarya*, *Liquidambar*, *Alnus*, *Salix*, *Ulmus*, *Zelkova*, *Sciadopitys*, Ericaceae, etc.);

DI: *Microtropis fallax* (a subtropical tree requiring a dry season), plus all the Mediterranean sclerophyllous plants (*Olea*, *Phillyrea*, *Quercus ilex*-type, *Cistus*, etc. (complete listing in Suc et al., 2018) plus sub-desert plants (Agavaceae, *Prosopis*) and steppe elements (*Artemisia*, *Ephedra*, *Erodium*, other Compositae than *Artemisia*).

(The complete listing of the taxa concerned is provided for each record in Supplementary information)

Climate Model Experiments

Model components

Model experiments were carried out using the coupled climate model GFDL CM2.1⁴⁷. This model consists of dynamic ocean, atmosphere, land and sea ice components. The ocean component is updated to use the Modular Ocean Model version 5.1.0 (MOM5). The ocean uses a resolution of 1° latitude x 1° longitude x 50 vertical levels, with latitudinal refinement within $\pm 30^\circ$ latitude down to 0.33° at the equator, as in ref.⁴⁷. The ocean and sea ice horizontal grid uses a tripolar configuration, consisting of a regular latitude-longitude grid from 85°S to 65°N, and a bipolar grid north of 65°N with poles over North America and Eurasia. The other model components are the same as in GFDL CM2.1, namely the GFDL Atmosphere Model 2, Land Model 2 and Sea Ice Simulator. The atmosphere resolution is 2° latitude x 2.5° longitude x 24 levels, as in the original GFDL CM2.1.

Boundary conditions

This study uses 3 experimental configurations, representing (i) the Early Pliocene (5.3-3.4 Ma), (ii) mid-Pliocene glacials (3.27-3.0 Ma) and (iii) mid-Pliocene interglacials (3.27-3.0 Ma). A summary of these configurations is shown in Extended Data Table 1. The Early Pliocene simulation is set up using the PRISM4 boundary conditions, as used in the Pliocene Model Intercomparison Project 2 (PlioMIP2)⁶. The paleogeography, including topography and bathymetry, ice sheet extents, and vegetation types are all set according to the PRISM4 protocol. The Early Pliocene simulation serves as a “control” experiment for this study, i.e. a reference case which can be compared with other Pliocene model experiments using the same boundary conditions.

The mid-Pliocene glacial and interglacial simulations use the PRISM4 boundary conditions as a starting point, with modifications to the ice sheets to match the total ice volume from the compilation of ref.⁵, for mid-Pliocene glacials and interglacials between 3.0 and 3.27 Ma.

Mid-Pliocene glacial simulation

For this case, we imposed Northern Hemisphere ice sheets derived from the ice sheet reconstruction of ICE-7G_NA⁴⁸ using their 8 ka timeslice, in order to achieve a total NH ice volume of 10.17 m sea level equivalent (SLE). For the Southern Hemisphere, we used ref.⁴⁹, using their RCP4.5 scenario at year 5000, in order to achieve a total SH ice volume of 55.32 m SLE. These snapshots are chosen to represent a physically realistic representation of a target ice volume, rather than an exact reconstruction of Pliocene ice sheets. A similar approach of reconstructing ice boundary conditions was used in the Pliocene modelling experiments of ref.²⁷, where they used ice model reconstructions from different time periods to match their targeted ice volume for the Pliocene M2 scenario.

Mid-Pliocene interglacial simulation

The Northern Hemisphere ice sheets were configured using the simulated ice sheet of ref.⁵⁰ using their 410 ka timeslice, to achieve a total NH ice sheet volume of 4.15 m SLE. The Southern Hemisphere ice sheet was configured using the simulated ice sheet of ref.⁴⁹ in order to achieve a SH ice volume of 50.78 m (SLE). Both of these previously simulated ice sheets are targeted at different time intervals than the Pliocene interglacial that we aim to simulate, so they should not be considered an exact match. But, they both represent physically realistic ice sheet configurations with total volumes that match the global sea level record. In the absence of a publicly available 3D ice sheet reconstruction for the Pliocene interglacials, these boundary conditions are a “best guess” at a realistic forcing of a fully coupled climate model.

Initial conditions and spinup

The climate model runs were initiated using idealised temperature and salinity initial conditions for the ocean. The salinity was set to a uniform global value of 34.7 psu. The initial temperature was constructed using (i) surface values of sea surface temperature (SST) from the PRISM4 dataset, (ii) a uniform deep ocean value of 6 °C everywhere below 500 m depth, and (iii) a linear interpolation between 0-500 m from the PRISM4 SST and deep ocean temperature. The deep ocean value was chosen in order to be slightly warmer than the anticipated equilibrium, in order to enable the start of deep ocean circulation that tends to initiate when the ocean is

losing heat. The atmosphere and land components were initiated using a “cold start” condition. Since these components have a much lower heat capacity than the ocean, they quickly reach quasi-equilibrium and the long-term spinup depends largely on the ocean evolution. All three simulations were spun up from the idealised initial conditions for a total of 2000 years, using CO₂ forcing demarcated in Extended Data Table 1. The analyses use the mean of the last 50 years of simulation, in order to reduce the impact of short-term variability.

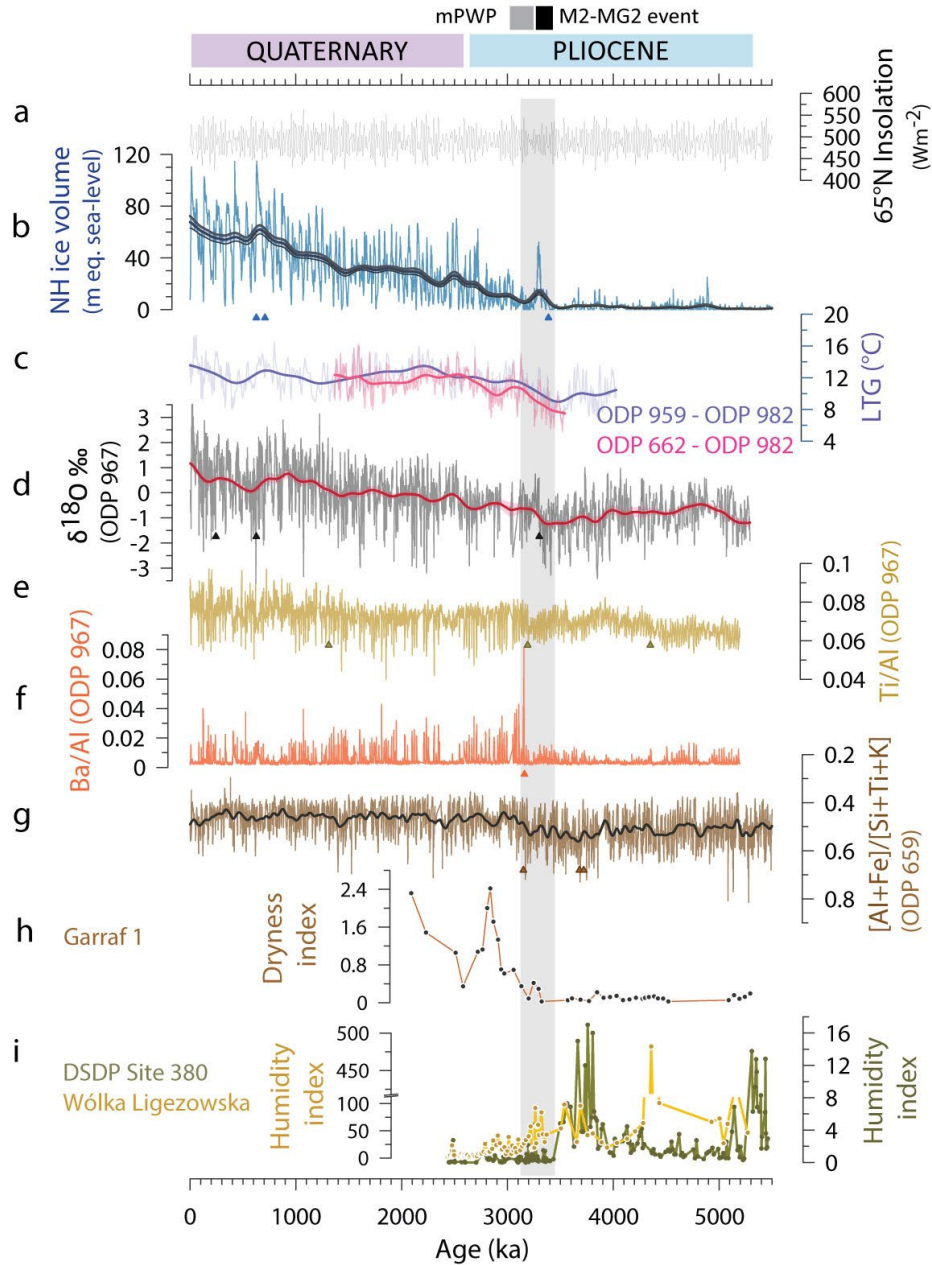


Figure 1| Evidence of environmental shifts over the Northern Hemisphere across the Early-Mid Pliocene transition. **a**, Boreal summer 65°N insolation curve. **b**, Northern hemispheric ice volume reconstruction for the past 5.5 Ma period²⁸. Thick black line represents the 60 ka moving average. Grey envelope represents the 95% higher and lower confidence intervals. **c**, North Atlantic latitudinal temperature gradient (LTG) calculated using sea surface temperature reconstructions from ODP Sites 662, 959 and 982^{refs. 34,35}. Thick lines represent the 60 ka moving average. **d**, ODP Site 967 $\delta^{18}\text{O}_{\text{calcite}}$ record¹². Thick red line represents the 60 ka moving average. **e**, **f**, ODP Site 967 Ti/Al and Ba/Al records, which are proxies for aeolian vs fluvial input to the eastern Mediterranean and original organic carbon burial, respectively. **g**, ODP Site 659 $[\text{Al}+\text{Fe}]/[\text{Si}+\text{Ti}+\text{K}]$ record, which is a proxy for dust input³⁴. Black line represents the 60 ka moving average. **h**, North-western Mediterranean dryness index, developed using pollen counts. The increased dryness after ~3.3 Ma is mainly attributed to the strengthened summer aridity over the Mediterranean¹⁰. **i**, Humidity/dryness indices for DSDP Site 380 (Southwest Black Sea) and Wólka Ligezowska (Northern Europe), indicating an increase in dryness after after ~3.3 Ma¹¹. The vertical shading indicates the Early-Mid Pliocene transition. For all plots, triangles represent the linear change points. mPWP, mid-Pliocene warm period.

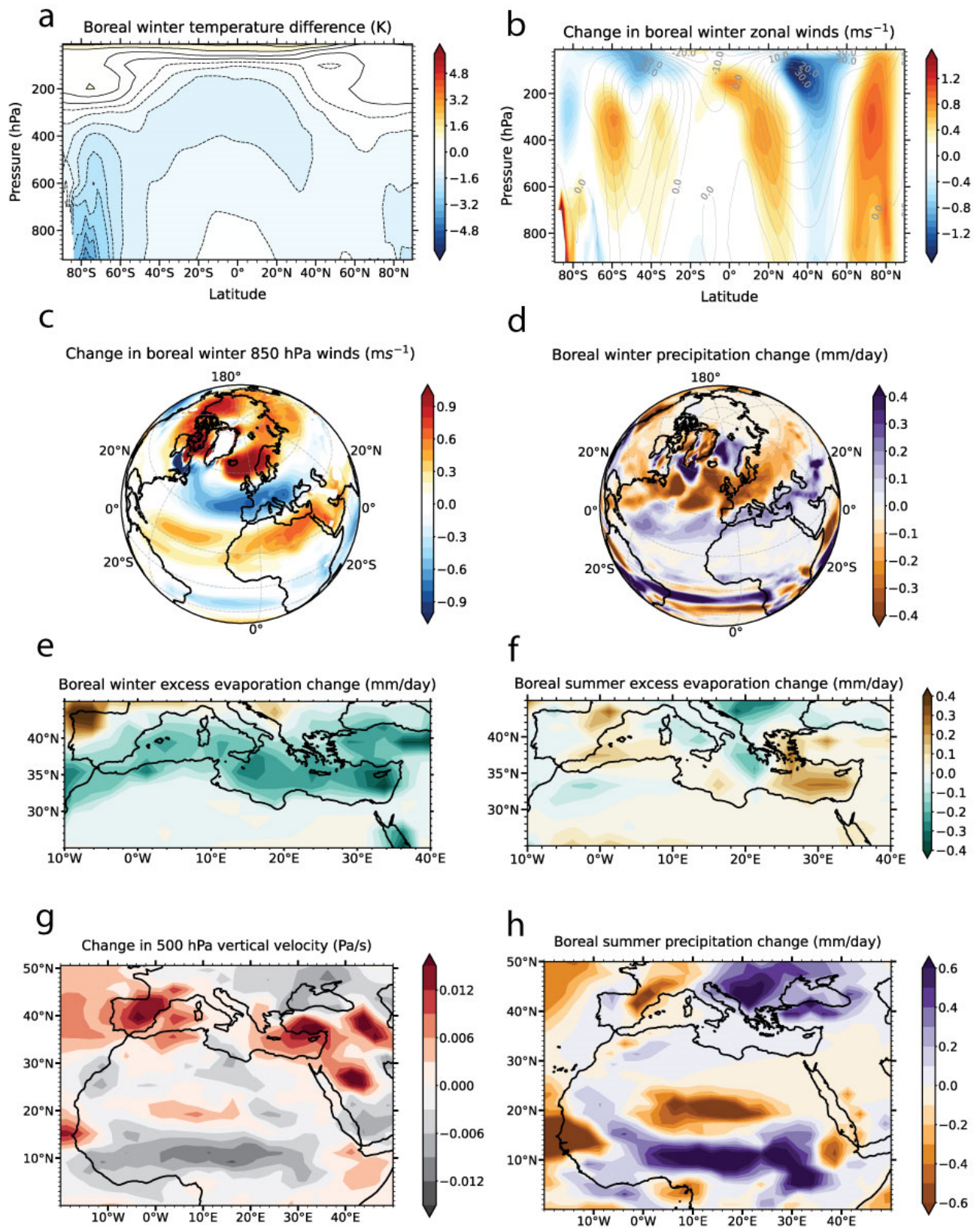


Figure 2| Climate modelling results showing the change in climate parameters (Mid Pliocene glacial mean- Early Pliocene). **a**, Boreal winter zonal mean vertical atmospheric thermal structure, indicating TUT, Arctic and Antarctic lower tropospheric cooling. **b**, Boreal winter zonal winds, indicating the weakening core of the NH upper tropospheric jet, while the jet flanks strengthen. Grey contours represent the wind velocities of the control run (Early Pliocene). Positive/negative values are for westerly/easterly winds. **c**, Boreal winter 850 hPa zonal winds, indicating a decrease of wind velocity over Europe. **d**, Boreal winter precipitation over Europe decreases as the storm track density decreases (weaker westerlies). Winter precipitation over Mediterranean increases due to the poleward strengthening of the westerlies. **e, f**, Winter versus summer excess evaporation over the Mediterranean. Winter-summer seasonal contrast increases due to the increase of Mediterranean winter precipitation, and the increase of summer excess evaporation driven by stronger subsidence (see Fig. 2 g). **g**, The change in 500 hPa vertical velocity over North Africa and the Mediterranean. Stronger subsidence over the Mediterranean and strengthened ascent over Sahel indicates strengthened local Hadley cell. The ascending region has contracted towards the equator at $\sim 20^\circ\text{N}$. **h**, Boreal summer precipitation change, showing a strong drying over North Africa.

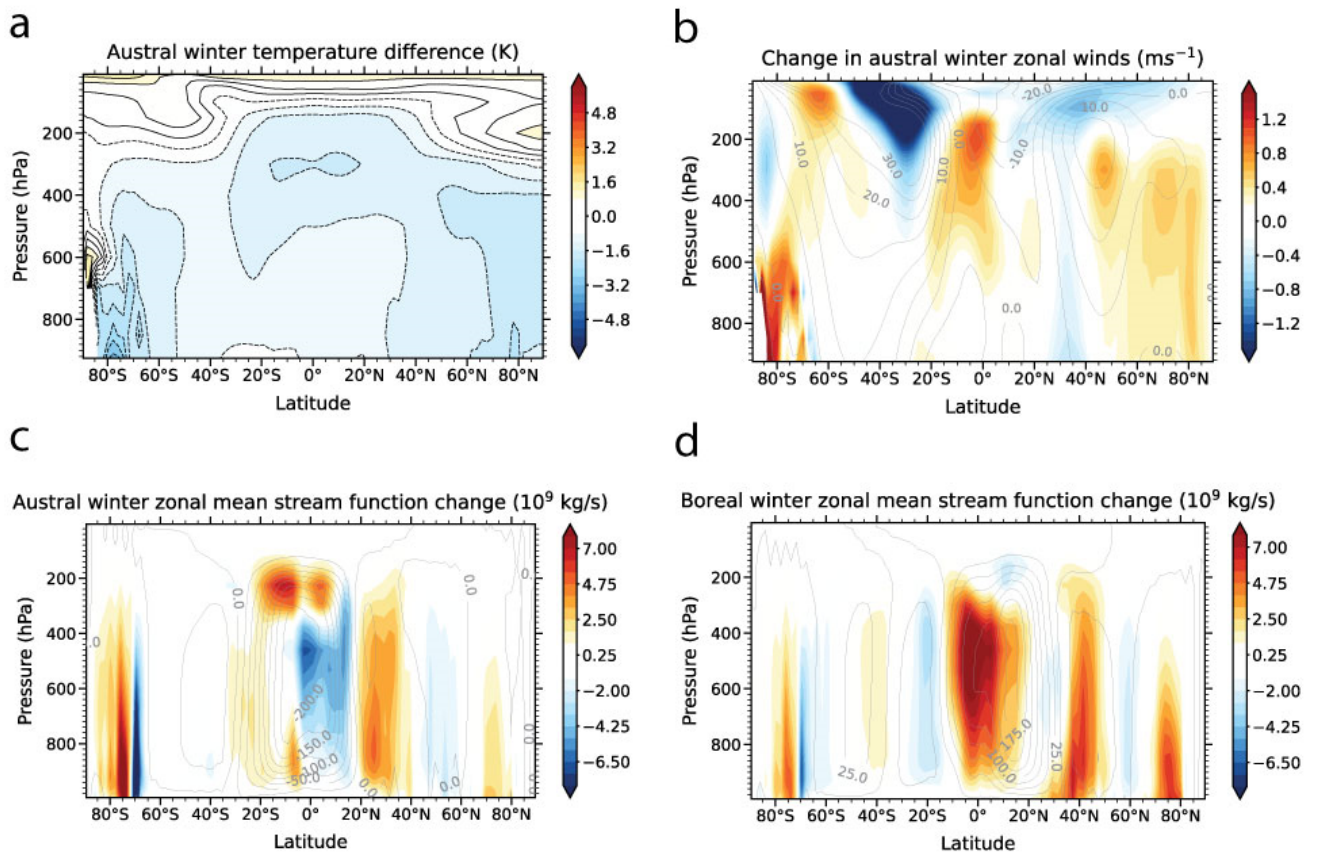
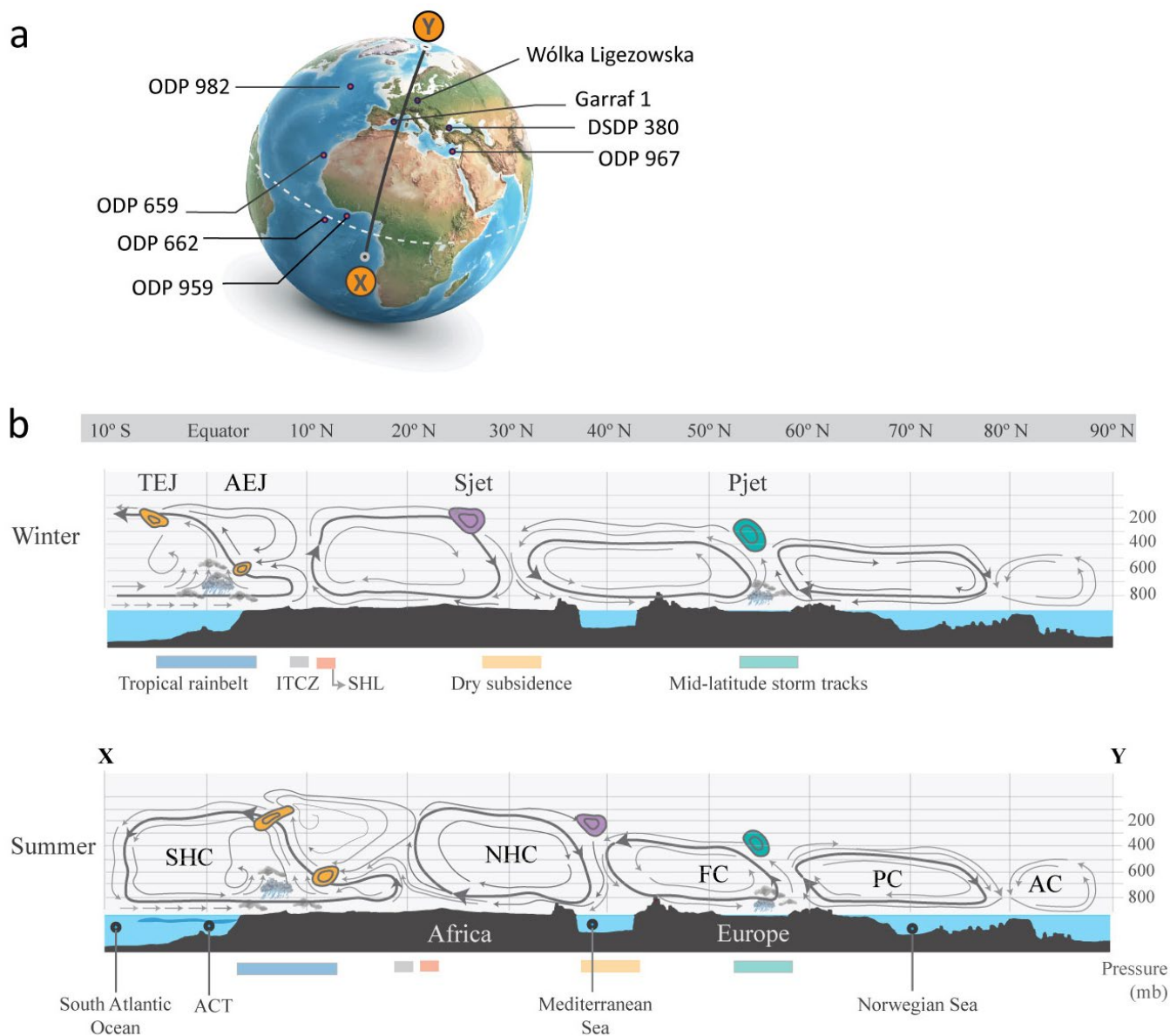
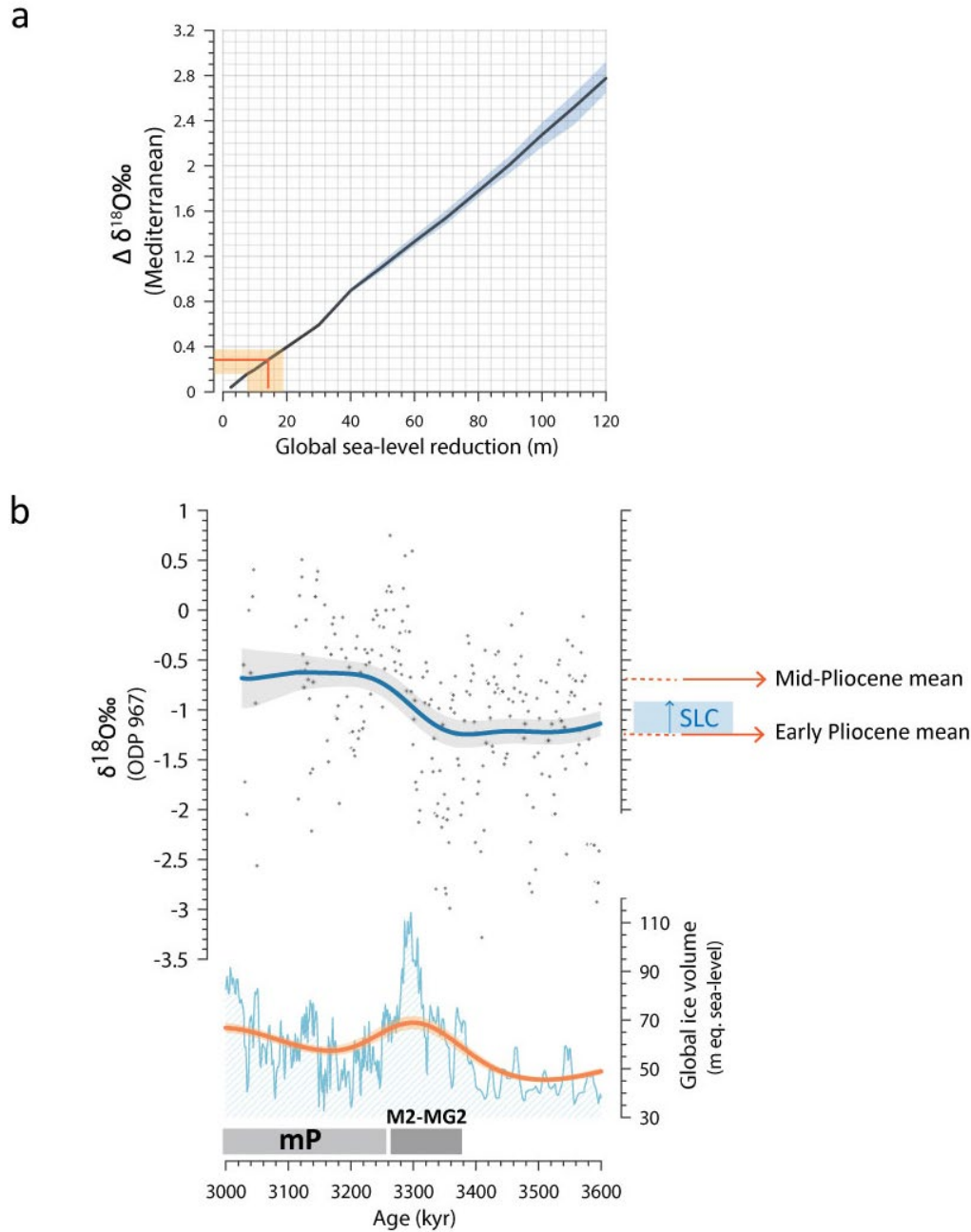


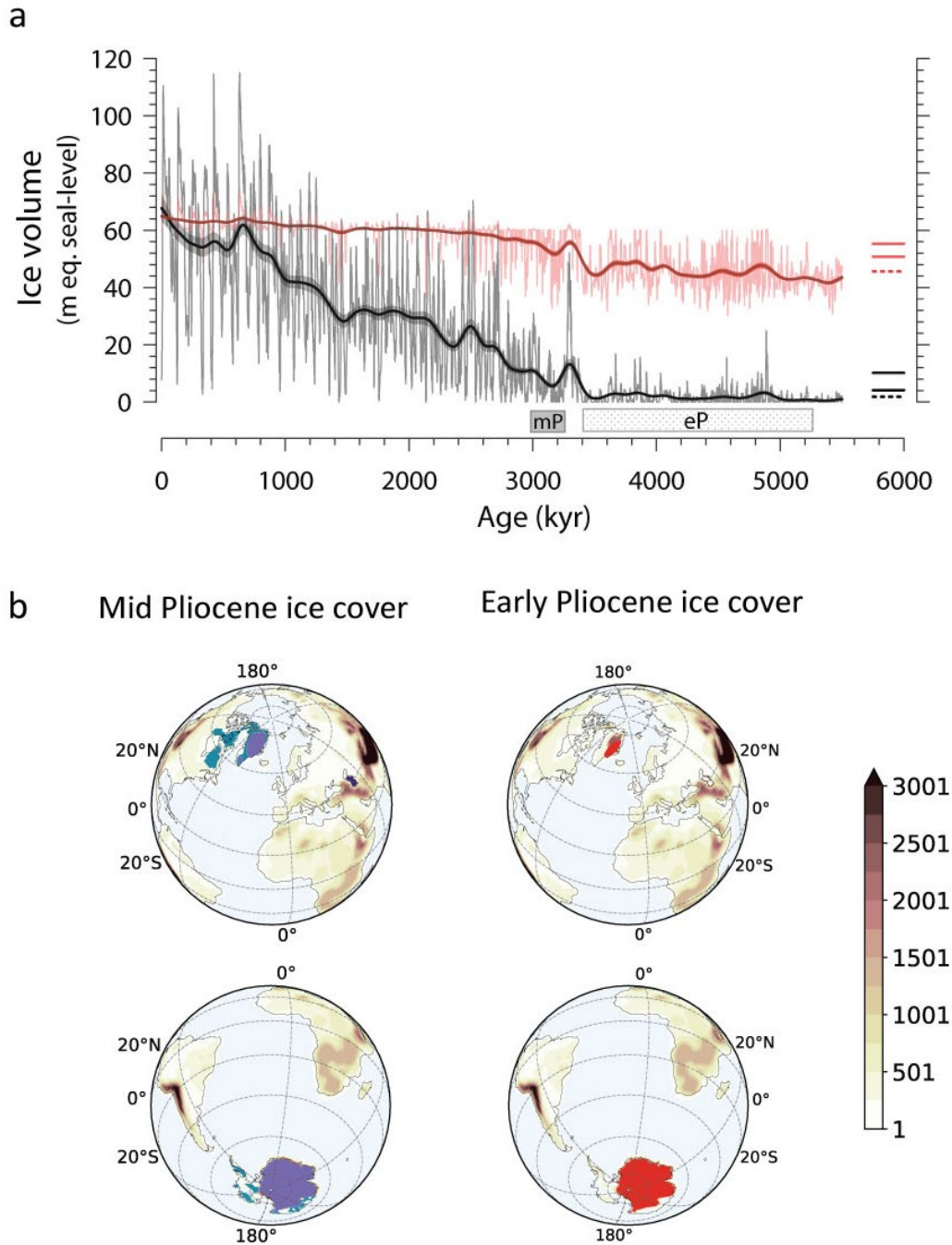
Figure 3| Climate modelling results showing the change in climate parameters (Mid Pliocene glacial mean- Early Pliocene). **a**, Austral winter zonal mean vertical atmospheric thermal structure, indicating TUT, Arctic and Antarctic lower tropospheric cooling. **b**, Austral winter zonal winds, indicating the weakening core of the SH upper tropospheric jet, while the jet flanks strengthen. Grey contours represent the wind velocities of the control run. Positive/negative values are for westerly/easterly winds. **c, d**, Change in zonal mean meridional stream function for austral and boreal winters, respectively. Grey contours represent the wind velocities of the control run. Austral and boreal winter Hadley cells strengthen and contract, while the tropopause height decreases due to the contraction.



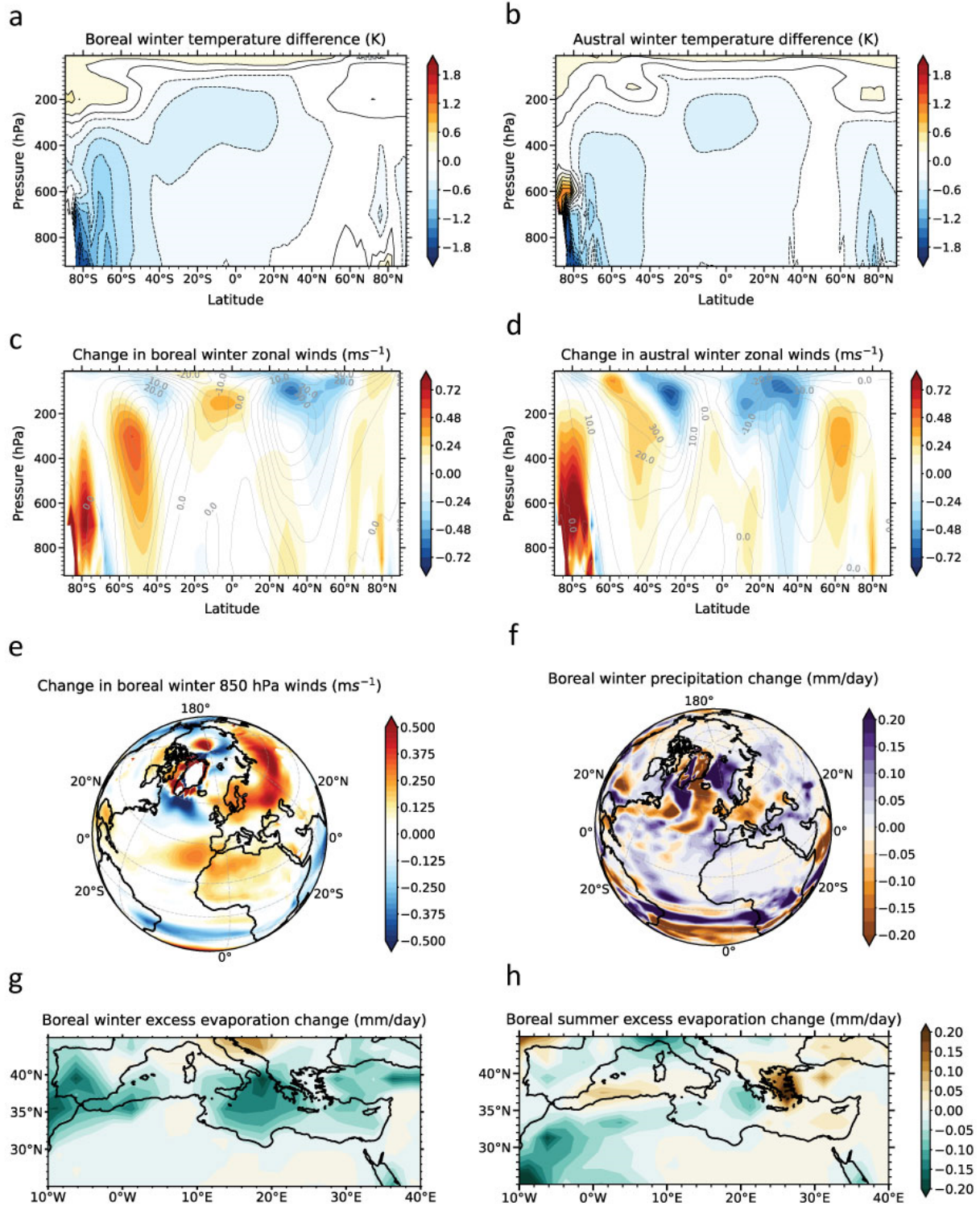
Extended Data Fig. 1 | A schematic representation of Northern hemispheric meridional circulation along 6°E longitude, resolved for boreal winter and summer. a, Map showing the main sites selected for data generation and compilation. b, Summer-winter dynamics across the XY cross section. Only the major modes of tropospheric climate variability across the section are considered here (North Atlantic Oscillation (NAO) and African monsoon system). The figure is drawn for a year with positive winter NAO, which induces the negative mode of summer NAO (see supplementary information). Cross section is drawn along the AB line shown in the map. TEJ; Tropical easterly jet, AEJ; African easterly jet, Sjet; Subtropical jet stream, Pjet; Polar jet stream, ITCZ; Inter-tropical convergence zone, SHL; Saharan heat low, SHC/NHC; Southerly/Northerly Hadley cells, FC/PC/AC; Ferrell/Polar/Arctic cells, ACT; Atlantic cold tongue. See the supplement for explanations.



Extended Data Fig. 2 | ODP 967 $\delta^{18}\text{O}$ shift at the Early-Mid Pliocene transition. **a**, Mediterranean box model $\delta^{18}\text{O}$ response to changing global sea-level. Upper and lower lobes (blue) represent 5% and 95% confidence intervals. Thick orange line indicates the mean sea-level change across the Early-Mid Pliocene transition. Orange shading indicates the range of values between mean interglacial and mean glacial ice volume differences compared to the Early Pliocene. **b**, ODP 967 $\delta^{18}\text{O}$ and global ice volume change²⁸ across the Early – Mid Pliocene. Dark grey dots indicate $\delta^{18}\text{O}$ data points. Thick blue line indicates the 60 ka moving average for $\delta^{18}\text{O}$ curve. Thick orange line represents the 60 ka moving average for global ice-volume reconstruction. The shading for each curve represents high/low (95%/5%) confidence intervals. Dotted lines (orange) at the right side $\delta^{18}\text{O}_{\text{‰}}$ axis show the mean mid and early Pliocene $\delta^{18}\text{O}$ values. Blue color square indicates the sea-level drop contribution (SLC) to the increase in mean $\delta^{18}\text{O}$ value (read from panel a). The remainder ($\sim 0.2 \text{ ‰}$) may result from factors such as an increase in excess evaporation³² (eg: stronger summer Hadley cell subsidence), or a decrease in freshwater runoff to the Mediterranean^{28,32} (eg: glacial North Africa drying). mP; mid-Pliocene.

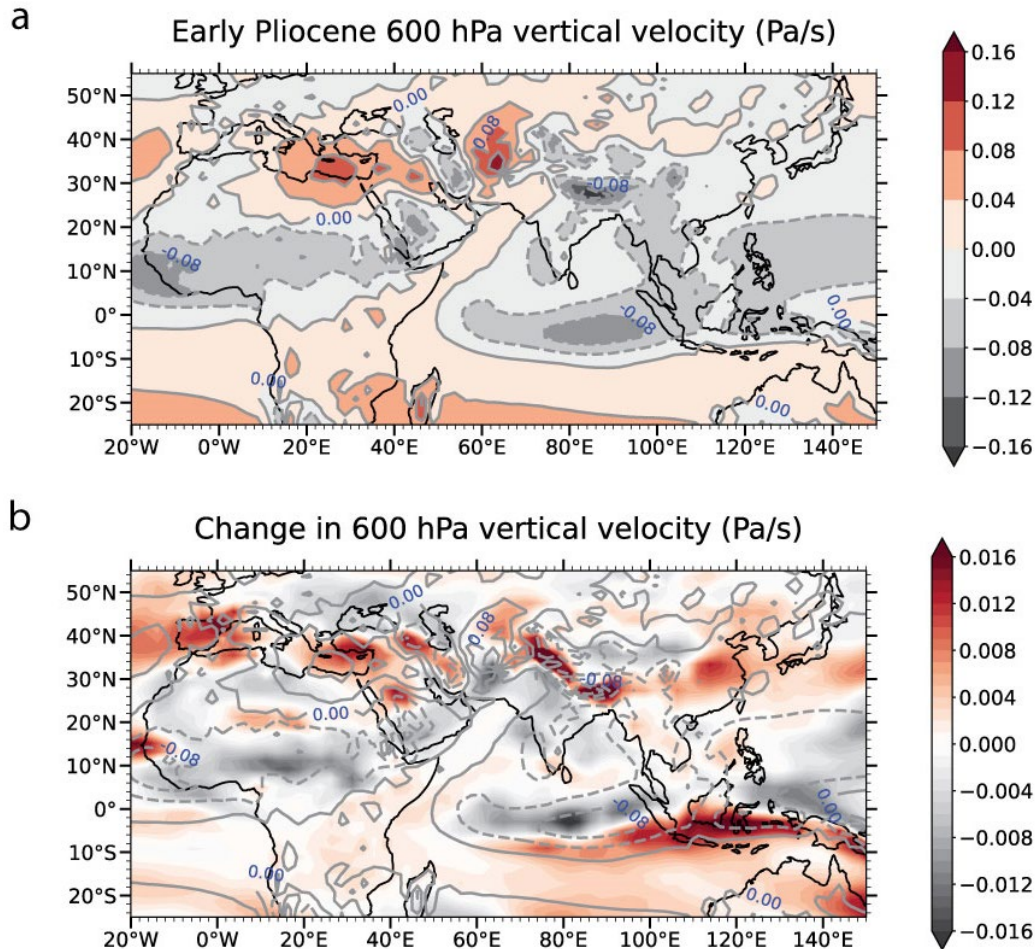


Extended Data Fig. 3 | Pliocene to present global ice volume evolution and reconstructed ice masks. a, Northern (black) and Southern (red) hemispheric ice volume evolution²⁸. Thick black and red lines represent 60 ka moving average for each record. The grey and red envelopes represent the 95% higher and lower confidence intervals for each curve. Horizontal lines next to the right side vertical scale represent the mean mid Pliocene glacial (upper solid lines), mid Pliocene interglacial (lower solid lines) and Early Pliocene (dotted lines) ice volumes for each hemisphere. mP, mid-Pliocene; eP, Early Pliocene. b, Ice masks employed for the model runs, developed based on the calculated mean ice volumes for Mid and Early Pliocene for both hemispheres. Red overlay = Early Pliocene mean, Purple overlay = mid Pliocene interglacial mean, Green overlay = mid Pliocene glacial mean. The color bar indicates the Pliocene topography.

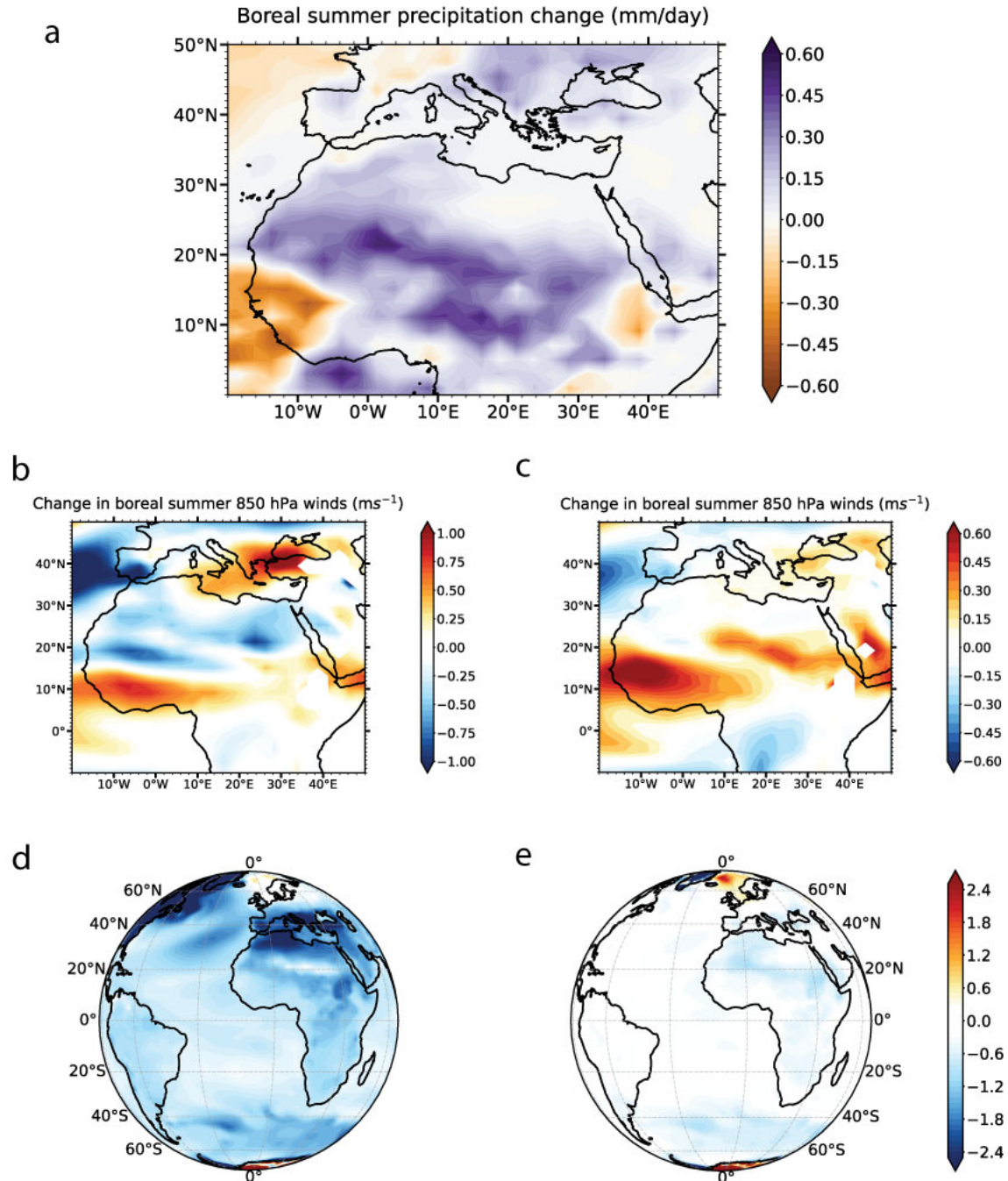


Extended Data Fig. 4 | Climate modelling results showing the changes in climate parameters (Mid Pliocene interglacial mean- Early Pliocene). **a, b**, Boreal and austral winter zonal mean vertical atmospheric thermal structure, indicating TUT, Arctic and Antarctic lower tropospheric cooling. **c, d**, Boreal and austral winter zonal winds, indicating the weakening core of the NH and SH upper tropospheric jets, while the jet flanks strengthen. Grey contours represent the wind velocities of the control run (Early Pliocene). Positive/negative values are for westerly/easterly winds. **e**, Boreal winter 850 hPa zonal winds, indicating a decrease of wind velocity over the North Atlantic. Patches of

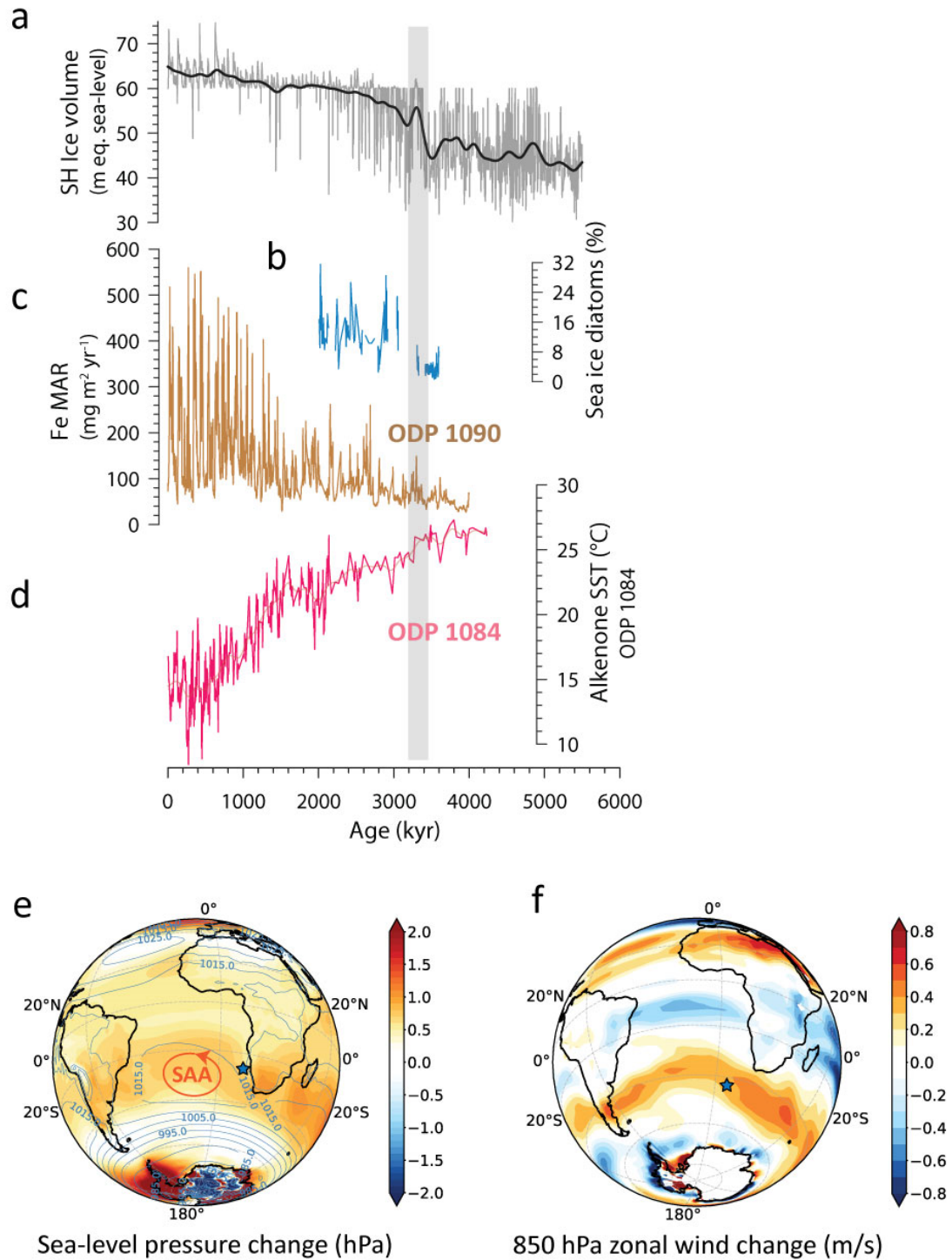
decreasing values exist over Europe **f**, Boreal winter precipitation over Northern Europe decreases as the storm track density decreases (weaker westerlies). Winter precipitation over Mediterranean increases due to the poleward strengthening of the westerlies. **g, h**, Winter versus summer excess evaporation over the Mediterranean. Winter-summer seasonal contrast increases due to the increase of Mediterranean winter precipitation, and the increase of summer excess evaporation driven by stronger subsidence.



Extended Data Fig. 5 | Strengthened subsidence over the eastern Mediterranean. a, Early Pliocene (control run) 600 hPa vertical velocity. Summer subsidence over the eastern Mediterranean is driven in combination by the North African summer Hadley cell and the Walker-type circulation origination over the 80°-120°E, 25°-35° N band over East Asia³⁷. **b**, Mid Pliocene glacial-Early Pliocene 600 hPa vertical velocity, indicating strengthened subsidence over the Mediterranean. Over the eastern Mediterranean, a stronger contribution likely comes from the Hadley cell, as the central ascending over East Asia weakens (contracts toward the equator) across the transition. Dashed and solid grey lines indicate the contours from the control run. The 600 hPa level was chosen due to topographic disturbances.

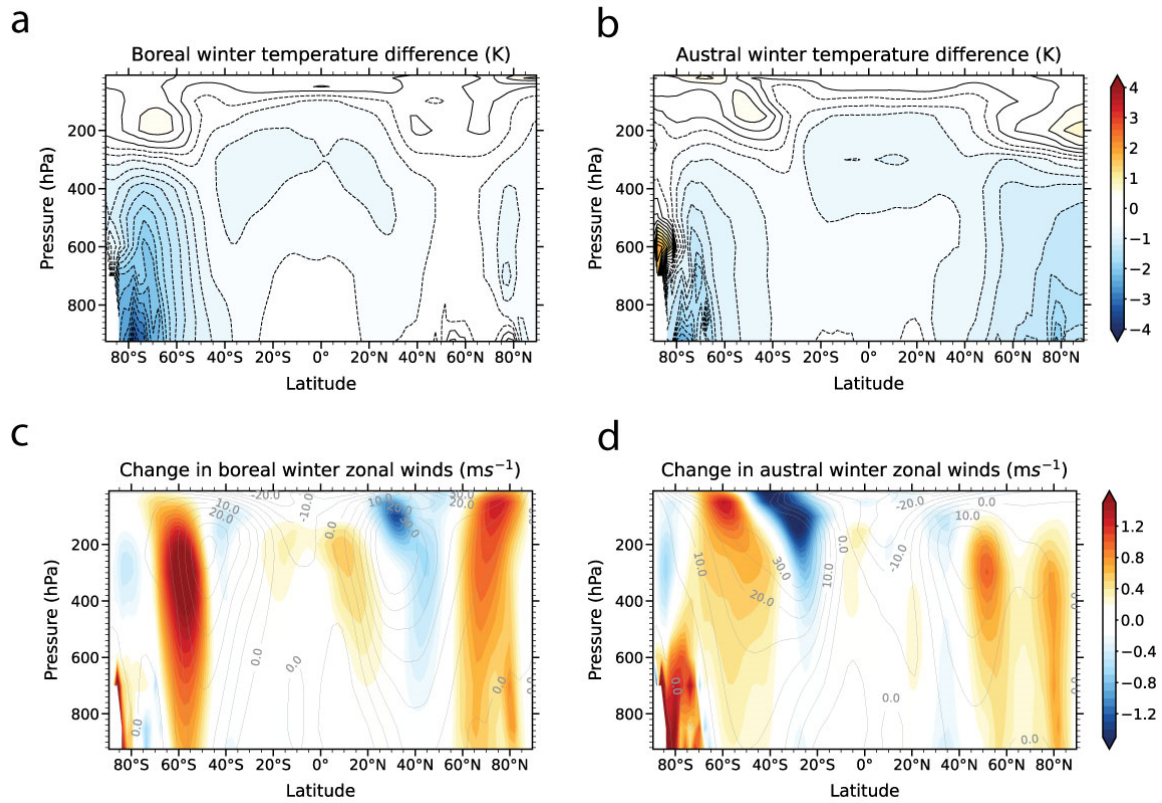


Extended Data Fig. 6 | Mid Pliocene Glacial-Interglacial precipitation contrast over North Africa. **a**, Boreal summer precipitation change (mid Pliocene interglacial – early Pliocene) over North Africa. **b**, Mid Pliocene glacial – Early Pliocene boreal summer 850 hPa zonal winds, indicating southward penetration of North African easterlies. Positive/negative values indicate stronger westerly/easterly winds. **c**, Mid Pliocene interglacial – Early Pliocene boreal summer 850 hPa zonal winds, indicating northward penetration of North African monsoonal winds, mainly driven by warmer temperatures over the North Atlantic and colder conditions in the South Atlantic. **d**, Mid Pliocene glacial – Early Pliocene boreal summer surface temperature difference (K). **e**, Mid Pliocene interglacial – Early Pliocene boreal summer surface temperature difference (K).



Extended Data Fig. 7 | Proxy-based evidence and climate model agreement on Early-Mid Pliocene global cooling influence on Southern Hemisphere **a**, Pliocene – present Southern Hemispheric ice volume reconstruction. **b**, Sea ice-indicative diatom abundance from Ross ice shelf ANDRILL AND-BI sediment core²⁷ **c**, Southern Ocean Fe mass accumulation rate (MAR) from ODP Site 1090, indicating higher glacial dust input after 3.3 Ma, followed by a major increase after 2.7 Ma^{refs.27,41} **d**, ODP Site 1084 Alkenone sea surface temperature reconstruction⁴⁰, indicating a sudden drop of temperature at 3.26 Ma, and continuous cooling afterwards. Vertical grey shading represents the Early-Mid Pliocene transition. **e**, Mid Pliocene glacial- Early Pliocene austral winter sea level pressure change, showing a strengthening of the South Atlantic anticyclone (SAA), which is the main driver

behind Benguela upwelling system intensification. Dark blue color star represents the ODP Site 1084 location. **f**, Mid Pliocene glacial- Early Pliocene austral winter 850 hPa wind change, indicating strengthened westerlies over the Southern Ocean. Dark blue color star represents the ODP Site 1090 location.



Extended Data Fig. 8 | Change in atmospheric temperature and zonal winds with no CO₂ forcing (Mid Pliocene glacial mean- Early Pliocene). **a, b**, Boreal and austral winter zonal mean vertical atmospheric thermal structure, indicating TUT, Arctic and Antarctic lower tropospheric cooling. Here, the Early Pliocene and mid-Pliocene glacial simulations were run using identical CO₂ concentrations (405 ppm). Therefore, the changes are considered solely be due to bipolar glaciation **c, d**, Corresponding boreal and austral winter zonal winds, indicating the weakening core of the NH and SH upper tropospheric jets, while the jet flanks strengthen. Even though smaller in magnitude, bipolar and TUT cooling alone are capable of widening and weakening the upper tropospheric jetstreams.

Extended Data Table 1: Ice sheet boundary conditions used for the early Pliocene (control) simulation, and the two perturbation experiments for the Mid Pliocene interglacial and glacial periods.

Experiment	NH ice volume (m SLE)	NH ice boundary conditions	SH ice volume (m SLE)	SH ice boundary conditions	CO2 forcing (ppm)
Early Pliocene (3.312 – 5.3 Ma)	25% of modern Greenland ice volume	PRISM4 (ref. ⁴⁶)	70% of modern Antarctic ice volume	PRISM4 (ref. ⁴⁶)	405 (initial) 415 (final)
Pliocene interglacials (3.0-3.264 Ma)	4.15	410 ka timeslice from ref. ⁴⁹	50.78	RCP8.5 scenario, year 5000 from ref. ⁴⁸	405
Pliocene glacials (3.0-3.264 Ma)	10.17	ICE-7G_NA: 8 ka timeslice from ref. ⁴⁷	55.32	RCP4.5 scenario, year 5000 from ref. ⁴⁸	405 (initial) 375 (final)

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CHAPTER 7

Megaflood-driven coexistence of eastern Mediterranean ventilation and sapropel formation

This chapter is in preparation for Nature Geoscience

Incorporating a wide range of data generation from ODP sites 967 and 969, This chapter presents a detailed understanding of the mystery sapropel that was investigated in chapter 2. Combined with numerical modelling, it is revealed that the eastern Mediterranean may have experienced gradually changing redox conditions throughout mystery sapropel deposition.

Statement of Contribution

This thesis is submitted as a Thesis by Compilation in accordance with
https://policies.anu.edu.au/ppl/document/ANUP_003405

I declare that the research presented in this Thesis represents original work that I carried out during my candidature at the Australian National University, except for contributions to multi-author papers incorporated in the Thesis where my contributions are specified in this Statement of Contribution.

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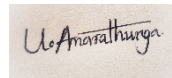
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Contribution to paper: U.A. designed and led the study, prepared samples for laboratory analyses, analyzed the data, generated the figures and wrote the paper; U.A. and J.J.B. developed the hypothesis; P.T.M. carried out paleodepth estimation; J.W.Z. performed biostratigraphy analysis; J.M.H., U.T., R.H., S.R., and I.C.vdH contributed to data generation; J.J.B., E.J.R. and G-J.R. advised on data interpretation; all authors contributed to manuscript development.

Senior author or collaborating authors endorsement: _____



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Mega-flood-driven coexistence of eastern Mediterranean ventilation and sapropel formation

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Collapse of the Gibraltar sill ~5.33 Myr ago generated a catastrophic mega-flood into the Mediterranean basin, which had partially desiccated during the Messinian salinity crisis (5.97-5.33 Myr). Previous work inferred that the mega-flood transferred dense western Mediterranean Messinian brines into the eastern Mediterranean across the Sicily sill, causing severe eastern basin salinity stratification. It was then hypothesized that anoxic conditions below the Sicily sill level due to hyperstratification caused the deposition of an anomalously long-lasting organic-rich layer ('mystery sapropel'). Here we present extensive proxy data and numerical modelling results to show that the eastern Mediterranean became oxygenated initially, due to the 1.5-kilometer-high, highly turbulent and aerated cascade that refilled the basin. We find that the oxygenation

enhanced gypsum deposition after the flooding, allowing preservation of only the most recalcitrant organic components. Next, oxygen was gradually depleted over a period of up to 12,000 years due to sinking organic matter remineralization, until organic matter deposition continued in a stratified, anoxic basin. It took a total of 33,000 years after flooding (7,000 years longer than suggested previously) for excess salt removal by turbulent diffusion to allow resumption of convective deep-water renewal, which marked the final return of normal and oxygenated marine conditions throughout the Mediterranean.

Main

Tectonic restriction of the Atlantic-Mediterranean gateway in the Late Miocene resulted in partial desiccation of the Mediterranean basin (Messinian salinity crisis; MSC, 5.97-5.33 Myr ago)¹⁻³. During peak MSC (5.6-5.55 Myr), both western and eastern Mediterranean basins were drawn down by more than 1.5 km, leading to the formation of giant evaporite deposits^{1,3-5}. Evidence for a massive drawdown come from the basin-wide presence of a Messinian erosional surface, and deep canyons beneath major river mouths such as the Nile and the Rhone rivers^{1,3,6}. The MSC ended ~300 thousand years later, as the Gibraltar gateway re-opened^{1,3}. However, the magnitude of drawdown during the terminal MSC and the mode of MSC termination remain highly debated, even after five decades of research^{1,7}.

Seismic data and sedimentological observations imply that prior to MSC termination, the Mediterranean still was largely drawn down and isolated from the Atlantic Ocean and other major water bodies^{3,8-11}. In contrast, paleontological evidence implies an intermittent presence of brackish biota across the Mediterranean sub-basins and biogeochemical evidence of Messinian brine dilution, indicating an influence of riverine and Paratethyan low-salinity waters^{7,12}. For a Mediterranean base level that was drawn down by ~2 kilometres, collapse of the Gibraltar sill at the MSC termination would have generated the most abrupt flooding event in recorded Earth history (the Zanclean megaflood)^{1,3}.

Recent modelling indicated that this highly energetic flood would have transferred remnant dense brine waters from the western basin into the eastern basin via a ~1.5 km high cascade across the Sicily sill¹. This established normal marine conditions in the western basin following the flooding event, while the eastern basin became salinity-stratified at the Sicily sill level¹. It was hypothesized that stratification led to deep-water anoxia, explaining the deposition of the anomalously long-lasting (26,000 years) organic-rich mystery sapropel following the

Miocene/Pliocene (M/P) boundary prior to re-establishment of normal marine conditions in the eastern Mediterranean¹.

At Ocean drilling program (ODP) Site 967, the mystery sapropel manifests as a dark layer with elevated Ba levels, following the M/P boundary¹. Ba is a proxy for original organic carbon burial, and is often used to detect Mediterranean sapropels even if they have been oxidized after deposition^{13–15}. It has long been established that Mediterranean sapropels formed during Northern Hemispheric precession minima (insolation maxima), due to curtailed deep water formation during extensive monsoon flooding phases into the Mediterranean^{16,17}. However, the Site 967 chronology indicates that the mystery sapropel spans the first two Pliocene insolation maxima, and the intervening insolation minimum; the only sapropel to span more than one insolation maximum in the entire Neogene¹. Here we combine high-resolution core-scanning XRF geochemical data and lower-resolution but diverse organic matter, mineralogical, and organic biomarker data for both ODP Sites 967 and 969 mystery sapropels¹, with numerical modelling of deep-water oxygenation, to obtain the first detailed characterization of this enigmatic final phase of the Mediterranean return to normal marine conditions.

New mystery sapropel data

In ODP Site 967, organic matter contents are very low throughout the mystery sapropel (<0.4%) (Extended Data Fig.1). Biomarker results indicate that only traces of recalcitrant higher plant lipids are preserved in the dark layer (Supplement). Although Site 967 today resides at a water depth of ~2,550 m, paleodepth reconstructions show that it resided at <400 m during the earliest Pliocene¹⁸, close to or above the level of the Sicily sill (Extended Data Fig.2). It is likely that more labile, algal organic remains were destroyed by post-depositional oxidation in such a shallow environment¹⁷. Furthermore, the first 0.6 m of the Site 967 mystery sapropel (ESU 2, see Extended Data Fig. 1) has a clastic nature with unusually elevated pollen/microcharcoal counts and low organic carbon contents, suggesting rapid sediment deposition following the Zanclean flooding, possibly representing or including reworked soil. Only the final 0.4 m (ESU 3, Extended Data Fig. 1) may be a true oxidized sapropel. Hence, we add data from deeper, more distal ODP Site 969.

ODP Site 969 (Mediterranean Ridge; Extended Data Fig.2) provides a well-preserved mystery sapropel equivalent. ODP Site 969 (Mediterranean Ridge crest) was deeper than present (>2,200 m) throughout the Pliocene¹⁹ (Extended Data Fig.2, Supplement). The Site 969 mystery sapropel is ~1 m thick and consists of 2 clear dark bands in a laminated, olive-grey

background (Fig.1). Our XRF results reveal 2 Ba peaks that correspond to the dark bands, with low Ba levels in between the peaks. However, organic carbon quantification indicates that, while the normal sapropel-like Ba peaks consist of high organic matter contents exceeding 1.7%, elevated levels (>1.0%) continue in between these peaks. Thus, we speculate that the Ba peaks correspond to the first 2 Pliocene insolation maxima, while the low Ba – high organic carbon values in between represent non-sapropelic preservation/productivity during the intervening insolation minimum. Our chronology based on this assumption agrees well with a re-evaluated biostratigraphy for Site 969 (Methods) and indicates that enhanced organic carbon preservation extended to the 2nd Pliocene insolation minimum (Extended Data Fig.3). Therefore, mystery sapropel deposition may have continued for ~33,000 years; ~7,000 years longer than previously estimated¹.

Sulphur (S) concentrations within the first half-precession cycle following the M/P boundary are up to 5 times higher than in the rest of the mystery sapropel (Fig.1). X-ray diffraction (XRD) analysis reveals that the high S values are caused by elevated gypsum contents in the sapropel. As the gypsum content reaches up to 20% after the M/P boundary, pyrite concentration reduces to values close to 0% (Fig.1). Elevated S contents continue for ~8-12 thousand years following the M/P boundary, until gypsum content reduces to <2.5 %, while pyrite content rises to values similar to those in the terminal Messinian sediments (~0.5 %). Pyrite is an end-product of the marine sulphur cycle, and is diagenetically stable in anoxic environments^{20,21}. Therefore, precipitation of the latest Messinian pyrite may have occurred in an anoxic, sulfidic water column²². However, we observe a sudden drop of pyrite content immediately after the M/P boundary (within the first Ba peak), which gradually increases to pre-Messinian values at the second Ba peak (Fig. 1). Unlike for normal sapropels (where pyrite maximum is correlated with high organic carbon), such a drop in pyrite: organic carbon ratio is suggestive of a largely oxygenated water column^{23,24}. Thus, we speculate that diminished pyrite contents following the M/P boundary with elevated organic carbon and gypsum contents, might indicate a shift in water column redox conditions.

Post-flood eastern Mediterranean oxygenation

Even though gypsum deposits have commonly formed in evaporitic environments (e.g., during the MSC)^{20,21,25,26}, the Mediterranean shifted from an evaporitic to a non-evaporitic basin across the M/P boundary^{1,3}. Gypsum precipitation in non-evaporitic environments requires additional high Ca^{2+} and/or SO_4^{2-} inputs^{20,21}. We infer that, in addition to sulphide oxidation,

Messinian brine accumulation in the eastern Mediterranean following the megaflood¹, combined with Messinian evaporite dissolution, may have provided excess Ca^{2+} and SO_4^{2-} to the basin.

Further evidence for a major sea-water influx comes from Site 969 Mo data (Fig.2e). In isolated anoxic basins, Mo will be depleted compared to the global ocean, due to sedimentary Mo enrichment^{27,28}, so that little Mo would have remained in the remaining Messinian waters. Thus, the isolated Mo peak immediately after the M/P boundary may suggest a sudden influx of Mo-bearing Atlantic waters to the eastern Mediterranean. Next, Mo is enriched throughout the mystery sapropel relative to normal marine sediments. Mo enrichment is commonly observed in euxinic, sulfidic settings, where water column MoO_4^{2-} is reduced to MoS, which is permanently buried in the sediment^{27,28}. Therefore, we suggest that anoxic conditions prevailed throughout mystery sapropel period in the deepest parts of the basin where ODP Site 969 is located. Bottom anoxia is supported by the absence of benthic fauna in the Site 969 mystery sapropel²⁹.

Our biomarker and pollen data provide evidence for Late Messinian hypersaline conditions, post-flood water column oxygenation, and the return of a largely anoxic basin within 8-12 thousand years (Fig.2a-d). Prior to Atlantic-Mediterranean reconnection, elevated relative archaeol, gammacerane and tetrahymanol concentrations (Fig. 2a) confirm high-salinity and stratified conditions³⁰. The relative abundances of these biomarkers rapidly drop toward zero at the M/P boundary coincident with opening to the Atlantic, cessation of Messinian hypersaline conditions and flux of algal and plant biomass to deep bottom sediments.

Even though the bottom sediments remained largely anoxic throughout the mystery sapropel deposition, notable changes in the relative abundances of algal and plant lipid classes support our hypothesis for a major long-term shift in water column redox conditions from the first to the second barium maximum. Accordingly, the lipid profile of the younger Ba peak points to minimal organic matter reworking typical of Pliocene sapropels³¹ (Fig. 2). In comparison, sediments within the first Ba peak are strongly depleted in labile phytoplankton lipids and enriched in recalcitrant biomarkers of terrestrial vegetation indicative of more intensive degradation under aerobic conditions. Notably, the ratio of C26:0 over C18:0 fatty acid is depressed in the first Ba peak relative to the second (Fig 2b), typical for aerobic reworking³². Similarly, the alcohol preference index (API) that demarcates the degradation of n-alcohols relative to more recalcitrant n-alkanes³³ (Fig 2b), the relative abundance of fatty acids over less

labile n-alcohols³¹, algal dinosterol over more recalcitrant land plant-derived sitosterol (Fig 2c), and the abundance of total sterols and C30 1,15-diol over relatively more stable n-alcohols^{31,32} (Fig 2d) markedly increase toward the younger Ba peak. More intense aerobic reworking of organic matter during deposition of the first Ba peak is also supported by up to 3 times lower pollen count in the first Ba peak compared to the second Ba peak³⁴ (Fig. 2e). The end of mystery sapropel deposition is marked by a sharp rise of (epi)brassicasterol abundances relative to dinosterol, pointing to a possible shift from dinoflagellates to haptophytes (or possibly diatoms) as dominant phytoplankton³⁵ (Fig. 2e). These combined data demonstrate a more oxygenated water column during the first ~8-12,000 years of mystery sapropel formation, followed by a shift to more reducing conditions typical of younger sapropels.

Oxygenation mechanism and modelling results

A likely source of oxygen to the eastern Mediterranean water column is the ~1.5 km high cascade that refilled the eastern basin through the Noto Canyon southeast of Sicily^{1,8,9}. The canyon opens at the Malta Escarpment, with a relief of 70° at its final 700m drop to the Ionian Basin^{8,9}. Modern experiments and observations have demonstrated a high potential for cascading, turbulent waters to increase the dissolved oxygen content, due to high aeration efficiency³⁶⁻³⁸. Increasing flood discharge rates rapidly increase the dissolved oxygen content, commonly reaching supersaturated conditions exceeding 180% O₂ further downstream³⁷.

Numerical models simulating the MSC-terminating megaflood indicate that at peak flood conditions, flood discharge may have exceeded 150 Sv, with velocities up to 50 m s⁻¹ in the Alboran basin^{1,3}. The cascade entering the eastern basin across the Sicily sill would have been even more energetic due to the steep drop at the Malta Escarpment, which would have generated highly turbulent conditions¹. It can therefore be expected that the eastern basin inflow was saturated (to supersaturated) in oxygen. In such a scenario, the eastern Mediterranean would have been filled with highly saline and oxygenated waters up to the Sicily sill level (Fig.3a) once the flooding phase was completed (within ~700 days)^{1,3}. We hypothesize that subsequent duration of O₂ presence beneath the pycnocline would depend on the rate of oxygen utilization by remineralization of the sinking organic carbon flux (hence, productivity). From our proxy evidence, we infer that O₂ may have existed for 8-12 thousand years following the flooding event, subsequently reaching anoxia throughout the water column (Fig.3d).

To test our hypothesis, we extend a published numerical model for the post-MSC basin developments¹ to quantify changing oxygen concentrations during and after the flooding event (Methods). We consider a scenario where a thin residual brine layer would remain in the eastern basin at flood termination (due to incomplete mixing with the inflow), to allow the observed mystery sapropel Mo enrichment^{27,28} (a starting brine salinity of 200 PSU, Extended Data Fig. 4). The first phase of the model calculates the flow-energy-dependent extent of mixing of incoming western Mediterranean waters with the eastern basin brines. This allows us to calculate the oxygen concentration of the western and eastern basin mixed layers through the refilling event, across a range of possible saturation states. The model indicates that at 20% mixing efficiency (Methods), ~95% of eastern basin brines will be completely mixed with the flood waters to create a hypersaline layer with ~90 PSU below the Sicily sill, while residual brines remain in the deepest basin at flood termination (Extended Data Fig.4). Assuming an O₂-saturated inflow during the refilling phase, the mixed layer reaches an O₂ concentration of 170 $\mu\text{mol kg}^{-1}$, which is ~90% of its O₂ saturation level (Fig.3b, Methods). Our sensitivity tests indicate that, for a range of 80-175% O₂ saturation of the inflow, the final eastern basin total O₂ content below Sicily sill depth can range between 280×10^{14} and 340×10^{14} mol (Extended Data Fig.5).

Salt removal back to the Atlantic after flood termination was suggested to occur through turbulent diffusion¹. Within a diapycnal diffusivity range of 1×10^{-5} to $5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, our model shows that eastern basin deep water renewal was inhibited for 12,000-44,000 years following the flooding event. Our revised proxy-based age estimate for the mystery sapropel (33,000 years; see above) agrees with this suggested duration of stratification (Fig.3c). To estimate the rate of post-flood O₂ consumption, the second phase of our model employs a published algorithm that links the Ba accumulation rate in sediments to surface-water productivity^{39,40} (Methods, Extended Data Fig.6). We estimate absolute organic carbon fluxes through time for a range of chosen maximum sapropel productivity values ($15\text{-}150 \text{ gC m}^{-2} \text{ yr}^{-1}$)⁴⁴⁻⁴⁶. We find that, for a basin refilled with an O₂ saturated inflow, complete O₂ consumption may take 0.4-13.5 thousand years within the $15\text{-}150 \text{ gC m}^{-2} \text{ yr}^{-1}$ surface productivity range (Fig.3d). This range covers the average surface productivity range of $30\text{-}60 \text{ gC m}^{-2} \text{ yr}^{-1}$ during Quaternary sapropel formation, the $120\text{-}140 \text{ gC m}^{-2} \text{ yr}^{-1}$ range of Late Pliocene sapropels^{41,42}, and the 5-7 times lower values for sapropels formed prior to 3.2 Ma derived from changes in Ba accumulation rates⁴³. For a 175% O₂ saturated inflow, the O₂ consumption period then ranges between ~0.5 and ~20.5 thousand years (Extended Data Fig.5). Our sensitivity tests indicate

that following a refilling event with saturated to supersaturated flood waters, and for maximum sapropel productivities lower than $\sim 45 \text{ gC m}^{-2} \text{ yr}^{-1}$, it is possible to maintain oxic to suboxic conditions in the eastern Mediterranean for the observed 8-12 thousand-year period (Extended Data Fig.5).

We employ wide-ranging data collection and box-model-type modelling, to explore the Mediterranean transitional phase to normal marine conditions following the catastrophic marine flooding that terminated the 600,000-year Messinian isolation of the Mediterranean from the global ocean^{1,3}. This rapid sea-water influx transformed the hypersaline, anoxic Messinian Mediterranean into a separated system comprising a normal marine western Mediterranean, and a severely salinity-stratified but largely oxygenated eastern Mediterranean with some residual (anoxic) brines in the deepest parts (Extended Data Fig.7). Following the flooding phase, eastern Mediterranean deep waters (below Sicily sill depth) gradually changed from an oxidizing to a reducing state in $\sim 8\text{-}12,000$ years, while remaining dissolved salts were removed to the Atlantic in $\sim 33,000$ years.

Methods

X-Ray fluorescence scanning

We present X-ray fluorescence (XRF) core-scanning data for ODP Site 969 Hole B (95.9-98.4 mbsf). Scanning was performed on archive core-sections at MARUM-University of Bremen on an Avaatech XRF core scanner. Core sections were covered with 4 mm-thick Ultralene film and measured at 50 and 30 kV with 0.55 mA current and with a Cu and Pd-thick filter, respectively, and at 10 kV with 0.035 mA current (no filter); count time for all runs was 7 s. Element 'counts' for the entire interval were converted into element concentrations by multivariate log-ratio calibration, using new wavelength dispersive (WD)-XRF reference element concentrations. For these, 38 bulk sediment samples were chosen to cover a range of lithologies based on the XRF scan, then 1 cm^3 dried ground sample was mixed with a lithium tetraborate/lithium metaborate flux and fused into 39 mm diameter beads. Major element abundances were analysed by WD-XRF using a Bruker S8 Tiger™ spectrometer at Geoscience Australia. Loss on ignition (LOI) was measured by gravimetry after combustion at 1000°C . One in every ten samples was duplicated along with multiple analyses of 3 international standards (NCS DC70306, MAG-1, ML-2) and an internal basalt standard (WG1). Quantification limits for all major element oxides are $<0.2\%$ and reproducibility is within 1%.

Biostratigraphy

To identify the M/P boundary, previous studies on the mystery sapropel employed shipboard stratigraphy and biostratigraphy based on post-cruise scientific reports of ODP Site 967 and 969. To generate a preliminary chronology for site 969, we tuned the Ba (and Ba/Al) peaks to June 21st 65°N insolation maxima⁴⁴, assuming the M/P boundary existence at a 97.11 m core depth. To validate our XRF-based chronology, site 969 biostratigraphy was re-evaluated.

The Zanclean global stratotype section and point (GSSP) and the base of the Pliocene Series is defined at the base of carbonate cycle 1 in section Eraclea Minoa in Sicily⁴⁵. Therefore, to determine whether the inferred position of the M/P boundary at site 969 corresponds with the true M/P boundary and whether the basal Pliocene section at Site 969 is complete, a comparison of 969 with section Eraclea Minoa in Sicily is required. To detect the earliest Pliocene biozones, a comparison of *Sphaeroidinellopsis* and left coiled *negloboquadrinid* species was carried out using 18 samples from core sections A11H4, A11H5, B11H5 and B11H6. To confirm the position of the M/P boundary, a comparison of Site 969 sapropels between Eraclea Minoa grey intervals was employed. Site 967 samples were not examined for biostratigraphy, as foraminifera preservation was poor within the designated mystery sapropel section.

X-Ray Diffraction analysis

A total of 10 and 8 samples were chosen from ODP 967 and ODP 969 sediments respectively, across the M/P boundary. Each sample was ground by hand in acetone with an agate mortar and dried. To enable the quantification of amorphous material, samples were spiked with 20 wt% corundum (Al₂O₃, 1 µm, Baikalo[®]), mixed in acetone, pipetted onto a quartz low-background-holder and dried.

Powder X-ray diffraction analysis was carried out with a Malvern Panalytical Empyrean Series 3 which is equipped with Bragg-BrentanoHD divergent beam optic and a PIXcel3D detector (1D scanning mode, 3.347° active length), using CoK α radiation. The sample was analysed over a range of 4-85° 2 θ , with step width of 0.0262606° 2 θ and a total dwell time of 300 s/step, while spinning horizontally. Phase identification was carried out with the software Diffraction Plus Eva 10 (2004) and ICDD PDF-2 database (2004). Siroquant V4 (2014) was used for phase quantification.

Organic carbon quantification

To determine the organic carbon percentage across the M/P boundary, 10 samples from Site 967 and 11 samples from Site 969 were chosen. All the samples were analysed at

Environmental Analysis Lab (EAL) at Southern Cross University. Approximately 0.2 g of dry, grounded samples were weighed into nickel lined ceramic LECO boats. An excess (approx. 2ml) of 5% Sulphurous Acid was added to every sample and reference. Then, the samples were placed on a hotplate at ~100°C until samples became dry. Analyses were carried out on the LECO SC832 as per QWORK18-70 and LECO SC832 Operation Manual. Determinations of carbon content were carried out automatically in the instrument software.

Biomarker analysis.

For biomarker analysis, ~2 g per sample was sampled from cores of both Sites (6 and 8 samples respectively, from Site 967 and Site 969). Chosen sediment samples were dried and finely ground using a mortar and pestle. Powdered sediments were extracted with a Dionex Accelerated Solvent Extractor (ASE 200) using 90% dichloromethane and 10% methanol. Each cell was heated to 100°C (2 min), pressurized to 1000 p.s.i (5 min thermal equilibration), static extracted (2 min), flushed and purged of solvent residue using pressurized nitrogen for a total of 5 cycles.

Preparation of the Total Lipid Neutral (TLN) extract for GCMS analysis. The Total Lipid Extract (TLE) was evaporated to dryness under nitrogen gas at 45°C (Caliper TurboVap LV) and hydrolyzed overnight with 3 mL of 6% KOH in methanol:water = 8:2. The solution was flushed with N₂, vortexed and left overnight at room temperature. The Total Lipid Neutrals (TLN) were obtained after three back-extractions with *n*-hexane (3 mL) and washing with MilliQ water (1 mL) to remove any remaining KOH. Solvent was removed from the TLN under a stream of purified nitrogen gas at 60°C. The aqueous layers were combined for FA extraction.

The TLN was taken up in dichloromethane and transferred to a 2 mL vial including a 100 µL insert and then reduced to dryness. BSTFA (sigma) (50µl) was added to derivatise the TLN, and the solution heated at 80°C overnight. Excess BSTFA was removed as above with a stream of purified N₂ gas. Hexane was added to the TLN for immediate GCMS analysis.

Preparation of the Fatty Acid (FA) extract for GCMS analysis. The combined aqueous phases from the TLN extraction were acidified to pH 1 with HCl (32%). The FA fraction was extracted from the acidified solution using dichloromethane and treated as above to derivatise with BSTFA.

Gas chromatography and mass spectrometry. Gas chromatography–mass spectrometry (GC–MS) analyses were carried out on an Agilent 6890 GC coupled to a Micromass Autospec Premier double-sector MS (Waters Corporation, Milford, MA, USA). The GC was equipped with a 60 m DB-5MS capillary column (0.25 mm i.d., 0.25 μ m film thickness; Agilent) and used helium as the carrier gas at a constant flow rate of 1 mL min⁻¹. The MS source was operated at 260°C in EI-mode at 70 eV ionization energy and with 8000 V accelerating voltage. Samples were injected in splitless mode into a Gerstel PTV injector, which was ramped from 60°C (hold for 0.1 min) to 300°C at 260°C/min and held at the maximum temperature for the remaining duration of the analysis. For full-scan analyses, the GC oven was programmed at 60°C (4 min), heated to 315°C at 4°C/min, with a final hold time of 22.3 min. The AutoSpec full-scan duration was 0.7 s plus 0.2 s interscan delay over a mass range of 55–600 Da.

All samples were injected in *n*-hexane to avoid deterioration of chromatographic signals by FeCl₂ buildup in the MS ion source through use of halogenated solvents (Brocks & Hope, 2014). All components were quantified relative to the 18-MEAME internal standard (*m/z* 340), using characteristic parent-to-daughter ion mass transitions (*m/z* in brackets, *n*-alkanes (85), *n*-alkanols (75), dinosterol (69), C30 diol (69), friedelin (205), gammacerane (191), tetrahymanol (191), archaeol (85) respectively). Peak areas are uncorrected for differences in GC-MS response. All the data required for calculation of indicated ratios in the main text are in Extended Data Table 1.

Pollen and microcharcoal analysis

To determine pollen and microcharcoal concentrations, about 1.25 cc of sediment was dispersed in Calgon (3%) and placed in a low temperature water-bath for ½ hour followed by placement on an agitator overnight to further loosen sediment, a Lycopodium tablet had been added (9666 spores) to calculate both the pollen and charcoal concentration. Samples were then treated with HCl (10%) in a warm bath to remove any carbonates and then sieved at > 125 μ m, the > 125 μ m fraction provided no relevant material (plant or seed material). HL (Heavy liquid/LST-Lithium heteropolytungstates) at a density of 2.01 SG was then used to separate mineral matter from the organic fraction which was followed by acetolysis which removes cellulose and stains the pollen. Samples were then mounted on slides with glycerine with the cover slip sealed with nail polish. Glycerine aids identification and provides movability on the slide. H₂O (distilled) washes, X 2/3, were completed across all steps.

Mediterranean Evolution

Flooding phase oxygen concentration

Following recent studies on the post-Messinian megaflood, we assume water level drops of 2,000 m and 1,750 m for eastern and western basin before the flooding event¹. We updated initial eastern basin Messinian brine salinity to 200 PSU, to generate a residual brine layer at flood termination (choice validated by ref.¹, because all western basin brines will be transferred to the eastern basin at salinities below 220 PSU). Flood velocity, energy, western and eastern basin salinity evolution are calculated according to published methods, using the most recent hypsometry for the Mediterranean^{1,3}. We use a mixing efficiency of 20% during the flooding phase (for mixing of less-saline waters with dense brines), as it was shown proxy data agrees well with this value¹.

During the first stage of the flood, western Mediterranean is rapidly refilled by Atlantic waters. Modern observations indicate that turbulent rapids and falling water rapidly becomes oxygen saturated, commonly reaching supersaturated levels up to 180% further downstream^{36–38}. Due to the high energy and turbulence of the flow, we assume that oxygen-saturated normal marine flood waters (36 PSU salinity, 15°C temperature) enter the western basin. To calculate the Atlantic inflow saturated oxygen concentration ($O_{X_{Atlantic}}$), we incorporated Gibbs Sea Water (GSW) Oceanographic Toolbox to our model. The GSW toolbox function *O2sol* calculates the saturated oxygen concentration, depending on the salinity and the temperature of the floodwaters.

The mixing extent of Atlantic waters with dense western basin brines depends on the available flow kinetic energy reaching the basin surface. If the flow energy is greater than the potential energy gain required for complete mixing, the whole brine column will be mixed with the incoming Atlantic waters. If the flow energy is not sufficient to mix with the brines completely, a portion of the brine column will be mixed, creating a ‘mixed layer’. Following ref.¹, we compute the extent of mixing using:

$$KE_{Av} = PE_{GP} = \int_{H+h-H_{Mix}}^{H+h} \rho_m g z dz A(z) - \left(\int_H^{H+h} \rho_s g z dz A(z) + \int_{H+h-H_{Mix}}^H \rho_b g z dz A(z) \right), \quad (2)$$

where KE_{Av} is the flow kinetic energy available for mixing, PE_{GP} is the potential energy gain during partial mixing, H is the total brine column thickness prior to mixing, h is the thickness of the seawater layer flooded into the basin per timestep (per day), H_{Mix} is the thickness of the mixed

layer, g is the acceleration due to gravity, $A(z)$ is the basin surface area with depth (z), and ρ_m , ρ_s , and ρ_b are densities of the mixed layer, Atlantic waters and Messinian brines, respectively.

The mixed layer thickness (H_{Mix}) can then be used to calculate the mixed layer volume ($V_{Mix[wMed]}$). Therefore, the oxygen concentration of the western basin mixed layer at each timestep will be:

$$Ox_{wMed} = \frac{Ox_{Atlantic} \times Q_{in}}{V_{Mix[wMed]}} \quad (3)$$

During flood stage 2, the eastern basin is filled by western basin mixed layer waters through the Noto Canyon¹. Thus, the oxygen concentration of the eastern basin inflow (Ox_{Noto}) is determined by the properties (salinity, temperature) of the western basin mixed layer. Thickness and the volume of the eastern basin mixed layer are calculated using eq. (1). Therefore, the oxygen concentration of the eastern basin mixed layer at each timestep will be:

$$Ox_{eMed} = \frac{Ox_{Noto} \times Q_{in}}{V_{Mix[eMed]}} \quad (4)$$

Once the eastern basin reaches the Sicily sill level, the cascade entering through Noto Canyon terminates. During the final flooding stage, both western and eastern basin levels rise to the Atlantic level. The eastern basin becomes salinity-stratified at Sicily sill level, while the western basin becomes a normal marine basin. We assume that oxygen contents in western basin, and in eastern basin below Sicily sill level, remained constant due to diminished flow energy during final flooding phase¹.

Post-flood eastern Mediterranean oxygen consumption

Our model for the flooding phase indicates that the eastern basin is mixed to a depth of ~3,300 m due to the energetic flood (at a 20% mixing efficiency as in ref.¹), and that oxygen concentration within the mixed layer can reach up to 170 $\mu\text{mol kg}^{-1}$. As density stratification prevents deep water formation, the consumption of oxygen will occur due to sinking organic matter below the stratification.

To estimate the rate of oxygen consumption with time, we calculated the relative Barium flux through time, in the eastern basin. Marine Barite (BaSO_4) is a major carrier of particulate Ba in water column, and is precipitated during phytoplankton decay, which results in a positive correlation between biogenic barium content and organic carbon flux to the ocean floor^{39,40}

(Eagle 2003). Algorithms developed on this relationship have widely been used to estimate past productivity of ocean basins, including the Mediterranean^{39,40}.

To estimate the biogenic Ba flux, the terrigenous Ba component should be removed, usually using conservative element concentrations such as that of Al. Therefore, the biogenic Ba flux can be written as:

$$Ba_{bio} = Ba_{total} - (Al \times \frac{Ba}{Al_{aluminosilicate}}) \quad (5)$$

where Ba_{bio} is the biogenic Ba content, Ba_{total} is the total Ba content and $Ba/Al_{aluminosilicate}$ is the terrigenous Ba/Al ratio, which is considered here to be 0.0019 for the eastern Mediterranean (Van Os). Then, the Ba_{bio} flux (F_{Ba}) can be estimated using:

$$F_{Ba} = \frac{Ba_{bio} \times \frac{MAR}{100}}{0.209 \log(MAR) - 0.213} \quad (6)$$

where MAR is the marine accumulation rate. New production (P_{new}) can then be estimated using:

$$P_{new} = \left(\frac{F_{Ba} \times 0.171 \times Ba_{dis}^{2.218} \times z^{(0.476 - 0.00478 Ba_{dis})}}{2056} \right)^{1.504} \quad (7)$$

where Ba_{dis} is the mean dissolved Ba concentration in the Mediterranean and z is the water depth at site of deposition. Surface primary productivity (PP) is then given by:

$$PP = 20(P_{new})^{0.5} \quad (8)$$

With above parameterizations, it is possible to calculate a range of export productivity estimates for the eastern Mediterranean. Calibrated XRF data for eastern Mediterranean ODP site 967 reveals that the change in elemental ratios is insignificant subsequent to calibration⁴³. On this note, we are using uncalibrated ODP site 969 XRF data for an export productivity reconstruction. Because the concentrations are only available in counts, it is necessary to construct a relative productivity curve, which subsequently can be converted to estimated absolute productivity curves.

Mediterranean paleoproductivity estimates infer that surface primary productivity during peak sapropel intervals generally ranged between 30-60 gC m⁻² yr⁻¹, while values low as 15 gC m⁻² yr⁻¹ and values exceeding 120 gC m⁻² yr⁻¹ have been recorded^{41,42}. To generate the relative productivity curve, we assume that the maximum absolute surface productivity was reached at the point of maximum Ba flux following the M/P boundary. Equations (5) -(7) are then used to

calculate relative PP values through the interval. Assuming a constant sedimentation rate through the mystery sapropel, we use a ratio of 1.3 for $MAR_{marl}/MAR_{sapropel}$, during precession maxima for equation (5). If PP_{Array} contains all the PP values calculated using Ba and Al concentrations in counts, then the relative productivity curve $PP_{R(Array)}$ will be:

$$PP_{R(Array)} = \frac{PP_{(Array)}}{PP_{(Array)}^{max}} \quad (9)$$

where $PP_{(Array)}^{max}$ is the maximum value in $PP_{(Array)}$, which occurs at maximum F_{Ba} . Therefore, the maximum value of $PP_{R(Array)}$ also occurs at maximum F_{Ba} ($PP_{R(Array)}^{max} = 1$).

Then, the absolute productivity curve ($PP_{abs(Array)}$) can be estimated using:

$$PP_{abs(Array)} = PP_{R(Array)} \times PP_{abs}^{max} \quad (10)$$

where PP_{abs}^{max} is the chosen maximum absolute productivity value. We estimate absolute surface productivity curves at chosen PP_{abs}^{max} values ranging between 15-100 gC m⁻² yr⁻¹.

In modern settings (including the Mediterranean), a maximum of about 25% of the surface primary production leaves the photic zone. It has been shown that a further 60-80% of organic carbon export below the photic zone is oxidized within the next several hundred meters^{46,47}. We use these values to estimate the organic carbon export with time, below Sicily sill level (present depth = 430 m), Therefore, the total organic carbon export to the deep basin ($C_{exp(deep)}$) through time can be estimated using:

$$C_{exp(deep)} = PP_{abs(Array)} \times 0.25 \times 0.3 \times A_{Sicily} \quad (11)$$

where A_{Sicily} is Mediterranean area at the Sicily sill level. A molar ratio of 1:1.4 for organic carbon: oxygen is employed to calculate cumulative oxygen consumption below the stratification. Because the upward turbulent diffusion of oxygen is significantly slow compared to the organic carbon sinking rate, the average rate of oxygen consumption (R_{ox}) below the Sicily sill is:

$$R_{ox} = \frac{C_{exp(deep)} \times 1.4}{12} \quad (12)$$

where the denominator is the molar mass of carbon in g mol⁻¹.

Because Ba_{bio} , Ba_{dis} and z in equations (5) and (6) are constants, the initial use of a relative productivity curve does not affect the end result. To avoid any uncertainties, we have used a range of maximum productivity values as mentioned under eq. (8).

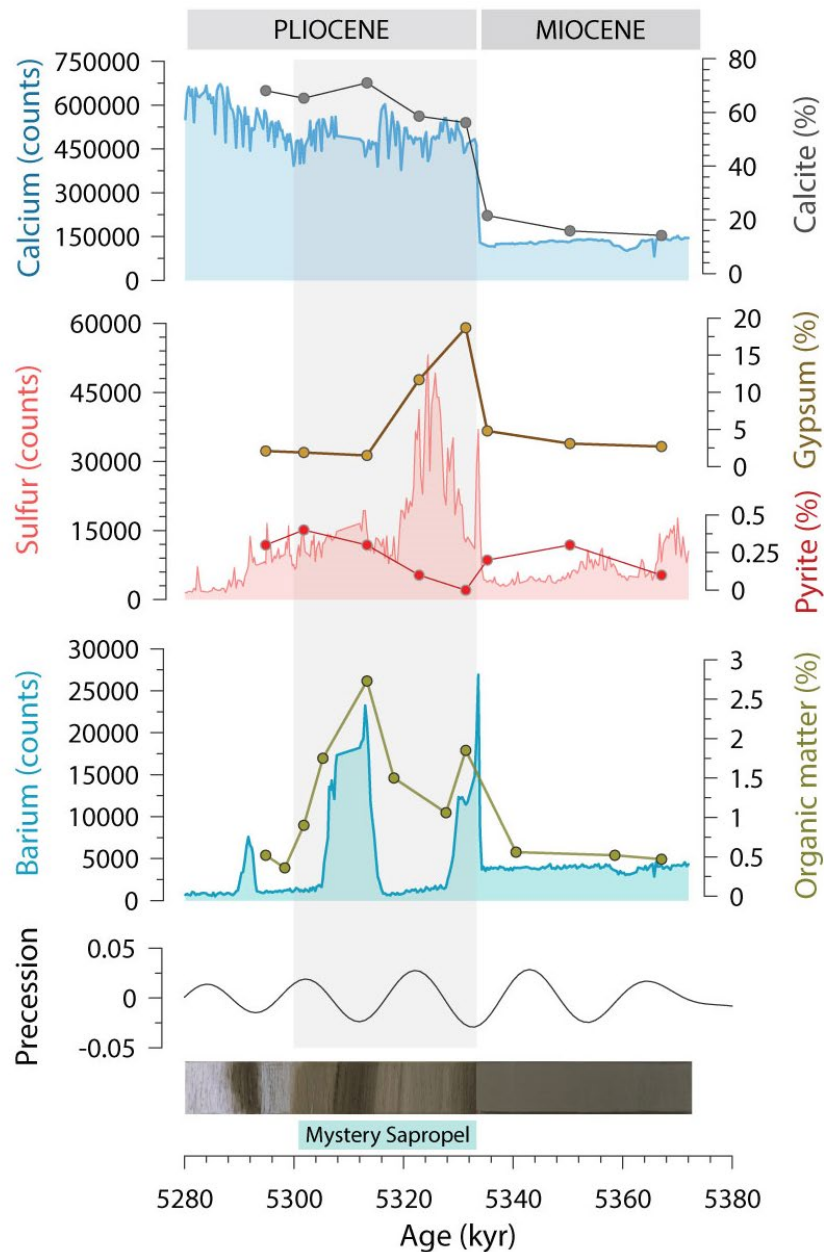


Figure 1| XRF core scanning, XRD and organic matter data across the Miocene/Pliocene boundary from ODP Site 969. The age model was developed by tuning the Ba peaks to 65°N insolation maxima, and was validated using biostratigraphy (see Methods, Extended Data Fig. 3). The M/P boundary is marked by a rapid increase in Ca (mainly calcite) concentration. The mystery sapropel interval consists of 2 dark olive-grey layers in an olive-green background. The 2 dark layers correspond to the first 2 Pliocene Ba peaks of the record. Organic matter concentration is >1 % within the mystery sapropel. High S contents following the M/P boundary is mainly caused by elevated gypsum contents.

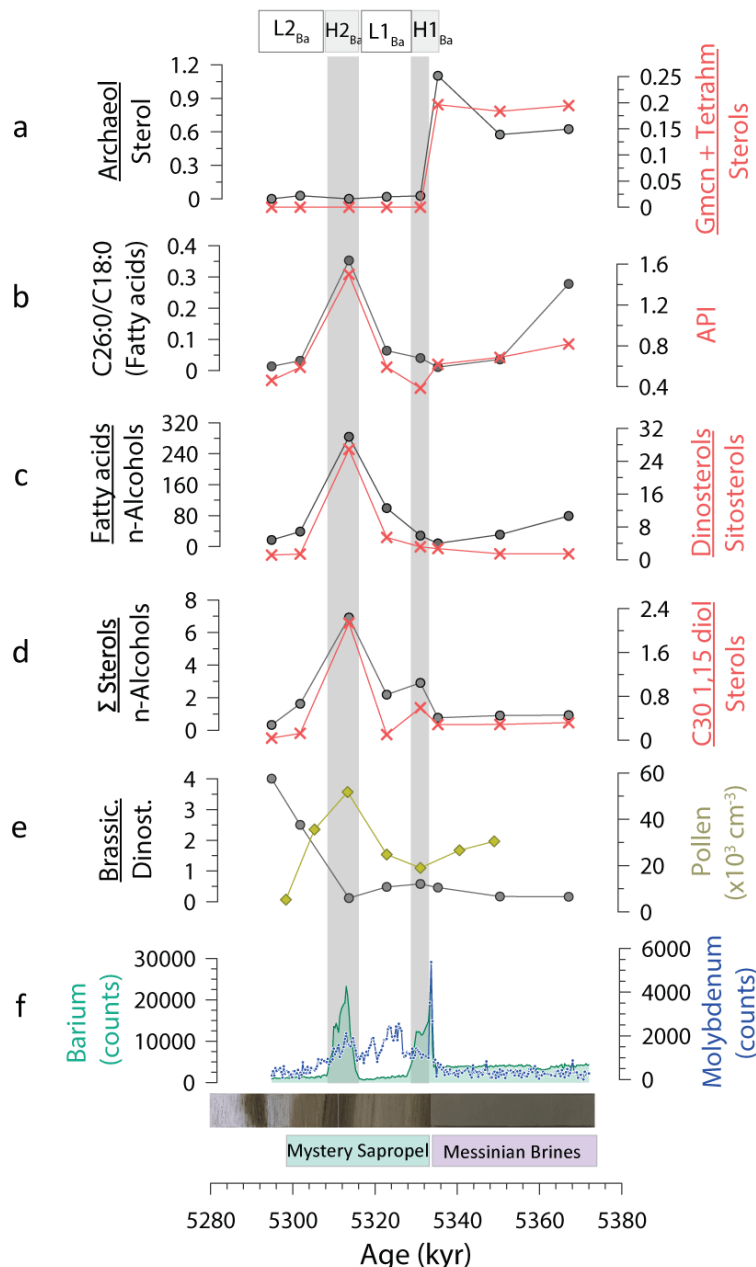


Figure 2| XRF, biomarker and pollen data indicating a gradual transition from a largely oxidizing to a reducing eastern Mediterranean water column. a, Relative abundances of archaeol, gammacerane and tetrahymanol normalized to sterol content. see Extended Data Table 1. **b,** Relative abundance of C26:0 and C18:0 fatty acids and the alcohol preference index (Methods). **c,** Fatty acid/n-alcohol and dinosterol/sitosterol ratios **d,** Total sterols/n-alcohols and C30 1,15 diol/sterol ratios **e,** Brassicasterol/dinosterol ratio and the pollen content **f,** Mo and Ba concentrations. The Mo peak immediately following the M/P transition may indicate a rapid influx of Atlantic waters. Ba record is plotted to show the high and low Ba regions through the mystery sapropel. H1_{Ba}, H2_{Ba} (shaded in light grey) and L1_{Ba}, L2_{Ba} are high and low Barium regions, respectively.

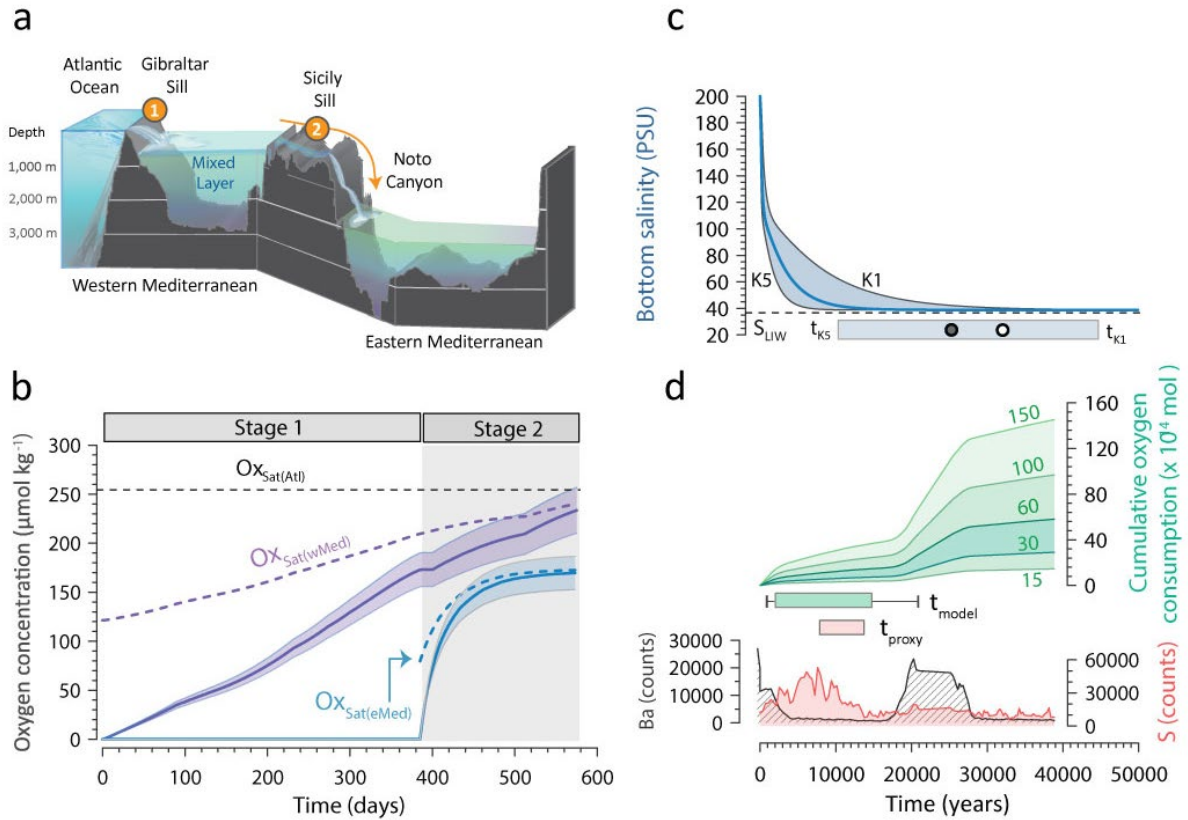
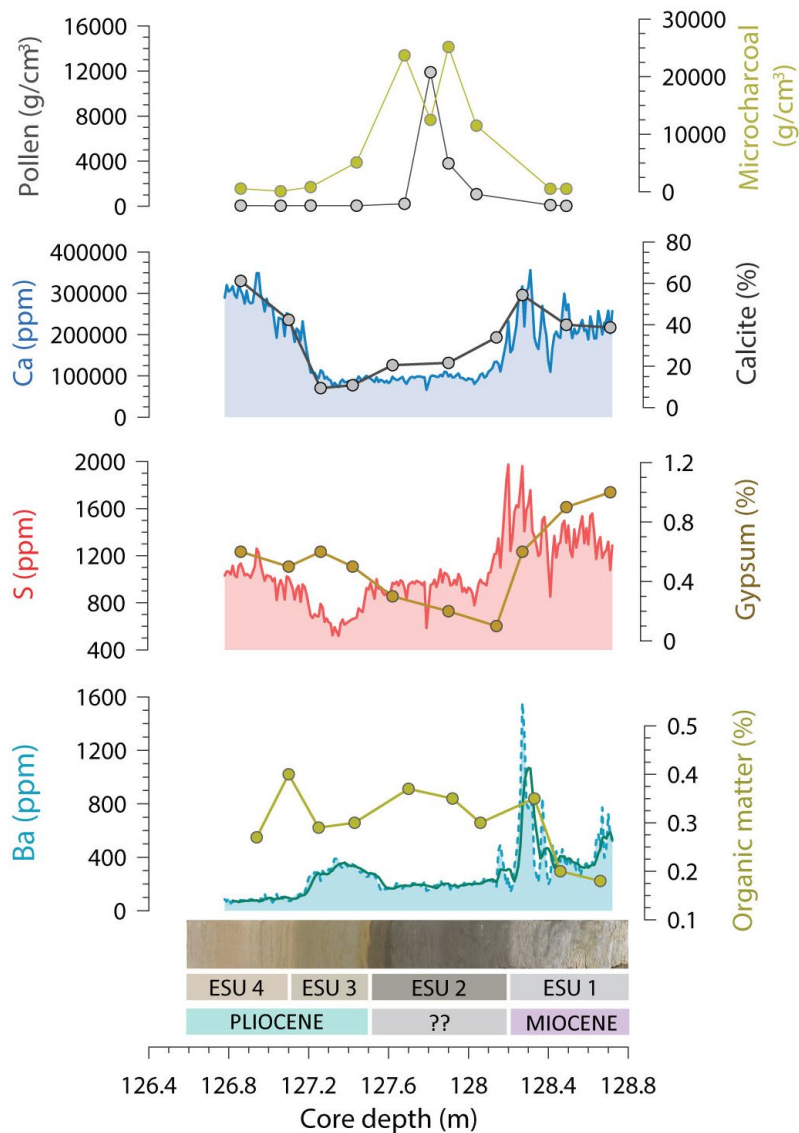
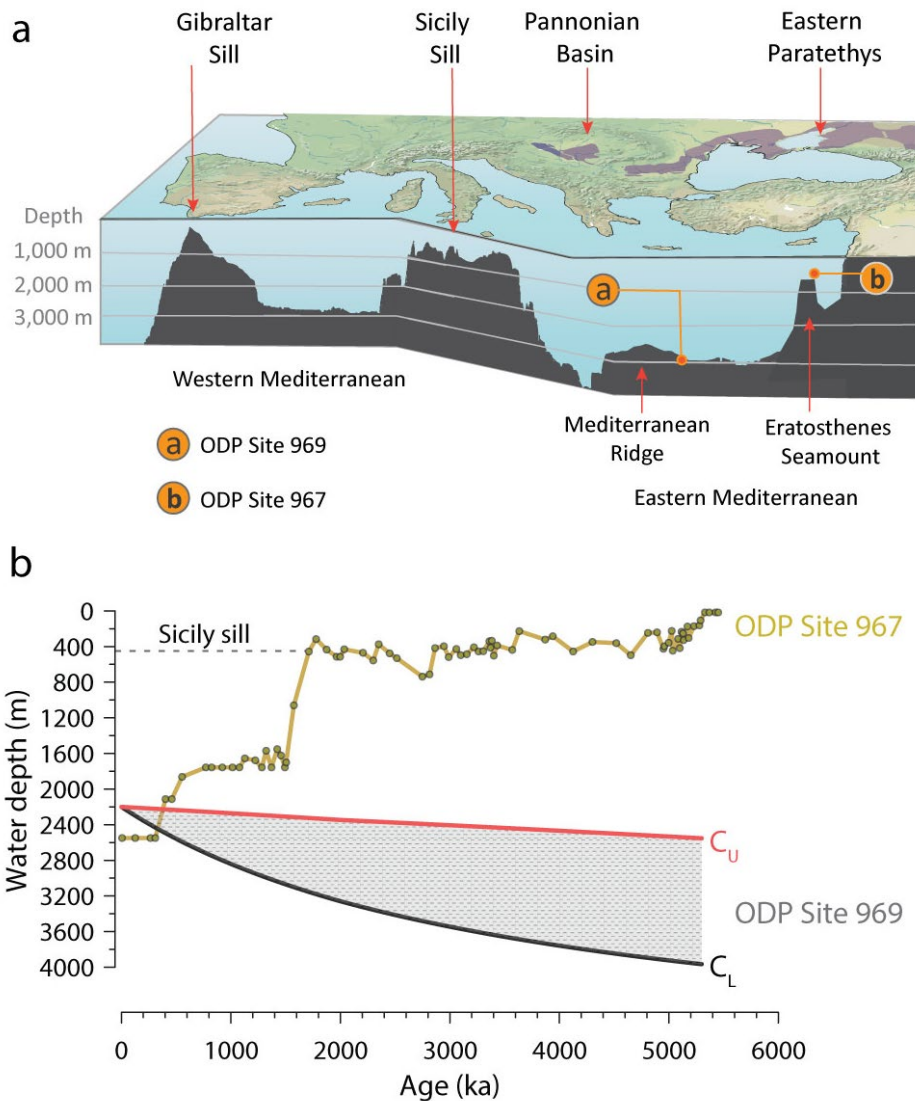


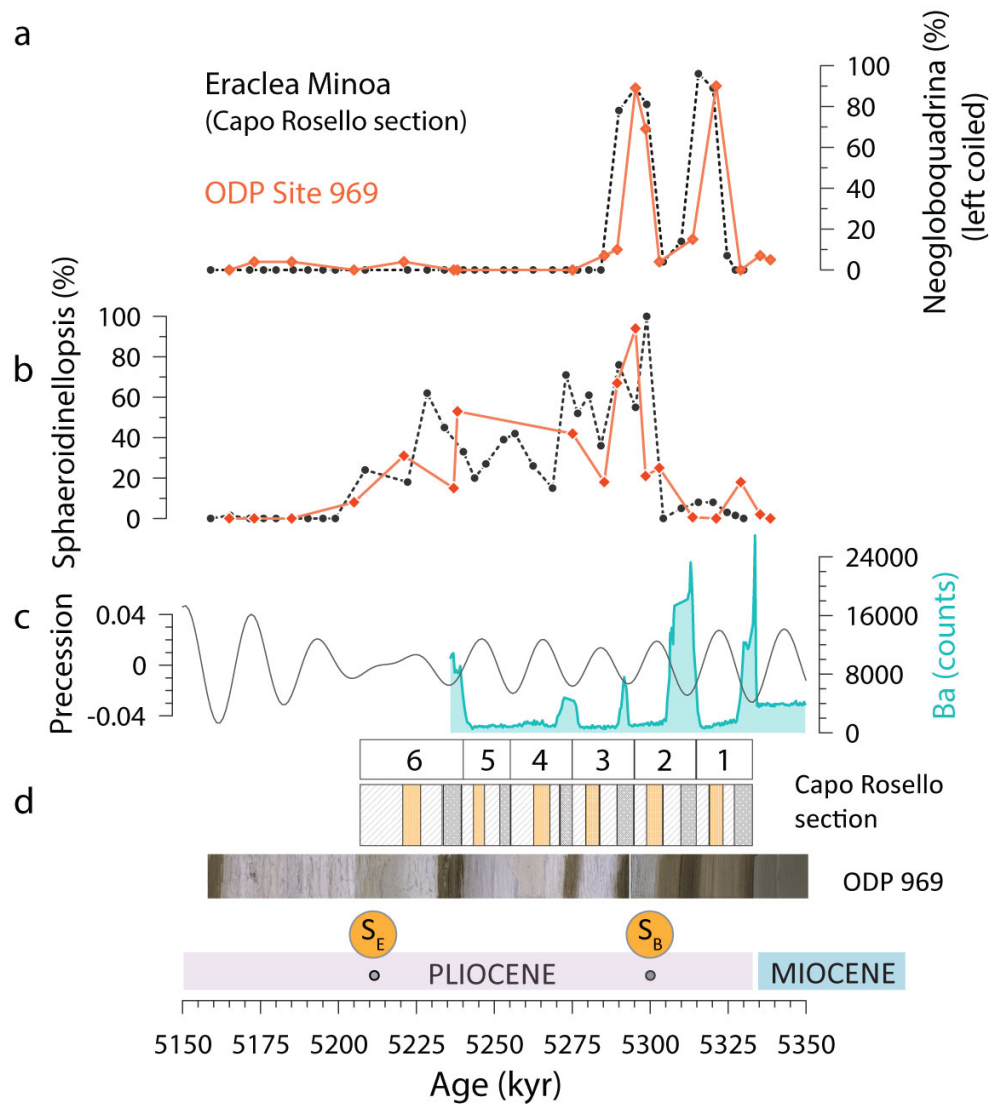
Figure 3| Flooding phase Mediterranean oxygenation and post-flood eastern basin oxygen consumption. **a**, Sketch showing the eastern basin refilling phase by western basin waters overflowing across the Sicily sill. Circled numbers 1 and 2 indicate ventilated inflows at the Gibraltar sill (the Zanclean channel) and the Sicily sill (Noto canyon). **b**, Evolution of the western (solid purple line) and eastern (solid blue line) basin mixed layer O₂ concentrations through the first two flood stages, for 100% O₂ saturated inflows. Shaded lower and upper lobes of each curve represents the range of O₂ concentrations for 90% and 110% O₂ saturated inflows entering each basin. The dashed lines represent O₂ saturation concentration for western (Ox_{Sat}(wMed), purple) and eastern (Ox_{Sat}(eMed), blue) basins. Ox_{Sat}(Atl), Atlantic water oxygen saturation concentration. **c**, Eastern basin post-flood bottom salinity evolution, indication a 10-40 thousand-year period to break the stratification by diapycnal diffusion. K1 and K5 curves correspond to salinity evolution at 1 and 5×10⁻⁵ m²s⁻¹ turbulent diffusivities, respectively. The light blue box indicates the time window, with the white dot representing the updated proxy-based mystery sapropel duration (black dot represents the salt removal time estimate from previous studies¹). S_{LIW}, Levantine intermediate water salinity. **d**, Cumulative oxygen consumption required to degrade all organic matter sinking below the Sicily sill level, at chosen maximum sapropel surface productivity values (ranging from 15 to 150 gC m⁻² yr⁻¹, as indicated by green numbers at each curve). Time initiates at the M/P boundary. The green box (t_{model}) indicates possible time range obtained from the model (for an O₂ saturated inflow), after which O₂ below Sicily sill will be consumed completely. The grey bars on the sides of green box indicate the minimum (0.5 kyr) and maximum (20.5 kyr) durations for oxygen persistence, at 80% and 175% O₂ saturation of the inflow. The orange box (t_{proxy}) indicates the proxy-based estimation of minimum (peak S) and maximum (S contents returning to base values) durations for an oxygenated eastern Mediterranean (8-12,000 years).



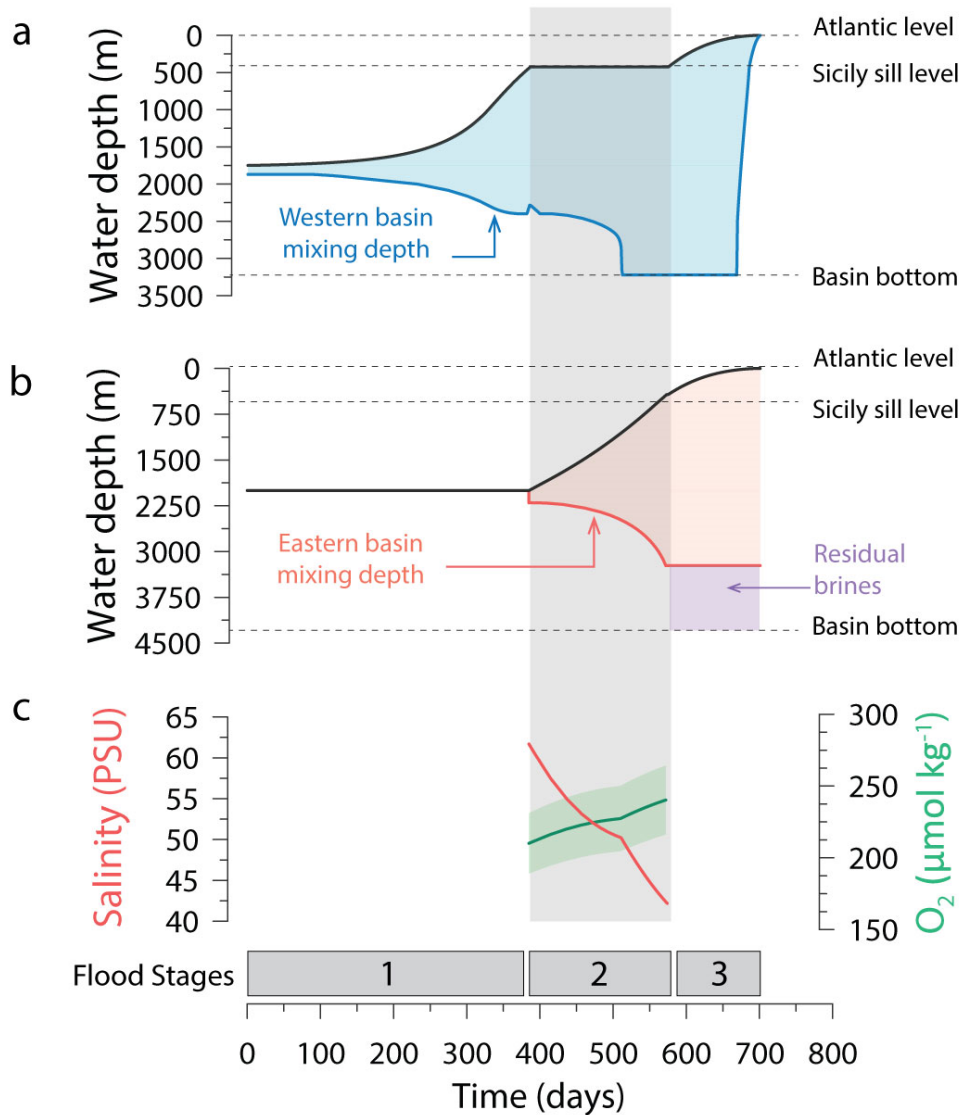
Extended Data Fig. 1| Proxy data across the ODP Site 967 M/P boundary. XRF data were published under ref.1, which were used to interpret the combination of ESU2 and ESU3 (ESU, Eratosthenes Seamount Unit) as a sapropel (one of 4 available eastern Mediterranean mystery sapropels¹). ESU3 has undergone post-depositional oxidation. New data indicate low organic matter contents across ESU2 and 3 (<0.4%). Sub-sampling during XRD analysis revealed the clastic nature of ESU2. Elevated pollen and microcharcoal contents are present within ESU2, while higher contents are usually expected during insolation maxima (ESU2 corresponds to an insolation minimum). The gypsum concentration is <0.8% through the earliest Pliocene. ESU2's siliciclastic nature, unusually elevated pollen/microcharcoal contents combined with low organic carbon, indicate the possibility of rapid sediment deposition following the Zanclean flooding, possibly including reworked soils. We infer ESU3 to be a secondarily oxidized sapropel. ESU1, Latest Miocene; ESU4, Pliocene normal marine sediments.



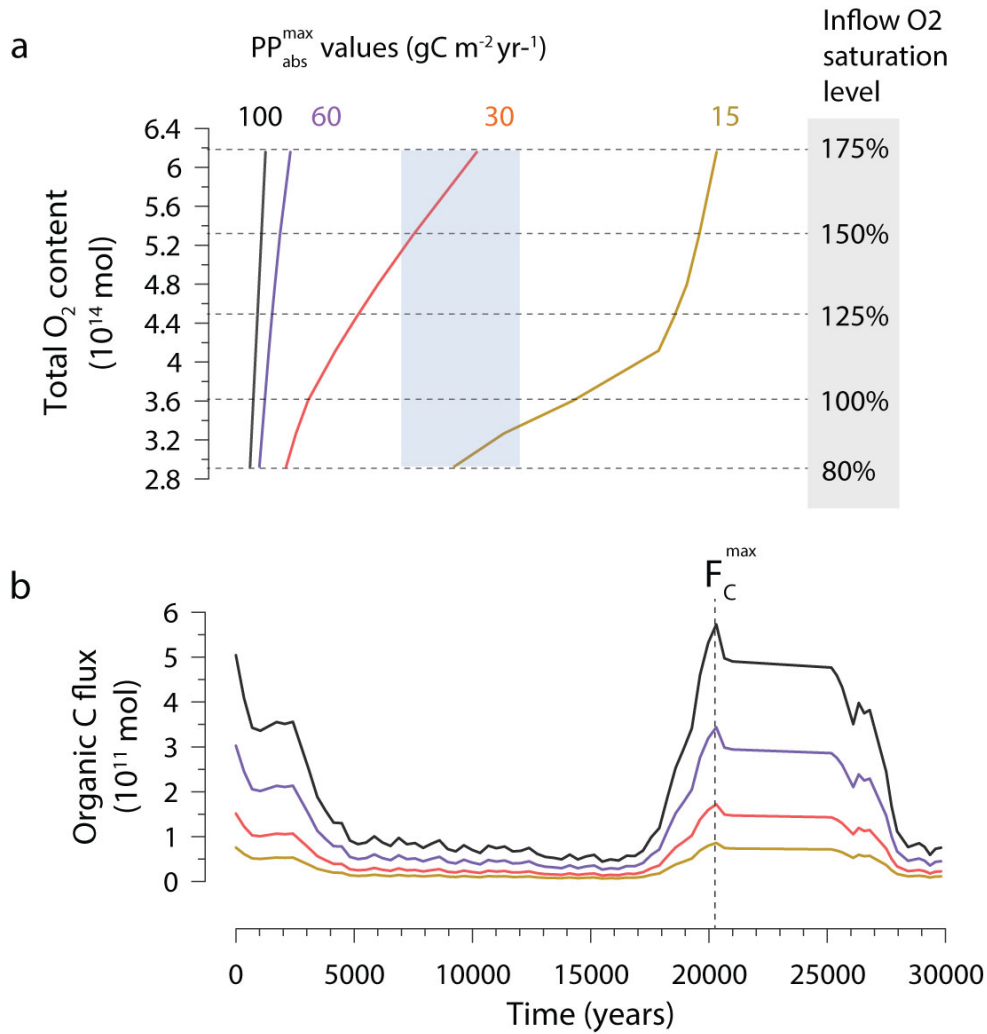
Extended Data Fig. 2| Proxy data across the ODP Site 967 M/P boundary. a, A conceptual diagram showing earliest Pliocene bathymetry and paleogeography of the Mediterranean, with estimated paleodepths for ODP site 967 and 969. **b,** Benthic foraminifera abundance-based ODP site 967 paleodepth reconstruction¹⁹ indicates significantly shallow depths during early Pliocene. Paleodepth estimation for ODP site 969 is based on tectonic convergence rates at the Mediterranean Ridge through the Pliocene (Supplement). The lower curve (C_L) and the upper curve (C_U) represent two end-member scenarios, where the abyssal plain between the African plate and Mediterranean Ridge outward growth edge has been totally consumed prior to Pliocene (C_L), or a scenario where the abyssal plain continued to exist through the whole Pliocene (C_U).



Extended Data Fig. 3| Re-evaluation of ODP Site 969 biostratigraphy across the M/P boundary. a-b, A comparison of left-coiled *Neogloboquadrina sp.* and *Sphaeroidinellopsis sp.* percentages with Capo Rosello section. **c,** Site 969 Ba record tuned to 65°N insolation maxima (precession minima). **d,** Capo Rosello section depositional cycles, showing repeating sapropel equivalents (grey layers), white and beige (orange) layers during each cycle. S_E , *Sphaeroidinellopsis* acme end; S_B , *Sphaeroidinellopsis* acme base¹.



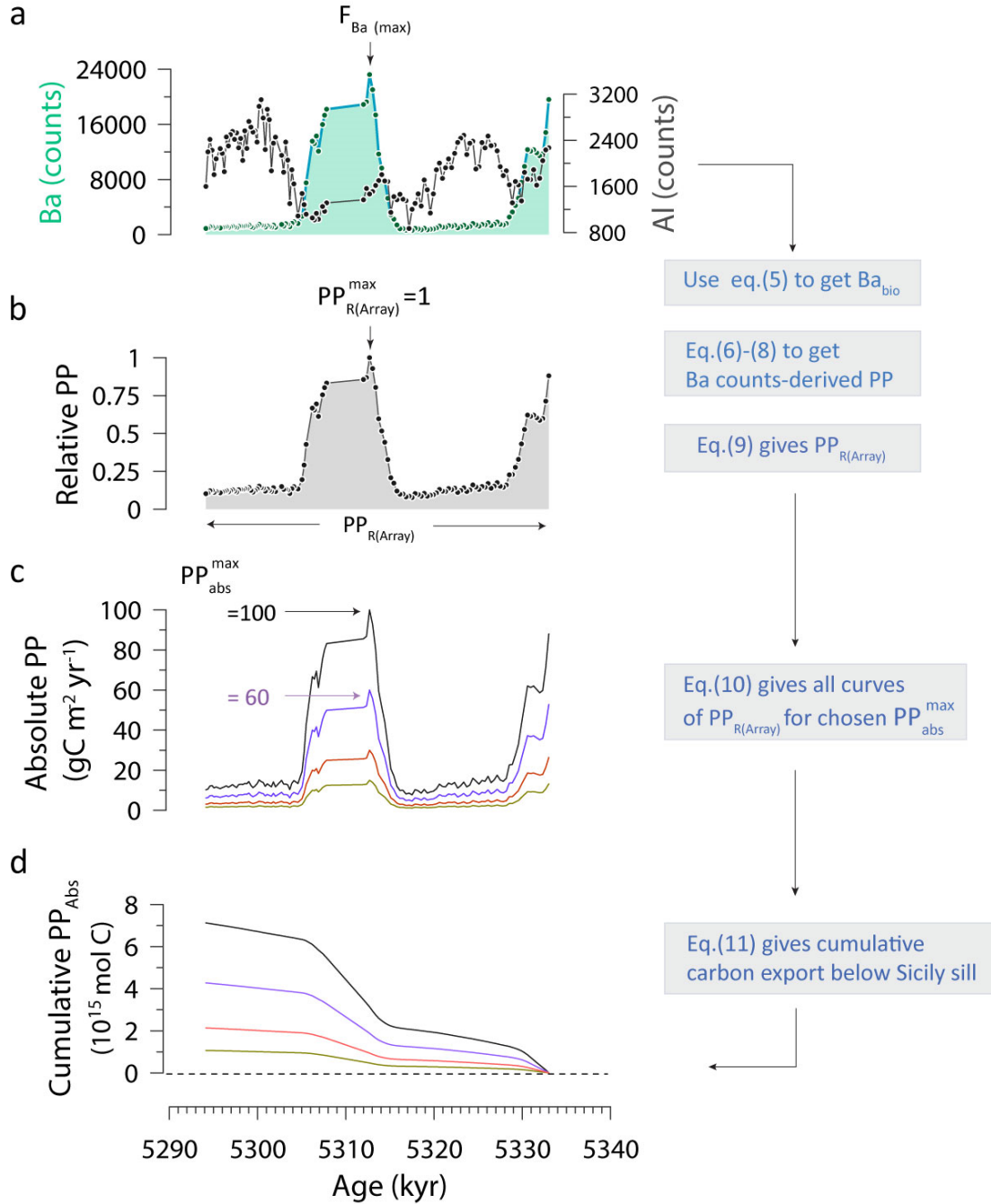
Extended Data Fig. 4| Mediterranean evolution during the flooding phase. a-b, Western and eastern Mediterranean water level (black lines) and mixing depth evolution through the flood, at a 0.2 mixing efficiency¹. Shaded area in each panel indicates the extent of mixing. For a starting salinity of 200 PSU, eastern basin residual brines remain at flood termination. **c,** Salinity and oxygen concentration of the cascade refilling the eastern basin through flood stage 2 (shaded in light grey). Dark green line indicates an O₂ saturated inflow. Lower and upper lobes indicate under-saturated (90%) and supersaturated (110%) O₂ levels for the inflow. During flood stage 1, the western basin fills up to the Sicily sill level. During flood stage 2, western basin brines refill the eastern basin up to Sicily sill level. Both basins rise to the Atlantic level, during stage 3. The flood is completed within ~700 days.



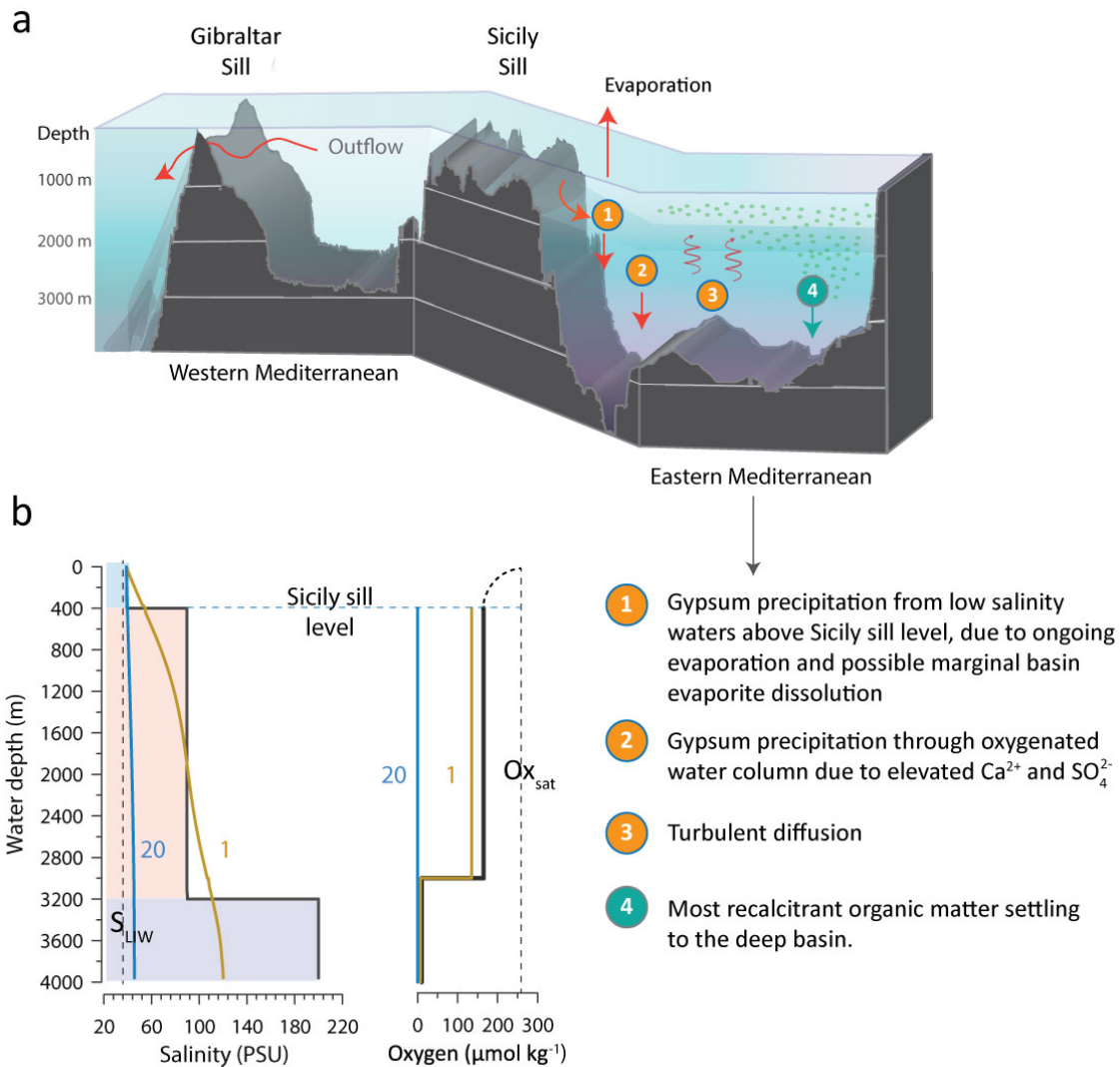
Extended Data Fig. 5| Eastern basin oxygen content and post-flood oxygen consumption.

a, Eastern Mediterranean total oxygen content below Sicily sill level at flood termination, for different O₂ saturation levels of the inflow. Black, purple, red and yellow curves indicate the time taken to consume all oxygen for a chosen inflow oxygen saturation level, at chosen maximum sapropel productivity values (PP_{abs}^{max}, 100, 60, 30, and 15 gC m⁻² yr⁻¹ as indicated for each curve). The shaded blue region represent the proxy based time window, during which the S content decreases to background values. It is assumed that all the oxygen is consumed within this period. For the chosen O₂ saturation range, a surface productivity <~40 gC m⁻² yr⁻¹ will be required to sustain oxygenated conditions for >8,000 years in the eastern Mediterranean.

b, Reconstructed organic carbon fluxes through time at chosen PP_{abs}^{max} values. F_C^{max}, point of maximum organic carbon flux.



Extended Data Fig. 6| Organic carbon flux estimation through the mystery sapropel. a, Ba and Al data are used to estimate the biogenic Ba flux to the deep basin. **b-d,** Estimated biogenic Ba accumulation rates are first converted to a relative primary productivity curve, which then is used to generate the cumulative organic carbon flux below the Sicily sill level through time, for chosen maximum sapropel productivity values (PP_{abs}^{max} , values in $gC\ m^{-2}\ yr^{-1}$; black=100, purple=60, red=30, yellow=15). F_{Ba}^{max} , point of maximum Ba flux; $PP_{R(Array)}$, relative productivity curve, $PP_{R(Array)}^{max}$, maximum value of $PP_{R(Array)}$, which equals to 1 (see Methods).



Extended Data Fig. 7| Sapropel deposition through a sulfate-rich, oxygenated water column. a, Sketch showing the possible pathways of gypsum precipitation and organic matter preservation. Late Messinian evaporite dissolution and the mixed layer salts may have contributed high Ca and sulfate ions to the water column, inducing gypsum precipitation. Evaporation of surface water during the precession maxima may have further increased surface gypsum concentration. A possible thin layer of residual Messinian brines existing in the deepest basin may have allowed pyrite precipitation and Mo enrichment during mystery sapropel deposition. Turbulent diffusion removes the excess salt back to the Atlantic. **b,** Salinity and oxygen profile (below Sicily sill) evolution through time. Only the profiles at 1,000 (dark yellow curves) and 20,000 (dark blue curves) years following the flooding event are shown. Shaded salinity profile shows the eastern basin condition at flood termination. Surface low salinity layer (blue) is underlain by a hypersaline mixed layer (orange). Residual brines remain at deepest parts (purple). For a O_2 supersaturated (at 175%), all oxygen will be consumed by ~20.5 thousand years. Ox_{sat} , Atlantic surface water oxygen saturation level.

Extended Data Table 1 |

Biomarker ratios for ODP 969 samples across the Miocene/Pliocene boundary.

Sample label	ODP 969 a	ODP 969 b	ODP 969 c	ODP 969 d	ODP 969 e	ODP 969 f	ODP 969 g	ODP 969 h
Core depth (m)	95.95	96.25	96.56	96.85	97.11	97.2	97.66	98.17
Age (kyr)	5295.8	5302.8	5314.7	5323.8	5331.0	5335.3	5350.4	5367.1
Mass extracted (g)	7.37	6.65	2.47	5.2	5.36	9.94	6.07	7.89
Archaeol	ND	0.09	ND	0.11	0.06	1.46	1.87	2.42
Gammacerane	ND	ND	ND	ND	ND	0.13	0.36	0.39
Tetrahymanol	ND	ND	ND	ND	ND	0.13	0.23	0.36
Dinosterol	0.43	0.44	2.83	2.35	0.75	0.51	1.22	1.45
Sitosterol	0.38	0.31	0.11	0.43	0.24	0.19	0.84	1.01
Brassicasterol	1.73	1.09	0.34	1.13	0.43	0.24	0.21	0.23
<i>n</i> -C _{26:0} / <i>n</i> -C _{18:0} FAs	0.014	0.032	0.353	0.064	0.040	0.011	0.036	0.278
API ^a	0.46	0.59	1.50	0.59	0.39	0.62	0.69	0.82
Σ <i>n</i> -alcohols ^a	12.60	1.92	0.59	2.68	0.83	1.73	3.59	4.18
Σ FAs ^b	213.53	74.22	167.10	265.86	23.53	14.17	110.53	330.50
Σ Sterols ^c	4.10	3.12	4.07	5.85	2.42	1.32	3.24	3.88

^aAlcohol preference index, API = (*n*-C₂₆ alcohol/ *n*-C₂₉ alcohol) ^bTotal alcohols, Σ *n*-alcohols = Σ (*n*-C₁₈: *n*-C₂₈ alcohols). ^cTotal fatty acids, Σ FAs = Σ (*n*-C₁₈: *n*-C₂₈ fatty acids). ^dTotal alcohols, Σ sterols = (sterol 129+ cholesterol+ brassicasterol+ ergosterol+ campesterol+ stigmasterol+ β-sitosterol+ dinosterol). All concentrations are given in ×100 μg per gram of sediment. Ratios are in their absolute values (API and *n*-C_{26:0}/*n*-C_{18:0} FAs). FAs, fatty acids; ND, component not detected.

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Author contributions

U.A. designed and led the study, prepared samples for laboratory analyses, analyzed the data, generated the figures and wrote the paper; U.A. developed the hypothesis with guidance from J.J.B.; P.T.M. carried out paleodepth estimation; J.W.Z. performed biostratigraphy analysis; J.M.H., U.R., H.K., U.T., R.H., S.R., and I.C.vdH contributed to data generation; J.J.B., E.J.R. and G-J.R. advised on data interpretation; all authors contributed to manuscript development.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this manuscript

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CHAPTER 8

Concluding Remarks

8.1 Thesis achievements

The objective of the project presented in this thesis was to develop a multi-proxy reconstruction for ODP site 967 for the Pliocene Epoch (5.3-2.6 Myr). The resultant 0-5.3 Myr proxy reconstruction is the first continuous record extending back to the Miocene-Pliocene boundary, from a single core site in the Mediterranean. It was proposed to use the developed proxy reconstructions, to explore the Pliocene evolution of Mediterranean oceanography and North African climate in response to globally important climatic and tectonic events.

Despite being broadly presented under a ‘paleoceanography and paleoclimate’ context, this thesis combines an array of disciplines (including physical oceanography, climate modelling, biogeochemistry, palynology and sedimentology), to establish hypotheses that are critical in addressing outstanding scientific questions of the Pliocene, ranging from climate and ocean sciences to hominin evolution and dispersal. To achieve this, collaborations were developed with expert scientists from several institutions in Europe (Utrecht University, Geoscience Barcelona, Sorbonne University, CNRS-France and ISAC-CNR in Italy) and Australia (ANU School of Culture, History and Language, University of New South Wales & University of Adelaide). Below, the main findings are summarized in chronological order.

The Messinian Salinity Crisis (MSC, 5.97-5.33 Myr) which resulted from tectonic restriction of Atlantic-Mediterranean gateway, provided the basis of two chapters of the thesis (chapters 2 and 7). As elaborated in the chapters, even after about five decades of research, the mode of termination of the MSC remains unresolved. Seismic and borehole data supports a catastrophic refilling of a partially desiccated Mediterranean, while geochemical and paleobiological evidence have been employed to suggest that the Mediterranean refilling event was less energetic and gradual. Numerical models developed in the two chapters, in combination with extensive proxy data from ODP sites 967 and 969 provide direct evidence of a catastrophic flooding event that reconnected the Mediterranean with the Atlantic Ocean at the Miocene-Pliocene transition (5.33 Myr). These studies indicate that the MSC-terminating Zanclean megaflood is the largest ever flood for which reasonable records exist and marked one of the most dramatic environmental-oceanic transformations in geological history. This finding helps to visualize the final phase of the Messinian Salinity Crisis, which will also provide important implications for an upcoming International Ocean Drilling Program (IODP) expedition (Expedition 401: Mediterranean-Atlantic gateway exchange).

The remaining chapters explored the North African climate and Mediterranean Sea evolution in response to the development of Pliocene global climate. ODP 967 Proxy data presented in this thesis (chapters 3)

indicate that North African wet-dry climate cycles existed throughout the past 5 Myr, in response to Earth's orbital cycles. The box-model deconvolution of ODP 967 planktonic foraminiferal oxygen isotope record (chapter 4) agrees with this observation, which confirm the eccentricity modulation of African monsoon runoff to the Mediterranean back to the Miocene-Pliocene boundary. However, proxy data reveal that North African climate was considerably more humid (especially during the dry periods) before 3.3 Myr. It was argued that the enhanced vegetation cover over the Sahel and Sahara during dry intervals resulted in decreased erodibility of North African landscape. The decreased erodibility was suggested to have reduced the nutrient input to the Mediterranean, which resulted in the observed 2-Myr-long sapropel-barren interval at site 967.

The work presented here shows that less frequent sapropel appearance within the 5.3-3.3 Myr period is common for all existing deep eastern Mediterranean ODP sites (chapter 3). However, it was later revealed that the sapropels are entirely absent in all core sites within the 3.8-3.3 Myr period (chapter 6). A proxy data synthesis and climate model results were combined to show that this period of sapropel absence (Pan-North African Humid Period; Pan-NAHP) corresponds to the most humid Pliocene climate phase over much of North -East Africa, during which freshwater runoff to the Mediterranean was maximized. Remarkably, the first known co-occurrence of an early hominin fossil in the Chad Basin with East African fossil sites, coincide with the Pan-NAHP. Therefore, it was argued that the increased surface water availability along the central African rift system may have facilitated the first known early hominin migration event to the Chad Basin, from their East African habitats.

The thesis employed climate model results (chapters 5, 6) to explain how the enhanced humid conditions over North Africa terminated, with the onset of major Northern Hemispheric glacial cycles since 3.3 Myr. The globally recognized M2 glaciation (3.3 Myr) and the mid-Pliocene glacials that followed, displaced the African monsoon front southward. The glacials generally correspond to the dry phase of North Africa's wet-dry climate cycles, which explains the enhanced aridity and landscape erodibility during dry phases after 3.3 Myr. Consequently, the nutrient runoff to the Mediterranean during intervening wet phases amplified, resulting in enhanced organic carbon burial observed across the ODP sites in the deep Mediterranean.

Further analyses of climate records revealed the global importance of the Earth's transition from unipolar to bipolar glaciation after 3.3 Myr (Chapter 5). It was shown that the expansion of both Northern and Southern Hemispheric ice sheets during the mid-Pliocene glacials resulted in global cooling events. Reduced global surface meridional temperature gradients strengthened atmospheric circulation, which resulted in sea and land surface environmental transitions that are embedded in proxy records from both

hemispheres. These findings suggest that globally coherent ecosystem changes occurred in the mid-Pliocene, about 0.5 Myr before the frequently cited Northern Hemispheric glacial intensification at 2.7 Myr.

8.2 Future directions

8.2.1 MSC termination

Implications on the nature of the final MSC phase were derived entirely from proxy data coming from the Messinian (Late Miocene). This is the first time the widespread occurrence of the earliest Pliocene mystery sapropel in the eastern Mediterranean was confirmed and was used to investigate the nature of MSC termination. The upcoming IODP Expedition 401 (for which the author will participate) will retrieve long sediment records from either side of the Strait of Gibraltar (from the Alboran Basin and Gulf of Cadiz). One of the main intentions of Expedition 401 is to generate a record of Mediterranean-Atlantic gateway exchange for the 5-8 Myr period. The records generated from this expedition will be useful in testing the hypotheses developed within this thesis, on the Zanclean megaflood.

8.2.2 Mediterranean box-model development

There is potential for development of the existing Mediterranean box-model, with the inclusion of more advanced physical oceanographic equations (eg: solving for maximal versus sub-maximal exchange across the Strait of Gibraltar). The results from the box-model can also be employed to study the past variations of Mediterranean outflow plume. The study presented in chapter 4 fails to resolve the contributions from surface layer temperature concentration and freshwater runoff, on observed oxygen isotope values. To resolve this, future studies may reconstruct surface and mid-layer temperature from foraminiferal shells of chosen species.

8.2.3 Climate modelling efforts

A majority of Pliocene climate modelling studies were focused on the warm intervals, which are considered as imperfect future global climate analogs (eg: mid-Pliocene interglacials and the Early Pliocene warm period). In this thesis, existing proxy data from various locations (some more than 40 years old) were extracted, to report the importance of mid-Pliocene glacials on key global environmental transformations as the global ice volume increased. Furthermore, the work presented shows implications of Early Pliocene – mid-Pliocene glacial transition on future global climate evolution. There is excellent potential for further studies (both modelling and proxy data generation) to deeply investigate the impacts of inception of mid-Pliocene glacial cycles on global climate.

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APPENDICES

Appendix Chapter 2

Supplementary information for:

Sill-controlled salinity contrasts followed post-Messinian flooding of the Mediterranean

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Contents:

Supplementary Figure 1: Evolution of the flooding event in the wMed and eMed – modelling results

Supplementary Table 1: A record of the Miocene to Pliocene transition recovered from Mediterranean DSDP and ODP sites.

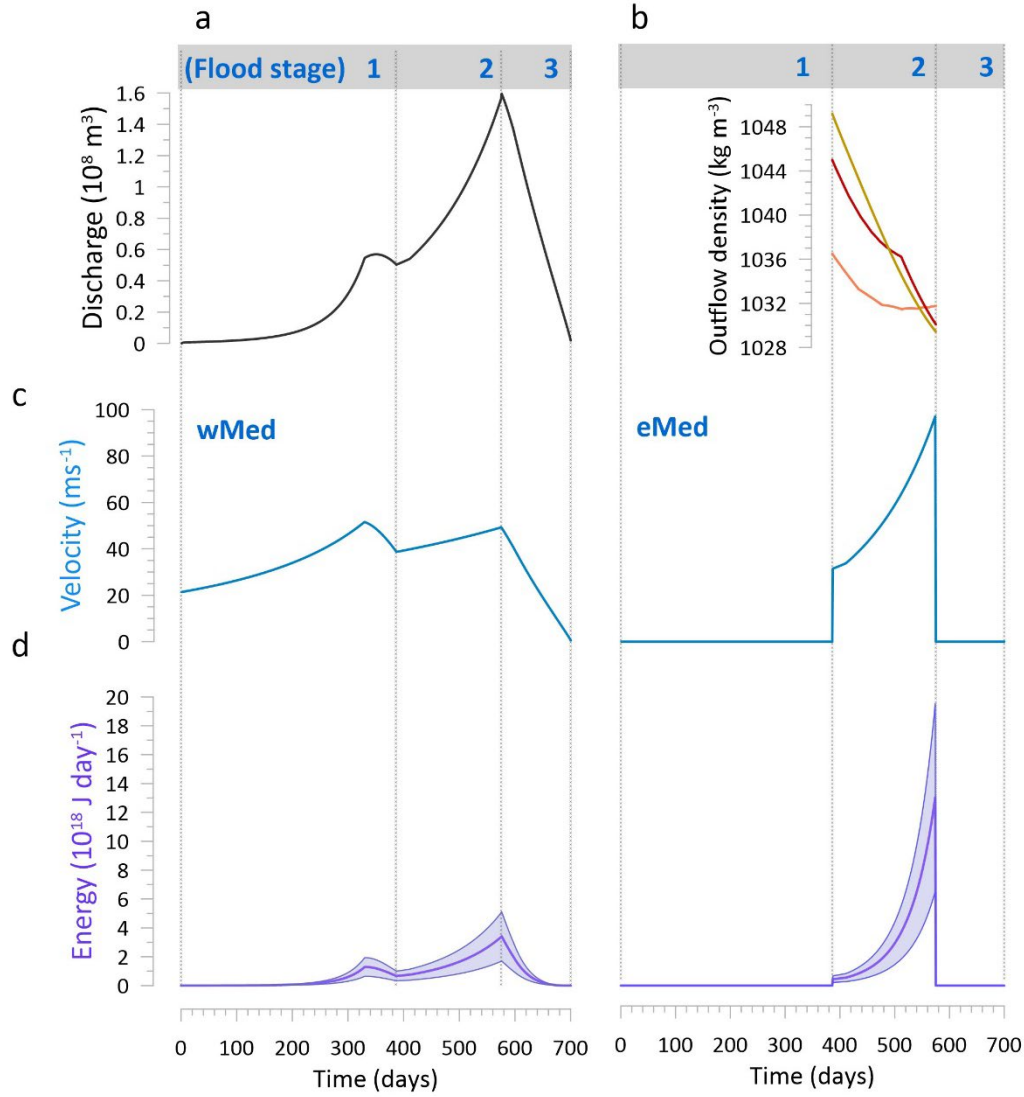
Supplementary Table 2: Biostratigraphic datums for ODP Site 967 for the interval shown in Extended Data Fig. 3. Ages given here are calibrated to the latest astrochronology.

The electronic supplementary information is available online (including links to data files), accompanying this published chapter:

<https://www.nature.com/articles/s41561-022-00998-z>

All the figures in this manuscript are reproducible via Jupyter notebooks and instructions provided in the Github repository Med_evolution_megaflow: <https://doi.org/10.5281/zenodo.6528768>

Supplementary figure 1 | Evolution of the flooding event in the wMed and eMed. a, Daily flood discharge through the Strait of Gibraltar. **b,** Evolution of eMed inflow water density during ZFS 2 at different mixing efficiencies (ME) in the wMed (orange = 10% ME; red = 20% ME; yellow = 30% ME). **c,** Flood velocity in the wMed and eMed. **d,** Kinetic energy available for mixing in wMed and eMed. Thick purple lines are energy availability at 20% ME. Upper and lower envelopes demarcate energy availability at 30% and 10% ME. ZFS 1, 2, and 3 are the three main Zanclean flooding stages (see main text Fig. 2).



Supplementary Table 1: A record of the Miocene to Pliocene transition recovered from Mediterranean DSDP and ODP sites. This includes a total of 46 sites⁶⁴: Deep Sea Drilling Project (DSDP) Leg 13 sites, DSDP Leg 42A – 8 sites, Ocean Drilling Program (ODP) Leg 107 – 7 sites, ODP Leg 160 – 11 sites, ODP Leg 161 – 6 sites.

Western Mediterranean					
Site	Location	Water depth (m)	Complete record across the M/P boundary		Nature of the boundary
			Present	Not Present	
Deep Sea Drilling Project (DSDP) Sites					
121	Western Alboran Basin	1163		✓	Suspected lower Pliocene to upper Miocene hiatus. Lower Pliocene <i>Sphaeroidinellopsis</i> acme zone was not recovered ⁶⁵ .
122	Valencia Trough	2146		✓	Basal Pliocene transgression is not recorded ⁶⁵ .
123	Valencia basement ridge	2290		✓	Basal Pliocene transgression is not recorded ⁶⁵ .
124	Balearic Rise	2726		✓	More than 1 million years of the earliest Pliocene record missing ⁶⁵ .
132	Tyrrhenian Sea	2835	✓		Pliocene foraminiferal pelagic ooze overlying calcitic-dolomitic-pyritic marl (Late Miocene evaporite series) ⁶⁵ .
133	Sardinia Slope	2563		✓	M/P boundary hiatus ⁶⁵ .
134	Balearic Abyssal Plain	2864		✓	About 0.8 million years of earliest Pliocene sediments missing ⁶⁵ .
371	South Balearic Basin	2792		✓	About 1 million year hiatus at the base of the Pliocene ⁶⁶ .
372	Menorca Rise, west Algero-Provencal Basin	2699		✓	MPI-1 and MPI-2 biozones missing; M/P boundary is recorded as a drilling artifact ⁶⁶ .
373	Tyrrhenian Basin	3517		✓	Only down to MPI 3 biozone recognized. No M/P boundary present ⁶⁶ .
Ocean Drilling Program (ODP) Sites					
650	Marsili Basin	3516		✓	Oldest sediments are late Pliocene (MPI 6 biozone) ⁶⁷ .
651	Tyrrhenian Basin	3578		✓	Oldest sediments are late Pliocene (Piacenzian stage, MPI 6) ⁶⁷ .
652	Central Tyrrhenian Sea	3446	✓		Mainly earliest Pliocene gypsiferous nannofossil ooze overlies Messinian Sediments ⁶⁷ .
653	Western Tyrrhenian Sea	2828	✓		Foraminiferal ooze of MPI 1 biozone overlies an upper Messinian unit characterized by brackish water facies ⁶⁷ .
654	Upper Sardinian Margin	2208	✓		Early Pliocene foraminifer-nannofossil ooze overlies Messinian grey marls and gypsum ⁶⁷ .

655	Gortani Ridge, Western Vavilov Basin	3290	✓	Pliocene biozone MPI 3 is present. No continuous M/P boundary recognized ⁶⁷ .
656	De Marchi Seamount	3597	✓	Oldest sediments probably of Messinian age. Pliocene record is not complete; a long gap is present ⁶⁷ .
974	Central Tyrrhenian Sea	3454	✓	Earliest Pliocene yellowish brown to olive grey nannofossil clay overlies Messinian sediments ⁶⁸ .
975	South Balearic Margin	2200	✓	Earliest Pliocene bioturbated nannofossil ooze and clay sequence overlies Messinian evaporative sequences ⁶⁸ .
976	Western Alboran Sea	1108	✓	Hiatus at M/P boundary ⁶⁸ .
977	Eastern Alboran Basin	1984	✓	Unclear whether the M/P boundary was reached because the earliest section is complex ⁶⁸ .
978	Eastern Alboran Basin	1929	✓	MPI 1 biozone (foraminiferal ooze) overlies Messinian sediments (not reliable) ⁶⁸ .
979	Southern Alboran Basin	1062	✓	Oldest sediments date to late Pliocene ⁶⁸ .

Eastern Mediterranean

Site	Location	Water depth (m)	Complete record across the M/P boundary:		Nature of the boundary
			Present	Not Present	
Deep Sea Drilling Project (DSDP) Sites					
125	Mediterranean Ridge	2782		✓	Sedimentation gap of 1.5 million years exists at the M/P boundary ⁶⁵ .
126	Cleft in Mediterranean Ridge, Ionian Sea	3730		✓	No Pliocene sediments recovered ⁶⁵ .
127	Hellenic Trench	4636		✓	Stratigraphic inversion detected; Cretaceous limestones overlying upper Pliocene oozes ⁶⁵ .
128	Hellenic Trench	4640		✓	Quaternary section penetrated; no M/P boundary present ⁶⁵ .
129	Strabo Trench, Levantine Basin	2832-3048		✓	No proper M/P boundary. Earliest Pliocene <i>Sphaeroidinellopsis</i> acme-zone present as downhole contaminants ⁶⁵ .
130	Mediterranean Ridge, Levantine Sea	2979		✓	Only Quaternary sediments present ⁶⁵ .
131	Western Nile Cone	3035		✓	Only Quaternary sediments present ⁶⁵ .
374	Ionian Sea	4078	✓?		M/P boundary obscured by diagenesis of earliest Pliocene horizons. Weakly defined boundary. Diagenetic gypsum included in Pliocene sediments.

				Sapropelic layers present in earliest Pliocene section ⁶⁶ .
375	Florence Rise, west of Cyprus	1900	✓	~1-million-year hiatus at basal Pliocene ⁶⁶ .
376	Florence Rise, west of Cyprus	2101	✓	Two M/P boundaries present as a drilling artifact. Prominent black layer present, rich in organic carbon, and finely laminated in its lower part dates to earliest Pliocene – Known as the “mystery sapropel” ⁶⁶ .
377	Mediterranean Ridge cleft	3718	✓	Quaternary sediments overlie Miocene sediments, no M/P boundary present ⁶⁶ .
378	Cretan Basin, Aegan Sea	1835	✓	Earliest MPI 1 zone missing. Olive grey marls of MPI 2 age in contact with selenitic gypsum ⁶⁶ .
Ocean Drilling Program (ODP) Sites				
963	Strait of Sicily	470	✓	Oldest recorded sediments date to early Pleistocene ⁶⁹ .
964	Near Calabrian Ridge, Ionian abyssal plain	3657	✓	Sediment record is complete only to 4 Ma ⁶⁹ .
965	Eratosthenes Seamount	1507	✓	Hiatus from middle to early Pliocene (tectonic instability) ⁶⁹ .
966	Eratosthenes Seamount plateau	940	✓	Hiatus at M/P transition ⁶⁹ .
967	Northern slope of Eratosthenes Seamount	2554	✓	Pliocene sedimentation begins with 1-m-thick layer rich in organic matter (this study). We relate this to the mystery sapropel.
968	Lower slope of Cyprus Margin	1960	✓	Hiatus from 3.57 Ma to late Miocene (inferred to result from tectonic uplift of southern Cyprus) ⁶⁹ .
969	Mediterranean Ridge	2000	✓	Pliocene sedimentation begins with a sapropel. This bed is considered an equivalent of the "mystery sapropel" described from the Florentine Basin, DSDP Hole 376 ^{ref.19} .
970	Mediterranean Ridge northern flanks	1953-2079	✓	Sedimentary record incomplete. Oldest sediments are early Pliocene ⁶⁹ .
971	Mediterranean Ridge	1933-2143	✓	Earliest recorded sediments are Pleistocene ⁶⁹ .
972	Mediterranean westernmost outer deformation front	3931	✓	Earliest sediments are late Pliocene ⁶⁹ .
973	Toe of the Mediterranean Ridge accretionary wedge	3694	✓	Earliest sediments are Pleistocene ⁶⁹ .

Supplementary Table 2. Biostratigraphic datums for ODP Site 967²² for the interval shown in Extended Data Fig. 3. Ages given here are calibrated to the latest astrochronology⁷⁰.

Location indicated in Extended Data Fig. 3	Biostratigraphic datum	Age (ka) (astronomically calibrated)	ODP 967 Hole A sample location ²²	Equivalent depth (m) in ODP 967 splice used here	Age (ka) of the location in the splice
a	Last Messinian sediments	5333 (flooding surface)	13H-4 109-111 cm	~128.16	~5330
b	MPL1 (influx of <i>Neoglobobadrina acostaensis</i>)	5320	13H-4 78-80 cm	127.86	5323.81
c	AB <i>Sphaeroidinellopsis</i>	5300	13H-3 113-115 cm	126.70	5280.68
d	AE <i>Sphaeroidinellopsis</i>	5210	13H-3 25-27 cm	125.79	5234.38

Events a and b agree closely with our chronology. Events c and d differ by ~-19 and ~+24 ka, respectively, compared to our chronology. It should be noted that the shipboard biostratigraphy was developed using samples from Hole 967A at 10-50 cm resolution, which is equivalent to ~5-25 ka age uncertainty based on events a and b. Therefore, we rely on our higher- (1-cm) resolution, calibrated XRF data to develop the new chronology. AE, Acme end; AB, Acme base.

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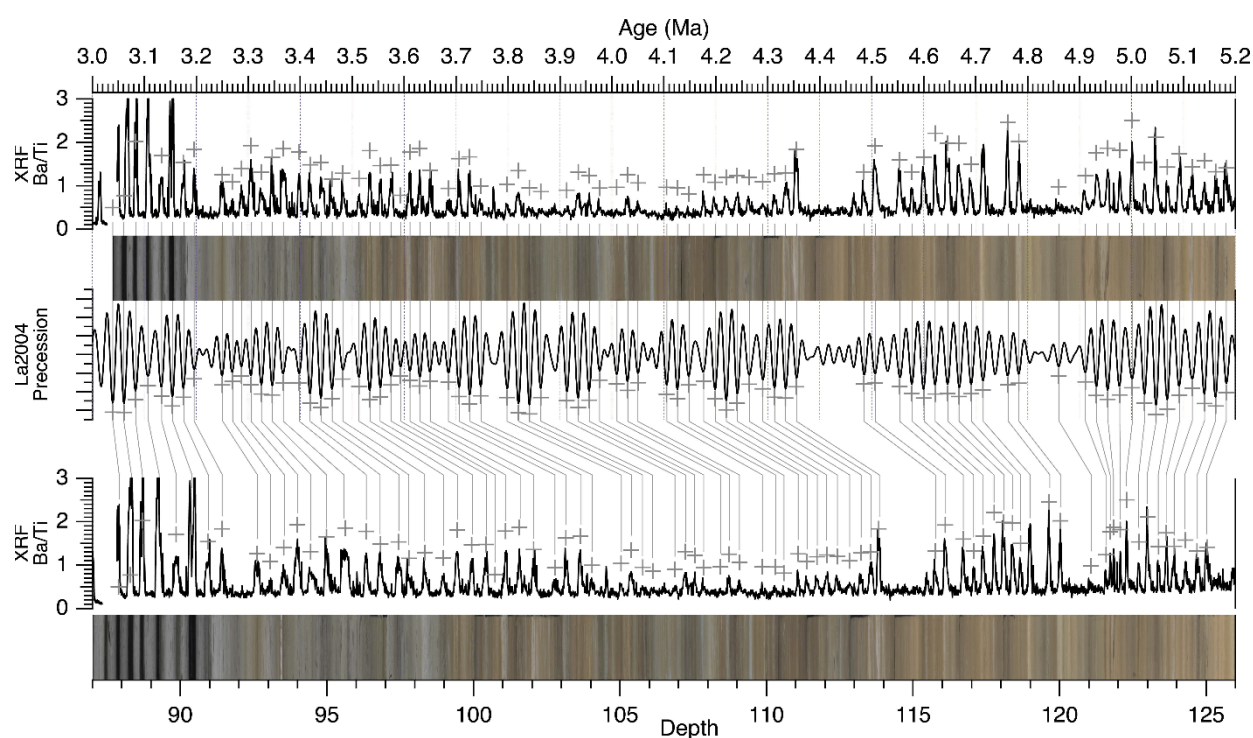
Appendix Chapter 3

Supplementary Data

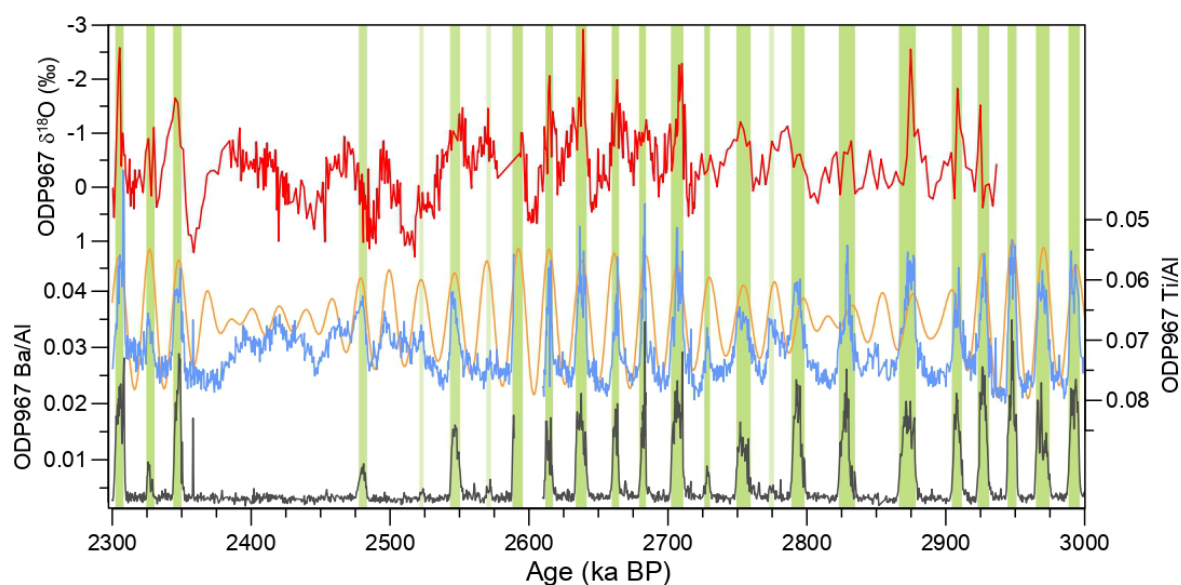
ODP Site 967 data from this study are available from Panagea (www.pangaea.de) under ‘Plio-Pleistocene scanning XRF, stable isotope and environmental magnetic data from ODP Site 967’ and are also available as online Supplementary Data accompanying this article.

<https://www.nature.com/articles/s43247-021-00339-9>

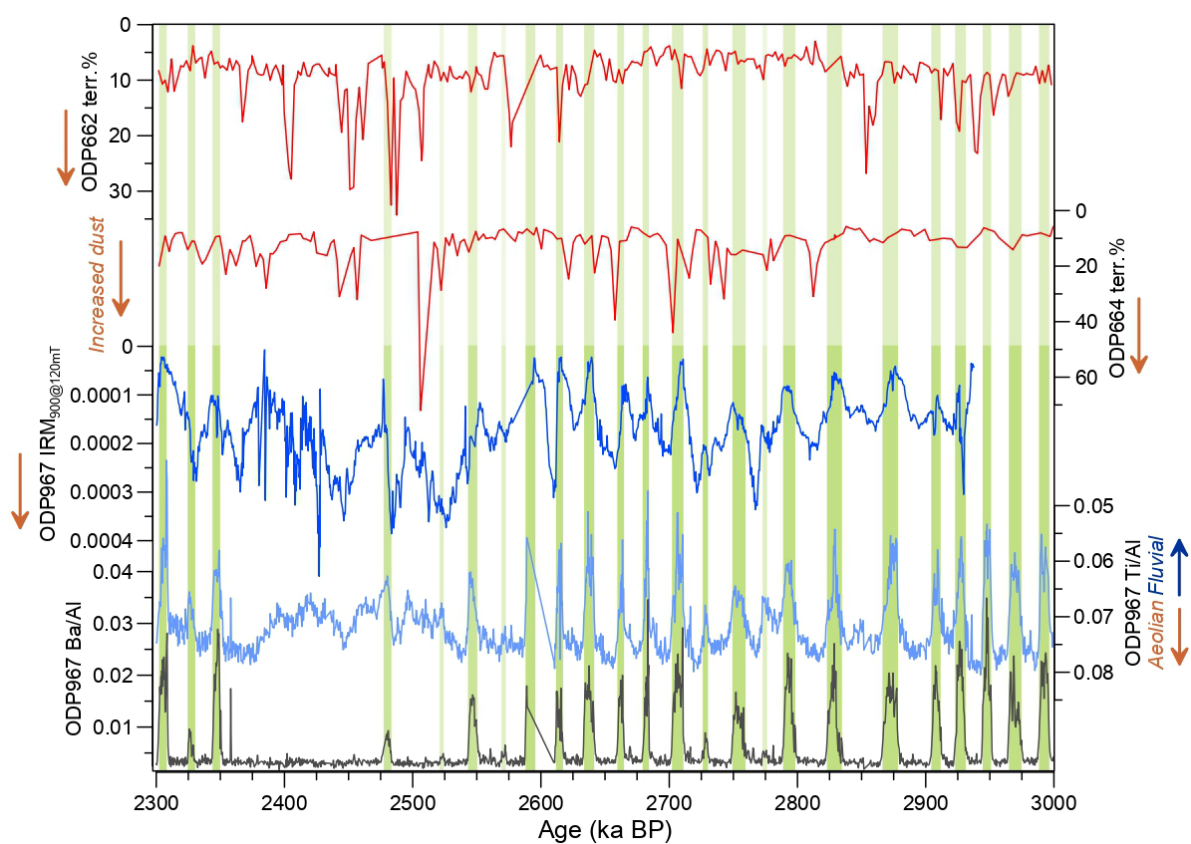
Supplementary Figures



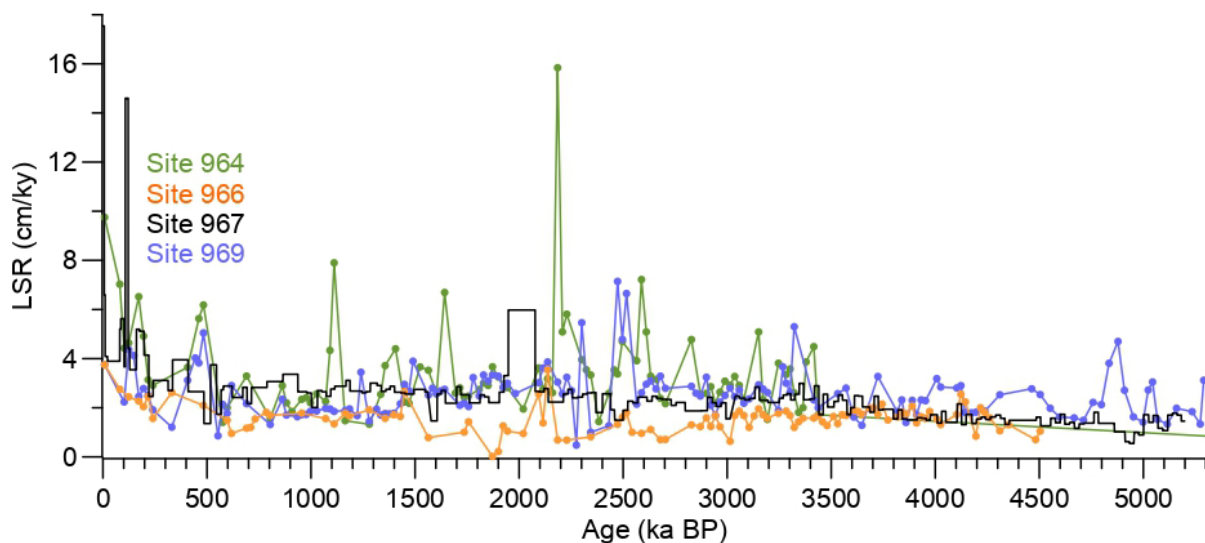
Supplementary Figure S1: Composite downcore image for ODP967 and astronomical tuning of scanning XRF Ba/Ti counts to precession for the 3-5.2 Ma interval. The published chronology for 0-3 Ma is also based on tuning to precession¹⁵.



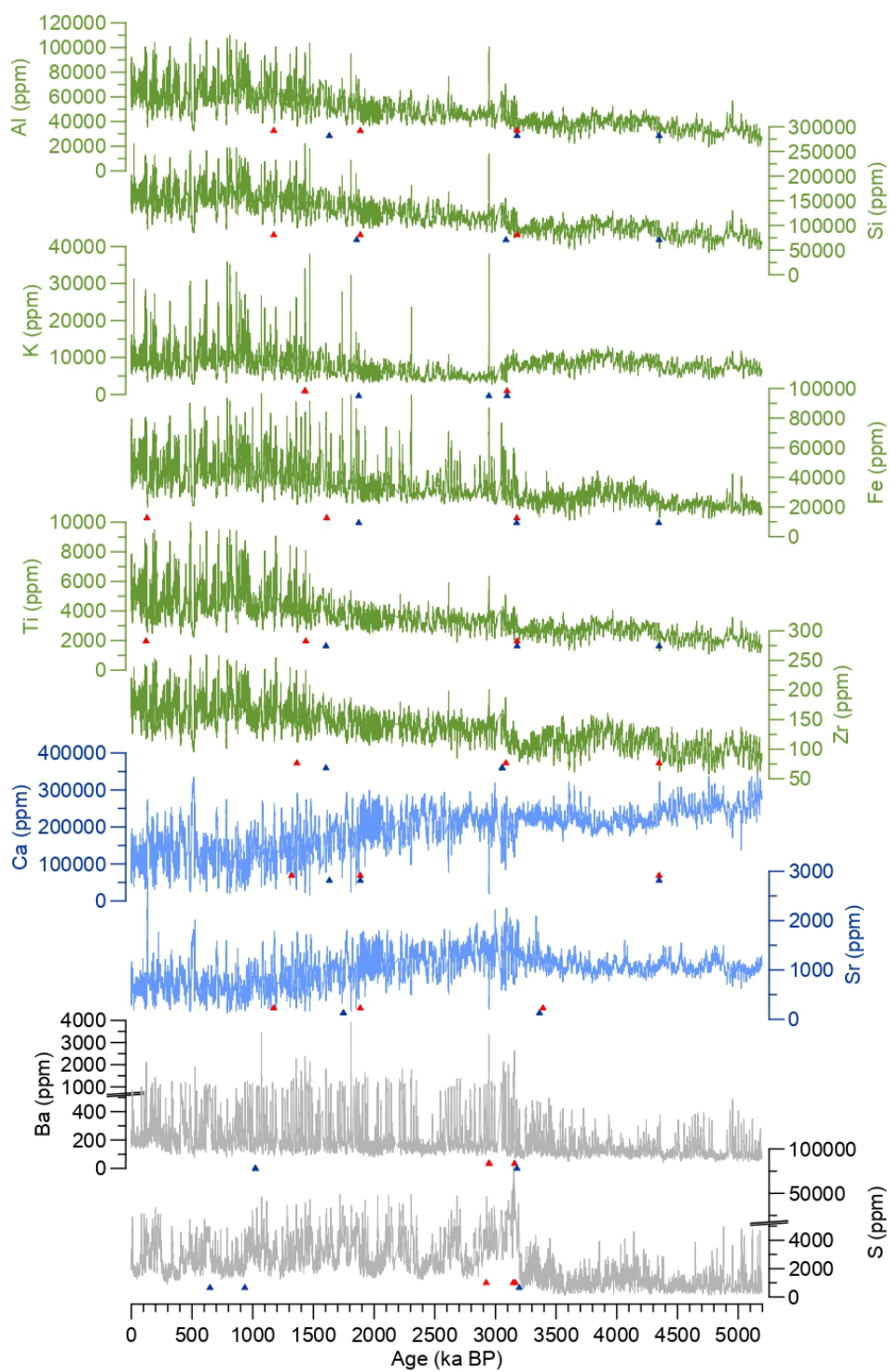
Supplementary Figure S2: Zoom-in of main-text Fig. 3 to show detail. ODP Site 967 records of planktic foraminifera (*G. ruber*) $\delta^{18}\text{O}$ (red), Ti/Al (blue), and Ba/Al (grey). Upward peaks correspond to precession minima (orange) and inferred Green Sahara Periods (green shading).



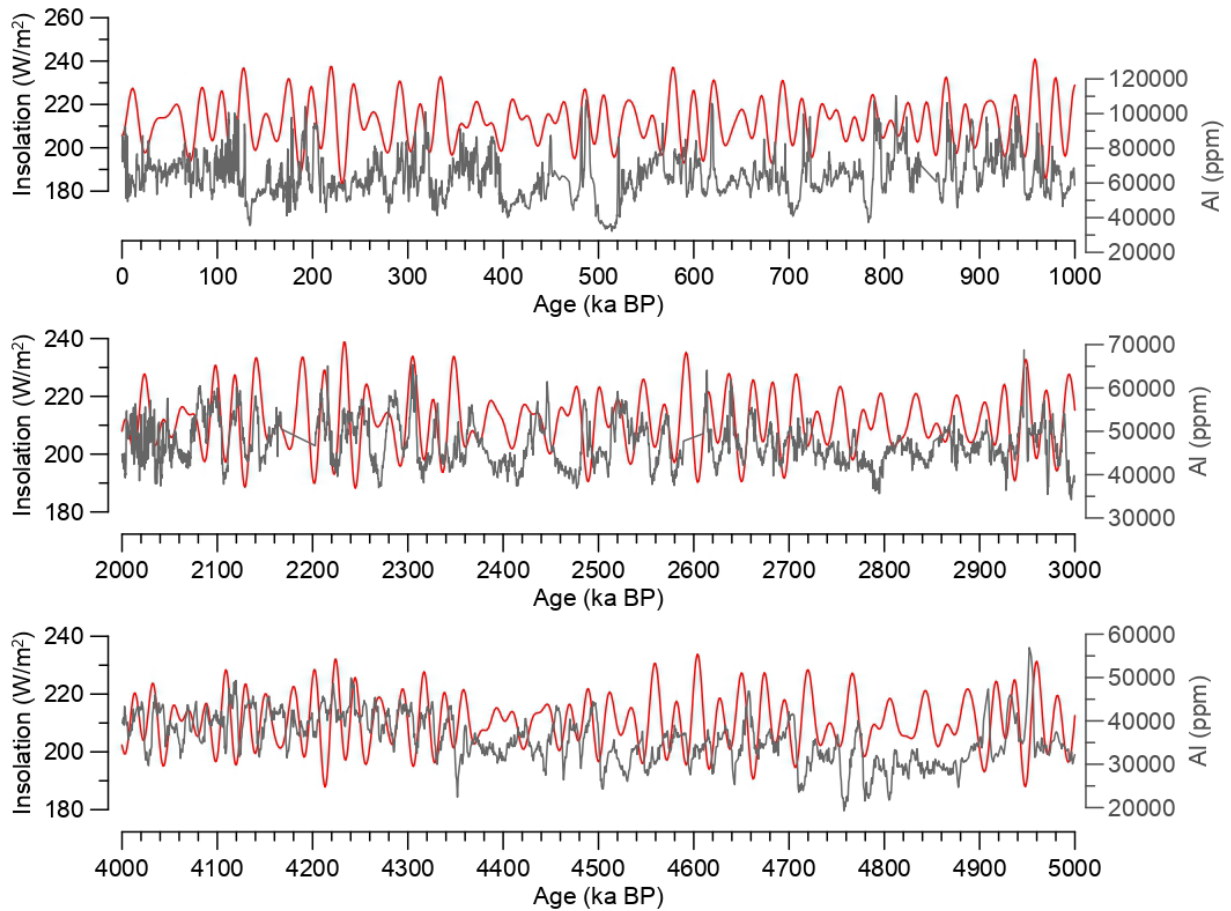
Supplementary Figure S3: Detail of dust records through Green Sahara Periods (GSPs). Terrigenous (aeolian dust) records from offshore West Africa (ODP Sites 662 and 664; red) on their original chronology^{24,25} and ODP967 magnetic dust proxy (IRM_{900@120mT}; deep blue) are shown with ODP967 Ti/Al and Ba/Al for comparison. GSPs (green bars) are based on this study.



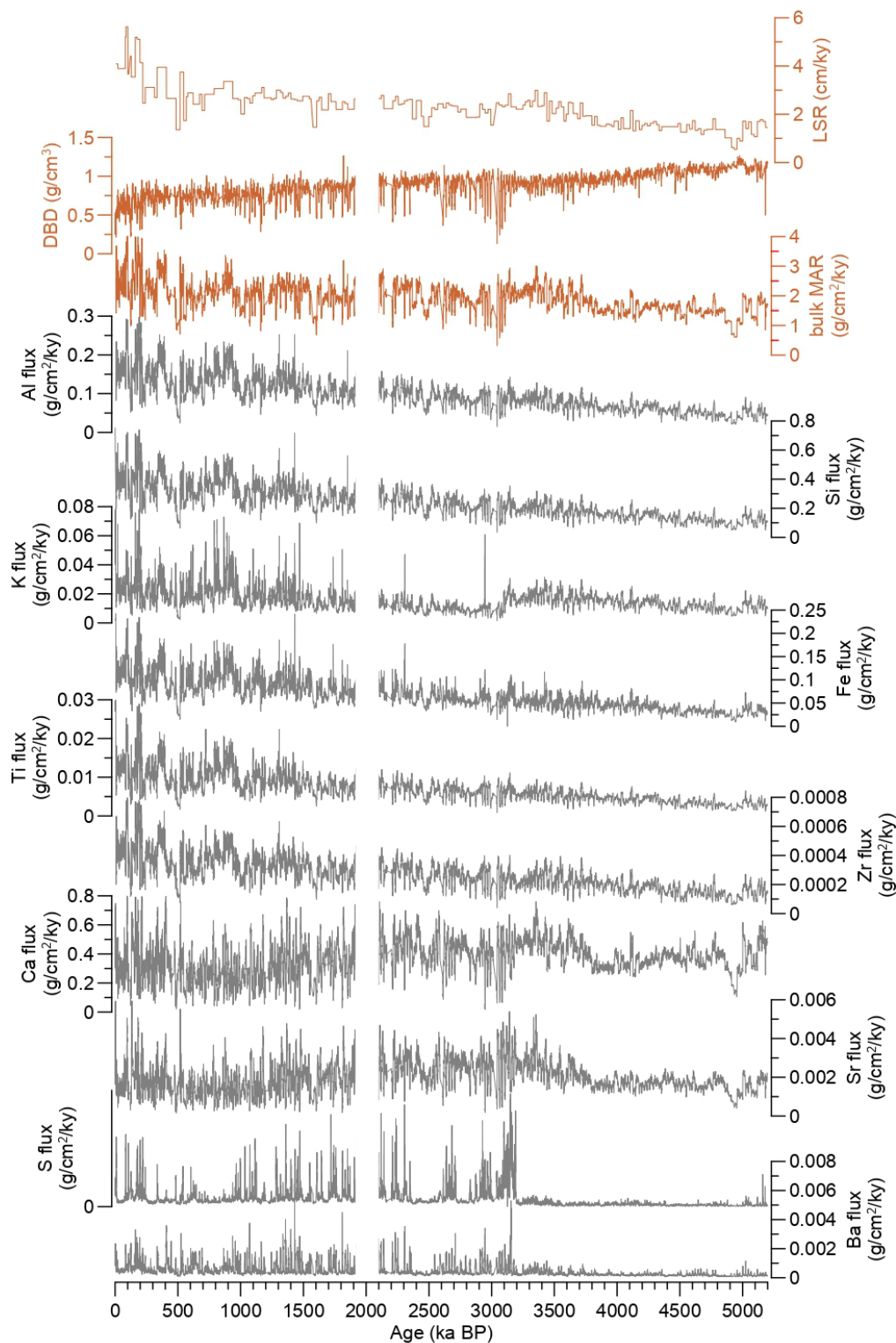
Supplementary Figure S4: Linear sedimentation rates (LSR) for ODP Site 967 (this study) and other Eastern Mediterranean ODP sites²⁹. There are no published depth-age data for Site 964 beyond 3.4 Ma, so we interpolate LSR for 3.4-5.3 Ma by assuming that the basal composite down-hole depth (133 m) corresponds to the base of the Zanclean at 5.33 Ma^{ref.81} (this is the case for Sites 967 and 969 where more depth-age data are available). Elevated rates at Site 967 at ~100 and 2000 ka BP are due to slumps; spikes in Site 964 LSR are likely due to turbidites.



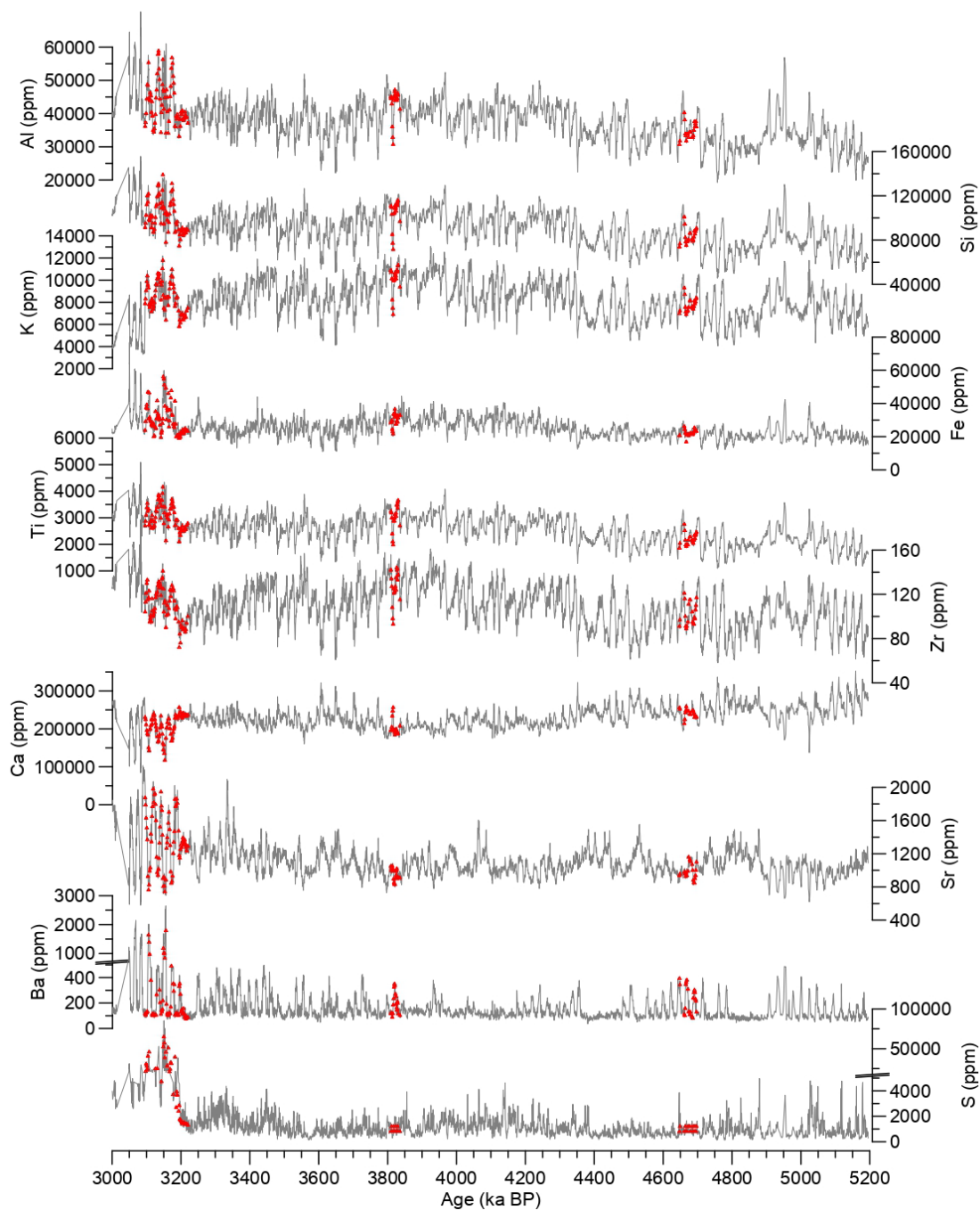
Supplementary Figure S5: ODP967 element concentrations (green = terrigenous; blue = biogenic) and change-points based on the mean (red triangles) and standard deviation (blue triangles).



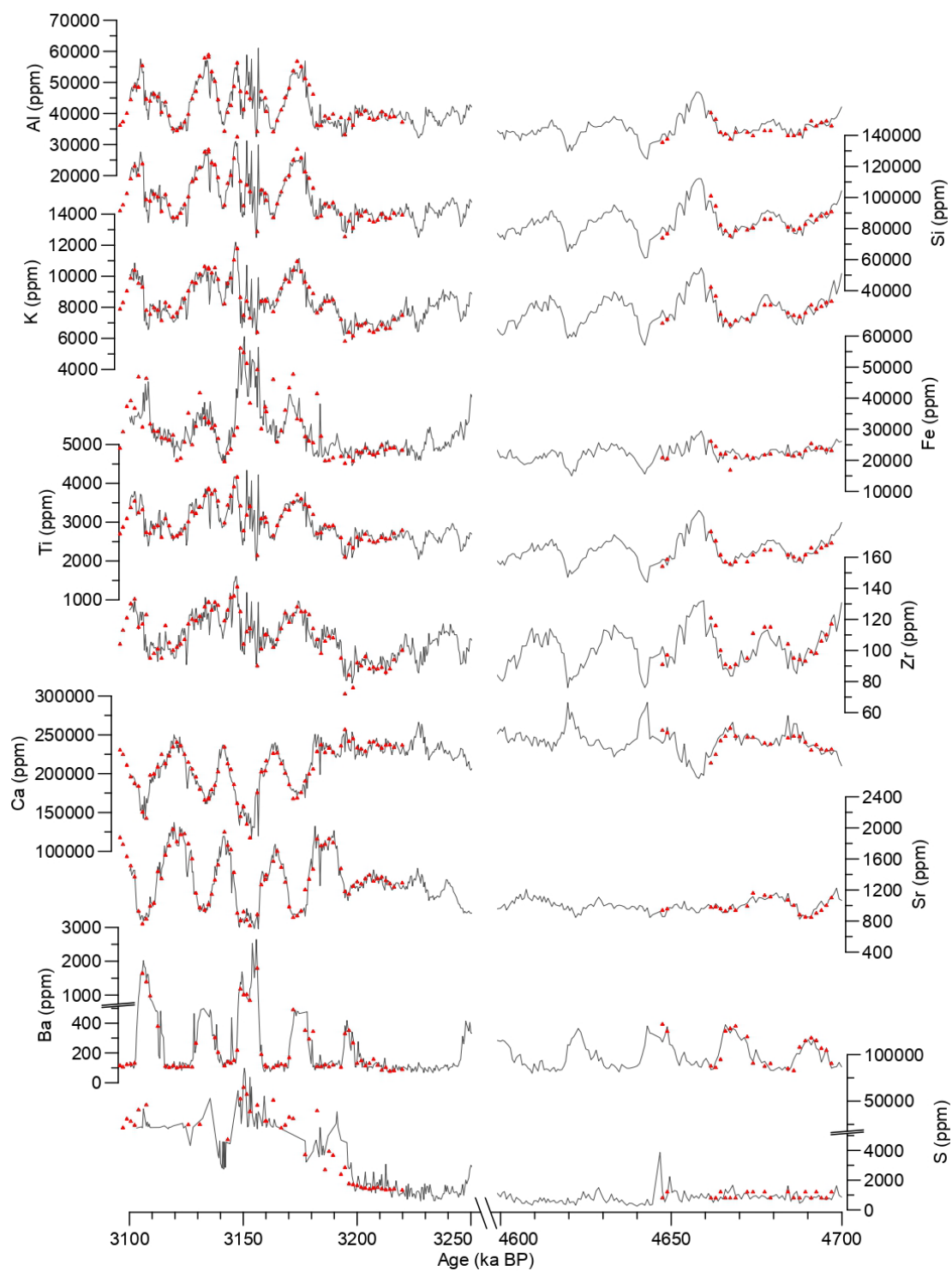
Supplementary Figure S6: Detail of ODP967 Al variability over three time periods (0-1, 2-3, 4-5 Ma) to illustrate how terrigenous element concentrations at ODP967 vary with insolation. The subtropical insolation gradient (21 June, 23°N-23°S; red) is near-identical to 21 June 65°N insolation and the best fit with Mediterranean sapropel sequences (see ref. 8).



Supplementary Figure S7: ODP967 linear sedimentation rates (LSR), dry bulk density (DBD), bulk sediment mass accumulation rates (MAR) and element fluxes (grey). A sediment slump at ca 2 Ma is blanked out. Element fluxes and bulk MAR reflect DBD changes (especially after 3.2 Ma when sapropels dominate) and a long-term increase in LSR.



Supplementary Figure S8: ODP967 element concentrations from WD-XRF (red symbols) and scanning XRF results converted into element concentrations (grey lines) based on a multivariate log-ratio calibration⁷⁵ (MLC; see Methods). A similar MLC was previously applied to scanning XRF results from ODP967 for 0-3 Ma^{ref.15}.



Supplementary Figure S9: The same as Figure S7 but zoomed into two intervals to show detailed comparison of reference (red) and predicted (grey) concentrations.

Supplementary Table S1: Sapropel preservation at Western Mediterranean ODP sites⁸²

Site	Water depth (m)	Location	Continuous visible sapropel record
974	3454	Tyrrhenian Sea	≤1.8 Ma
975	2416	Balearic Margin	≤1.8 Ma
976	1108	Alboran Sea	≤1.5 Ma
977	1984	Alboran Sea	≤1.5 Ma [†]
979	1062	Alboran Sea	≤3.0 Ma*

[†] Prior to 1.5 Ma, there are two sapropels at 2.7 Ma.

*Corresponds to basement of drilled site

Supplementary References

81. Andreetto, F. et al. Freshening of the Mediterranean Salt Giant: controversies and certainties around the terminal (Upper Gypsum and Lago-Mare) phases of the Messinian Salinity Crisis. *Earth-Sci. Rev.* 216, 103577 (2021).
82. Murat, A. Pliocene-Pleistocene occurrence of sapropels in the western Mediterranean Sea and their relation to Eastern Mediterranean sapropels. *Proc. ODP Sci. Res.* 160, 519-527 (1999).

Appendix Chapter 4

Appendix A: Decomposition approach

A flowchart is provided (Figure A1) to illustrate our proposed approach in a compact fashion. The following list explains the key terms used in the main text and Figure A1:

$\delta^{18}\text{O}_{\text{pf}}$: Planktonic foraminiferal $\delta^{18}\text{O}$.

$\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$: $\delta^{18}\text{O}_{\text{pf}}$ in monsoon upper summer mixed layer.

$Q_{0.1}^{\delta^{18}\text{O}_{\text{pf}}}(S)$: 0.1 quantile regression of $\delta^{18}\text{O}_{\text{pf}}$ in sapropel intervals.

$Q_{0.1}^{\delta^{18}\text{O}_{\text{pf}}}(M)$: 0.1 quantile regression of $\delta^{18}\text{O}_{\text{pf}}$ in marl intervals.

$Q_{0.9}^{\text{RSL}_{\text{Gib}}}(S)$: 0.9 quantile regression of RSL_{Gib} in sapropel intervals.

$Q_{0.9}^{\text{RSL}_{\text{Gib}}}(M)$: 0.9 quantile regression of RSL_{Gib} in marl intervals.

$\Delta\text{RSL}_{\text{Gib}}$: Difference in RSL_{Gib} in terms of marl and sapropel 0.9 quantiles.

ΔT : Temperature concentration effect in monsoon upper summer mixed layer.

ΔFWF : Monsoon freshwater flux via the Nile River and North African margin.

$\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{RSL}}$: Change in $\delta^{18}\text{O}_{\text{pf}}$ due to $\Delta\text{RSL}_{\text{Gib}}$.

$\Delta\delta^{18}\text{O}_{\text{mon}}$: $\delta^{18}\text{O}$ of monsoon freshwater flux.

$\Delta\delta^{18}\text{O}_{\text{pf}}^{\text{mon}}$: $\delta^{18}\text{O}_{\text{pf}}$ anomaly due to monsoon freshwater flux.

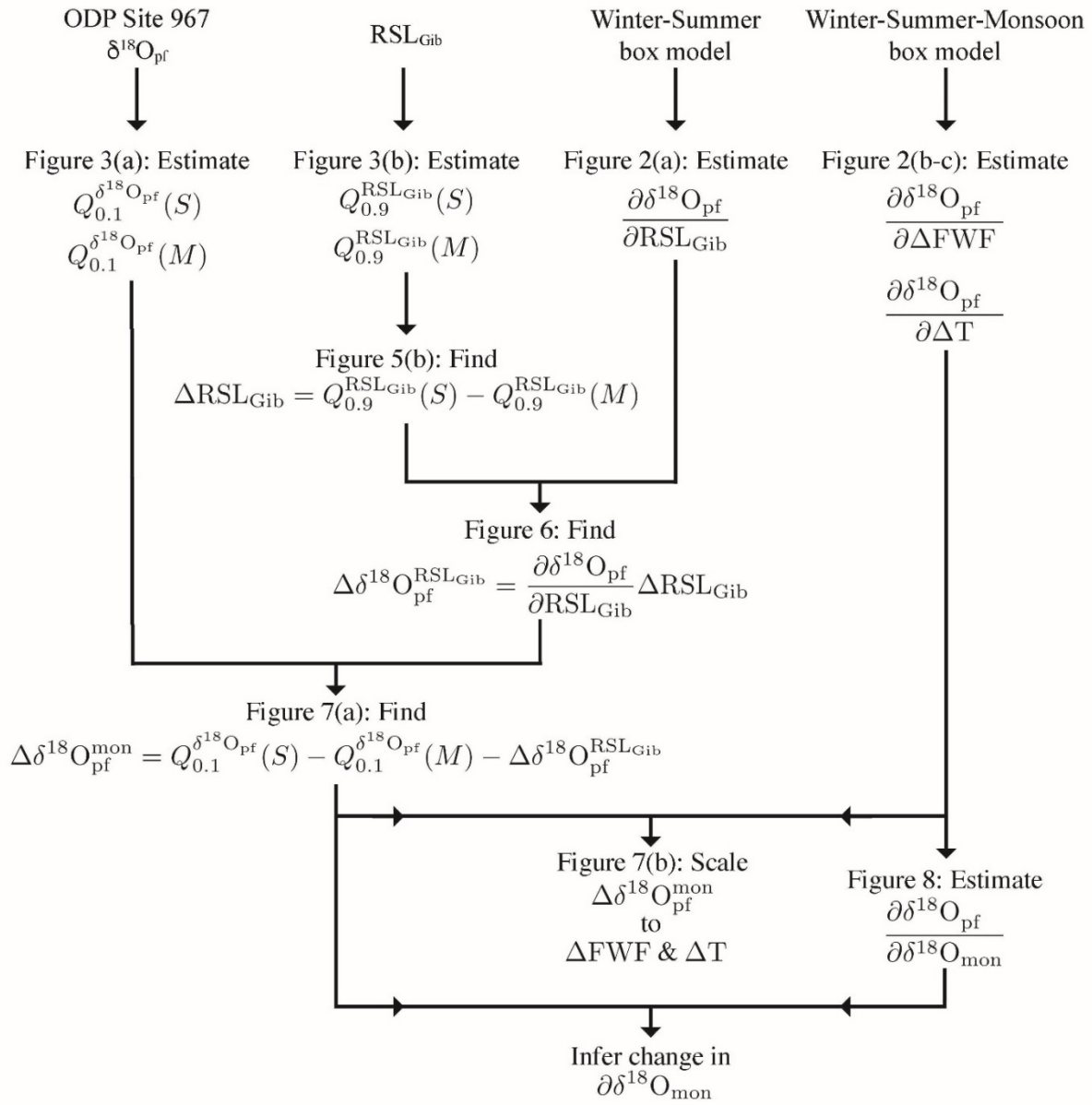


Figure A1. Flowchart of the proposed $\delta^{18}\text{O}_{\text{pf}}$ deconvolution procedure. A list of the abbreviations in the flowchart and main text is provided in Appendix A.

Appendix Chapter 5

Supplementary information for:

A 0.5 million-year North African humid period within the Pliocene

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Contents:

Supplementary Table 1: Nd isotope data for ODP site 967

Supplementary Table 2: Preserved sapropel record of eastern Mediterranean ODP sites

Supplementary Table 1| Nd isotope data for ODP 967 sediments.

Sample type	Age (kyr)	ϵNd	Error
Sapropels (Insolation maxima)	7.83	-6.61285	0.0000258
	604.613	-6.41235	0.0000289
	789.262	-4.73579	0.0000262
	1090.907	-5.85911	0.0000371
	1605.030	-4.35485	0.0000489
	2213.011	-5.31661	0.0002315
	2480.322	-5.75828	0.0000259
	2926.362	-6.24241	0.0000509
	3156.013	-5.00514	0.0000198
	3556.143	-4.48626	0.0000206
	4243.630	-6.34046	0.0000725
	5004.486	-6.22777	0.0000452
Marls (Insolation minima)	16.005	-6.52151	0.0000275
	608.773	-6.92463	0.0000508
	794.058	-4.01398	0.0000166
	1097.023	-5.12494	0.0000240
	1618.465	-7.02352	0.0000296
	2222.793	-6.06446	0.0000629
	2222.793	-5.98857	0.0000314
	2490.094	-8.35105	0.0009607
	2936.021	-6.02174	0.0000260
	3169.444	-5.60029	0.0000202
	3566.857	-8.02015	0.0001201
	3829.975	-7.99713	0.0000373
	4251.515	-5.53341	0.0000532
	5009.286	-6.18879	0.0000272

Supplementary Table 2| Preserved sapropel record of eastern Mediterranean ODP sites

ODP Site	Depth (m)	Age (kyr)	Composite depth (m)	ODP Site	Depth (m)	Age (kyr)	Composite depth (m)
964	0.78	8	0.78	966	0.3	8	0.3
964	5.49	81	5.91	966	3.35	124	3.36
964	6.26	102	6.84	966	4.44	172	4.45
964	7.28	124	7.86	966	4.9	195	4.92
964	10.89	172	10.99	966	5.45	217	5.46
964	12.02	195	12.12	966	19.44	1070	20.46
964	12.71	217	12.81	966	19.99	1111	21.01
964	13.38	240	13.48	966	20.93	1164	21.95
964	17.27	407	19.57	966	23.1	1280	24.12
964	21.85	461	22.61	966	24.29	1356	25.31
964	23.21	483	23.97	966	25.52	1429	26.54
964	24.94	597	25.7	966	24.67	1564	27.97
964	28.8	955	34.24	966	27.07	1923	30.37
964	29.33	977	34.77	966	27.29	1944	30.59
964	29.77	997	35.21	966	32.78	2137	34.28
964	30.54	1027	35.98	966	33.11	2185	34.61
964	31.51	1070	36.95	966	33.41	2229	34.91
964	31.3	1091	37.86	966	34.35	2344	35.85
964	32.88	1111	39.44	966	35.03	2588	38.99
964	48.14	1280	41.76	966	35.52	2632	39.48
964	38.62	1356	43.94	966	35.85	2679	39.81
964	40.82	1406	46.14	966	37.65	2828	41.61
964	39.64	1449	47.1	966	38.18	2871	42.14
964	40.12	1471	47.58	966	38.9	2921	42.86
964	43.47	1564	50.93	966	39.27	2943	43.23
964	44.47	1603	51.93	966	39.54	2965	43.5
964	48.24	1642	54.54	966	39.85	3014	43.81
964	45.67	1694	55.89	966	40.22	3036	44.18
964	46.26	1715	56.48	966	40.63	3058	44.59
964	46.77	1736	56.99	966	41	3080	44.96
964	47.29	1757	57.51	966	41.31	3105	45.26
964	48.69	1808	58.91	966	44.1	3129	45.66
964	49.32	1829	59.54	966	44.53	3151	46.09
964	49.57	1829	59.79	966	44.89	3172	46.45
964	50.73	1872	60.95	966	42.27	3193	46.78
964	50.82	1872	61.04	966	43.22	3246	47.72
964	53.28	1900	61.86	966	44.45	3322	48.97
964	54.52	1944	63.1	966	53.52	3702	55.3
964	56.6	2115	67.84	966	53.9	3724	55.68
964	57.9	2160	69.14	966	52.18	3817	57.26
964	57.98	2185	73.1	966	52.58	3839	57.66
964	59.15	2208	74.27	966	52.93	3859	58.01
964	60.37	2229	75.49	966	54.2	3932	59.28
964	72.97	2611	89.69	966	54.53	3953	59.61
964	73.65	2632	90.38	966	55.42	4007	60.5
964	75.5	2703	92.22	966	55.67	4026	60.75
964	76.71	2828	98.19	966	59.9	4103	62.08
964	77.81	2871	99.29	966	60.41	4123	62.59
964	79.17	2921	100.64	966	61.31	4195	63.49

964	79.64	2943	101.12	966	61.75	4217	63.93
964	80.22	2965	101.7	966	62.13	4238	64.31
964	80.96	2989	102.44	966	62.51	4262	64.69
964	82.95	3036	103.89	966	63.02	4310	65.2
964	83.59	3058	104.53	966	64.48	4482	66.66
964	84.1	3080	105.04	966	64.71	4504	66.89
967	1.19	8	1.19	969	0.3	8	0.3
967	4.31	81	4.27	969	2.4	102	2.4
967	5.44	102	5.51	969	3.36	124	3.36
967	5.67	102		969	4.94	172	4.94
967	6.89	124	7.57	969	5.58	195	5.58
967	8.95	172	9.63	969	6.13	217	6.13
967	9.67	195	10.79	969	13.57	483	13.29
967	10.56	217	11.68	969	14.64	575	14.36
967	10.71	240	12.21	969	15.03	597	14.75
967	13.55	331	15.05	969	21.09	955	21.33
967	16.51	407	18.01	969	21.47	977	21.71
967	18.52	461	20.02	969	21.84	997	22.08
967	20.09	483	20.85	969	22.4	1027	22.64
967	20.47	503	21.23	969	23.25	1070	23.49
967	22.16	575	22.92	969	23.66	1091	23.9
967	22.7	597	23.51	969	24.03	1111	24.27
967	24.53	668	25.29	969	25.03	1164	25.27
967	25.09	690	25.85	969	25.44	1185	25.68
967	31.18	934	32.6	969	27.26	1280	27.5
967	31.72	955	33.15	969	23.31	1356	28.89
967	32.35	977	33.79	969	28.83	1398	29.63
967	32.71	997	34.15	969	29.5	1429	30.3
967	33.44	1027	34.88	969	30.09	1449	30.89
967	34.51	1070	35.95	969	30.68	1471	31.48
967	34.99	1091	36.43	969	33.28	1564	34.08
967	35.62	1111	37.06	969	34.33	1603	35.13
967	37.17	1164	38.61	969	35.39	1642	36.19
967	36.01	1185	39.25	969	30.28	1736	38.18
967	38.59	1280	41.85	969	37.95	1757	38.61
967	39.54	1315	42.78	969	39.47	1808	40.04
967	40.08	1335	43.32	969	40.21	1829	40.74
967	40.71	1356	43.95	969	40.94	1851	41.42
967	41.32	1376	44.56	969	41.68	1872	42.12
967	41.88	1398	45.12	969	42.66	1900	43.04
967	42.72	1429	45.95	969	43.35	1923	43.69
967	41.98	1449	46.54	969	44.02	1944	44.32
967	42.44	1471	47	969	49.27	2094	48.68
967	44.59	1564	49.15	969	50.07	2115	49.44
967	45.14	1584	49.7	969	52.48	2185	51.75
967	47.71	1603	50.08	969	53.8	2229	53.02
967	48.67	1642	51.03	969	54.44	2252	53.64
967	50.23	1715	52.59	969	40.94	2301	55.17
967	50.65	1736	53.01	969	57.38	2344	55.6
967	48.24	1757	53.44	969	65.28	2565	63.18
967	49.37	1808	54.57	969	45.01	2588	63.78
967	49.88	1829	55.08	969	66.69	2611	64.46
967	50.41	1851	55.61	969	67.38	2632	65.11

967	50.87	1872	56.07	969	68.15	2658	65.83
967	51.48	1900	56.68	969	68.88	2679	66.52
967	52.03	1923	57.23	969	69.6	2703	67.19
967	53.92	1944	57.78	969	73.41	2828	70.78
967	62.38	2094	67	969	74.57	2871	71.87
967	65.01	2115	67.49	969	50.29	2900	72.81
967	65.64	2137	68.12	969	50.73	2921	73.25
967	63.37	2185	69.19	969	51.11	2943	73.62
967	64	2208	69.82	969	75.75	2965	74.11
967	64.6	2229	70.42	969	76.47	2989	74.71
967	66.39	2301	72.21	969	77.31	3014	75.41
967	70.21	2344	73.33	969	77.95	3036	75.95
967	65.51	2588	79.02	969	78.67	3058	76.55
967	66.04	2611	79.56	969	79.96	3105	77.62
967	76.55	2632	80.15	969	81.57	3151	78.97
967	77.11	2658	80.71	969	79.34	4310	107.13
967	77.78	2679	81.38	969	86.11	4552	113.36
967	78.5	2703	82.1	969	113.43	4597	114.09
967	81.27	2828	84.87	969	114.68	4667	115.2
967	82.22	2871	85.82	969	115.43	4712	115.87
967	82.95	2900	86.55	969	88.92	4758	116.89
967	83.45	2921	87.05	969	93.77	4909	122.01
967	83.97	2943	87.57	969	94.47	4952	122.71
967	84.47	2965	88.07	969	95.12	4998	123.36
967	84.99	2989	88.58	969	95.82	5023	124.04
967	73.63	3014	89.13	969	96.46	5044	124.68
967	74.05	3036	89.55	969	97.46	5115	125.67
967	74.5	3058	90	969	98.33	5159	126.54
967	74.88	3080	90.38	969	99.72	5234	127.92
967	89.01	3105	90.93	969	100.24	5273	128.44
967	88.24	3151	92.08	969	95.82	5290	128.97
				969	96.5	5310	129.65
				969	97.1	5330	130.25

Appendix Chapter 6

Supplementary information for:

Global cooling and atmospheric responses at the Early-Mid Pliocene transition

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Contents:

Supplementary Table 1: A list of environmental shifts detected across the Early-Mid Pliocene transition (3.4-3.2 Ma).

Supplementary Table 2: Summer and winter dynamics of major stratospheric and tropospheric components over Europe, the Mediterranean and North Africa.

Supplementary Table 1: A list of environmental shifts detected across the Early-Mid Pliocene transition (3.4-3.2 Ma).

Locations	Observations	Inferred implications
Gulf of Lions (Garraf 1) North-eastern Spain (Papiol, Torrente del Terme, Ciurana) South-western France (Le Boulou, Cap d'Agde 1 borehole)	The record demarcates a marked increase of Mediterranean sclerophyllous plant percentage across the MG2-M2, as subtropical elements declined, announcing their future extinction^{18,22}.	Garraf 1 borehole was drilled close to the Northwestern Mediterranean shoreline which was characterized by a prevalent subtropical to warm-temperate forest vegetation during the Early Pliocene¹⁸. The rapid replacement of subtropical elements by Mediterranean vegetation illustrates the onset of Modern-like Mediterranean seasonal rhythm (strengthening of the seasonal contrast)^{18,22}.
Southwest Black Sea (DSDP Site 380)	Herbs became dominant, while subtropical elements declined¹⁹.	DSDP Site 380 shows a low altitude Zanclean vegetation with subtropical to warm-temperate forests competing with continental steppe during the Early Pliocene. The domination of herbs across the Early-Mid Pliocene transition indicates the establishment of cooler and drier conditions associated with the MIS MG2 glaciation, leading to the development of open environments, coeval to the onset of Mediterranean seasonal climatic rhythm¹⁹.
Poland (Wólka Ligezowska borehole) The Netherlands (Susteren 752.2 borehole)	A gradual decrease in subtropical elements, which were replaced by warm-temperate elements such as <i>Quercus</i>¹⁹.	Wólka Ligezawska borehole, cored in a paleolake from lowlands in central eastern Poland, displays an Early Pliocene mosaic vegetation (forests and heather moors) dominated by warm-temperate plants including some subtropical elements in the Early Pliocene. Complete disappearance of subtropical elements across the Early-Mid Pliocene indicates the development of more continental climatic conditions, characterized by decreased humidity and decreased temperature¹⁹.
Eastern Mediterranean (ODP Site 967)	The onset of enhanced organic carbon (sapropel) preservation	An abrupt non-linear response of North African landscape

	in the eastern Mediterranean. Concurrently, fluvial terrigenous sediment input to the site was doubled ²⁰ .	associated with a dominant increase in arid:humid contrast between green Sahara periods and intervening dry periods ²⁰ .
Northwest Africa (ODP Site 658)	The sum of pollen taxa sourced from the Sahara continued to increase ²¹ .	Strengthening of Trade winds (regional Hadley cell) with the development of arid conditions over North Africa, related to the development of ice sheets in the Northern Hemisphere.
Northwest Africa (DSDP Site 397)	An increase of terrigenous matter accumulation rate, and a slight increase in the biogenic opal accumulation ⁵¹ .	Strengthened meridional atmospheric circulation intensified the Trade winds, leading to higher upwelling rates and productivity

Supplementary Discussion:

The North Atlantic Oscillation

The North Atlantic Oscillation (NAO) is the dominant, and the only year-long mode of atmospheric variability governing the weather patterns (precipitation, storm tracks, and heat waves etc.) across the North Atlantic and European regions^{52–55}. NAO is regarded to be the regional expression of its hemispheric equivalent, the Atlantic Oscillation (AO)⁵⁶. The spatial structure of NAO is most commonly defined using an empirically-determined orthogonal function (EOF), which detects mean distribution of sea-level pressure (SLP) anomalies over the North Atlantic⁵². SLP anomalies of greatest amplitude occur during the boreal winter, when low-pressure anomalies over Iceland (Icelandic Low) and high-pressure anomalies over subtropical Atlantic (Azores High) persist⁵⁴. However, temporal variability of pressure centers clearly depicts the existence of a year-long pressure dipole, which seasonally changes its orientation and position^{52,55}. The NAO exerts minimum spatial extent and the percentage of total SLP variability during the boreal summer, when the pressure centers are located substantially northeast compared to the winter⁵⁵.

Modern NAO indices are derived from the difference in SLP anomalies between low and high pressure centers over the North Atlantic⁵³. During the winter, strengthening of the stratospheric polar vortex (SPV) establishes the positive mode of winter NAO^{57,58}. When the winter NAO index is positive, stronger than normal SLPs prevail at Icelandic Low and Azores High pressure centers, shifting the axis of moisture transport (winter storm tracks) to a more southwest to northeast orientation over the Atlantic⁵³. This results in wetter than normal conditions over Scandinavia and northern Europe, whereas southern Europe, the Mediterranean and North Africa become drier than normal⁵³. When the winter NAO index is negative, the SPV is weaker than normal, the SLP difference between the pressure centers diminishes, resulting in opposite weather conditions in the aforementioned regions (as the storm tracks shift southwards)⁵³.

Both modeling and observations have shown that the winter AO/NAO influence remains through the subsequent months, modulating the summer NAO conditions^{53,59,60}. High (positive) indices of NAO results in thinning of Arctic sea ice in the winter, leading to enhanced heat loss during the spring⁶⁰. As a result, summer sea ice content decreases with the aid of an anomalous Ekman drift of ice from marginal seas towards the central Arctic^{59–61}. This supports the development of the negative mode of summer North Atlantic Oscillation (SNAO). The negative SNAO mode is characterized by low pressure anomalies over northern Europe and a

high pressure center over Greenland⁶². Similar to the positive winter NAO, negative SNAO leads to cooler, wetter than normal conditions over northwest Europe, and warmer, drier conditions over southern Europe, the Mediterranean and North Africa⁵⁵ (Folland 2009). Consequently, a negative winter NAO should yield a positive SNAO, developing opposite to negative SNAO weather conditions in the region⁵⁵.

Supplementary Table 2 | Summer and winter dynamics of major stratospheric and tropospheric components over Europe, the Mediterranean and North Africa. Details discussed in the table were employed in constructing the Extended Data Figure 1b.

Feature/ component	General description	Boreal summer	Boreal winter
Stratospheric features			
Arctic stratospheric polar vortex (SPV)	A seasonally reversing circumpolar vortex of the stratosphere, which exist from 15 to 50 km over the Arctic region ^{63,64} . The SPV variability can extend to the troposphere, affecting the jet streams, storm tracks and surface weather patterns ⁶⁵ .	Strong westerly Arctic SPV breaks down in the spring, which consequently supports the development of an anticyclone over the Arctic ⁶⁴ . This easterly circumpolar vortex is weaker compared to the winter westerly vortex ⁶⁴ . The easterly vortex dominates from May to August, which subsequently reverses in late September as the mid-stratospheric cooling begins ⁶⁶ .	Wintertime Arctic SPV is composed of strong westerly circulation ⁶⁷ . Strengthening of winter SPV results in positive phases of winter AO and the NAO ^{67,68} . Weakening of the winter SPV is known as sudden stratospheric warming (SSW) events, which results in the negative mode of AO and NAO ⁶⁹ .
Tropospheric features			
Arctic cell	The fourth meridional cell (not well-studied) in the Northern hemisphere (NH), in addition to the 3 main meridional cells (Hadley, Ferrell and Polar cells). Occurs in the troposphere north of the Polar cell, with weaker circulation compared to the main cells ^{70,71} .	Boreal summer Arctic cell-Polar cell boundary exists near ~80°N. Stands alongside the polar cell, with a more vertical boundary between the two cells compared to the winter ⁷⁰ .	Boreal winter Arctic cell-Polar cell boundary exists near ~82°N (Closer to the North pole compared to boreal summer) ^{70,72} .
Polar jet stream and mid-latitude storm tracks	An upper-tropospheric, quasi-zonal, high velocity wind stream ⁷³ . Located at the poleward edge of the	The polar jet stream is located at ~300 hPa level ⁷⁶ .	The polar jet stream is located at ~200-250 hPa.

	Ferrell cell, where cold, polar air is separated from warm, tropical air⁷⁴. Driven by perturbations of baroclinic eddies which generate westerly jets⁷³. In the lower troposphere, the region of baroclinity associated with strong temperature gradients consist of mid-latitude storm tracks⁷⁵.	North Atlantic/European summer storm track position can be related to the prevailing mode of SNAO. When SNAO is in positive mode, storm tracks shift polewards from west Atlantic to northern Scandinavia (~65°N). Low pressure anomalies with increased cloudiness exist over the Mediterranean, which increases summer rainfall. When the SNAO is in negative mode, storm tracks are displaced southwards over the UK and northwestern Europe (55°N). Mediterranean storm activity decreases (drier than normal summers)^{55,59,77}.	A significant correlation has been observed between the WNAO index and the polar jet latitude. When the WNAO index is largely positive, polar jet over North Atlantic can be shifted poleward up to 56°N, whereas when the WNAO index is extremely negative, the jet stream can be displaced towards the subtropical jet to about 40°N⁷⁸. Positive WNAO results in a stronger jet stream which is zonally elongated. When the WNAO is in its negative phase, the polar jet stream becomes weaker and may combine with the subtropical jet. Consequently, winter storm tracks also shift meridionally⁷⁴.
Subtropical jet	Driven by the transport of angular momentum from the tropics, northward through the Hadley cell in the Northern hemisphere⁷³. It forms along the poleward edge of the Hadley cell, as a zonal component (Krishna 1961). Jet axis is more frequently found at ~200 hPa, with a mean speed of 70 ms⁻¹ ref.⁷⁹.	Subtropical jet stream is less intense compared to the winter. The core of the jet is located at 200 hPa, 38-40°N over the Mediterranean⁸⁰.	Subtropical jet main axis over northwest Africa lies between 20– 30°N during the winter⁸¹. When the WNAO is in negative mode, equatorward displacement of the polar jet can result in cyclogenesis over the Mediterranean due to the interaction with the subtropical jet stream⁷⁹.
Saharan heat low (SHL)	A shallow thermal depression with exceedingly high temperatures, generated below 700 hPa⁸² (Nicholson 2003). Dry convection in the SHL helps to maintain the African easterly jet (Northern component)^{83,84}.	Plays an important role in the west African monsoon system. Progress north-westward between June and July from a core position of 15-20°N and 5°E. Becomes quasi-stationary until August at 22-27°N and 2°W.	Shifts southeastward from its summer position. Located south of Darfur mountains (mean position 9°N and 14°E) as an elongated heat trough. The heat trough extends from 15°W to 25°E⁸³.

		Strongly developed wind fields and enhanced surface temperatures compared to the boreal winter ⁸³ .	
ITCZ	Most definitions state the ITCZ as the east-west oriented low-pressure region where trade winds converge. This is true over the Oceans. Over tropical landmasses, trade winds do not exist. Therefore, over Africa the ITCZ is defined by the surface impression of the convergence between shallow, moist southwesterly monsoon flow and the dry northeasterlies (Harmattan winds over the Sahara) ⁸⁵ . The ITCZ is decoupled (separated by ~1,000 km) from the tropical rainbelt ⁸⁶ .	Mean position over west Africa is ~18-20°N, some 8° north of the tropical rainbelt. This region also corresponds to the dry ascent of air masses formed by the convergence of shallow southwesterly flow and the northeasterly flow of air from the SHL ^{82,87} .	Southwesterly monsoon weakens during the boreal winter. The ITCZ is displaced equatorward from its summer position. Zone of convergence roughly lie 8-10°N over Africa. In January, east part of the ITCZ traverse through equatorial Africa and migrates to ~20°S. Zone of convergence in west Africa lies ~6-10°N ⁸⁵ .
Tropical rainbelt	A year-long southerly moisture flux enters western Africa through the equatorial Atlantic region. The rainbelt is formed due to the strong ascending core associated with deep meridional circulation between the axes of the African easterly jet (Northern component) and the tropical easterly jet ⁸⁶ . Frictional uplift of air masses when southwesterly winds encounter the land surface may play a role in initiating the ascending motion ⁸⁷ . Dry air from the SHL is also transported towards the rainbelt at mid-tropospheric levels through the shallow circulation cell ⁸⁷ .	During the first half of July (<i>Transitional phase</i>), coastal rainfall reduces due to sea-surface temperature reduction induced by the development of the ACT and intensified upwelling. The main moisture flux convergence lies 7°N during the transitional phase. From mid-July to September (<i>Sahelian phase</i>), moisture flux convergence moves towards Sahel (10°N) and strengthens as the rainy season begins ^{87,88} .	From November to mid-April (<i>Oceanic phase</i>), the main rain belt lies in vicinity of the equator, with peak rainfall at ~1°N over the equatorial Atlantic Ocean. From mid-April to May, moisture flux convergence intensifies while moving away from the equator to ~4°N (<i>Coastal phase</i>). This phase is concurrent with the Atlantic cold tongue (ACT) development ^{87,88} .

African easterly jet-Northern component (AEJ-N)	A zonal jet stream in the mid-troposphere at 600-700 mb (hPa). Plays a major role in generating African easterly waves. AEJ-N is produced from the thermal contrast between the Sahara (hot) and the coast of Guinea (humid) (AEJ-S also develops due to a similar mechanism). The rainbelt is more intense when both AEJ-N and -S are well-developed ⁸² .	AEJ-N core lies at ~600 hPa during the boreal summer. Core speed is ~12 ms ⁻¹ as the mean zonal wind field strengthens. Shifts northward from its winter position to ~10-12°N over west Africa ^{82,87,89} .	AEJ-N core located at ~700 hPa during the boreal winter. Relatively weak compared to the boreal summer. Located around 3-5°N over west Africa. Core speed is ~8 ms ⁻¹ refs. 82,87,89.
Tropical easterly jet (TEJ)	A zonal jet stream in the upper-troposphere at 200 mb (hPa). Develops due to the extensive temperature gradient between the Himalayan Plateau and the Indian Ocean. Maintained by a combination of east-west Walker circulation and a north-south Hadley circulation. TEJ core lies over the Indian Ocean, which extends over and exits through west-central Africa. TEJ over west Africa is associated with an upper level divergence, which has been linked to regional rainfall intensity. A stronger TEJ is linked to a more intense rainbelt ^{82,87} . The annual cycle of TEJ magnitude shows a double maximum in July and February, of which the July maxima is the strongest ⁸² .	Core over west Africa lies at ~8-10°N. Mean speed over the eastern Sahel is ~18 ms ⁻¹ ref.87.	Shifts southward from its summer position. Core over west Africa lies at ~6°S. Mean speed over the eastern Sahel is ~14 ms ⁻¹ ref.87.
Atlantic cold tongue (ACT)	The ACT is developed by SST reduction in eastern equatorial Atlantic (EEA) during the boreal summer. Ocean surface off the coast of Guinea is under the influence of southerlies of the southern Hadley cell	West African landmass heating after the spring equinox leads to an increased surface temperature and pressure gradient with the equatorial Atlantic, resulting in an acceleration of	Peak development of the ACT is followed by slow warming, starting from August ^{90,91} . Warming takes place until March ^{90,91} . Meridional wind stress over the EEA starts to reduce

	year-around. These southerly winds strengthen during the boreal summer, which enhances vertical mixing, upwelling and surface evaporation, lowering the equatorial SST. West African monsoon onset follows the ACT development by few weeks. Anomalously warm summer EEA SSTs result in below average precipitation over the Sahel and enhance precipitation over the coast of Guinea⁹⁰⁻⁹².	southerly winds⁹⁰. This induces Oceanic upwelling in the EEA. Enhanced upwelling may result in a SST drop of 5-7°C, leading to the development of ACT (cooling proceeds 3 months from May to July)⁹¹. Maximum cooling of EEA is reached by the end of July-August. Accelerated southerlies push the rainbelt (and ITCZ) to the north over west Africa⁹⁰.	from August, reaching a minimum from December to March⁹⁰ (Okumura). Average SST increases, hindering the development of the ACT⁹¹.
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Appendix Chapter 7

Supplementary information for:

Mega-flood-driven coexistence of eastern Mediterranean ventilation and sapropel formation

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Contents:

Supplementary Methods

Supplementary Figure 1

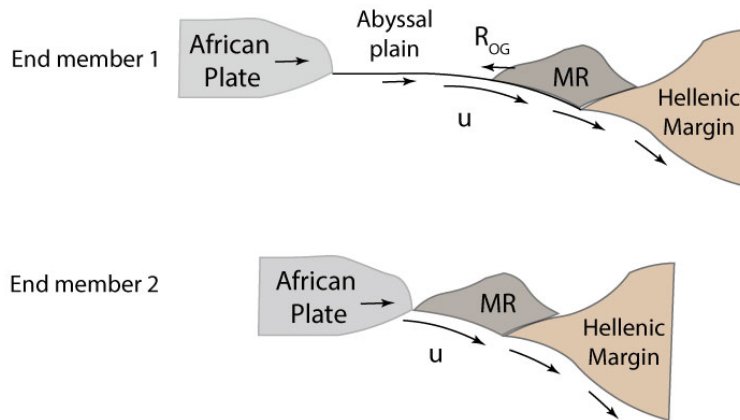
Supplementary Tables 1 & 2 – Organic matter contents and XRD results

Supplementary Methods

Mediterranean Ridge paleodepth estimation

The Mediterranean Ridge (MR) has formed by the subduction of the African Plate beneath Eurasia, leading to scraping off and accretion of sediments in front of the Hellenic Margin^{1,2}. Several attempts have been made to reconstruct the rate of outward growth of MR accretionary complex¹⁻³. Previous studies suggest that at the central MR, entire abyssal plain between the African plate and Hellenic Margin may have been consumed due to plate convergence, sometime between 3-5 Ma ago³. In such a scenario, as the outward growth of the wedge is hindered, the wedge behaviour is similar to that of an uplifted plug and retrowedge, where sediment accretion mainly contributes to an increase of thickness of the wedge^{3,4}.

To estimate the minimum and maximum possible paleodepth values for the MR crest in the Early Pliocene, we assume 2 end-member scenarios. End-member 1: An abyssal plain was always available for MR wedge outward growth during the past 5 Myr. To obtain an upper limit of paleodepth estimation (lower rate of uplift), we consider a constant breadth of MR, assuming no outward growth of the wedge. End-member 2: Abyssal plain was already consumed prior to the M/P boundary. Therefore, MR height increase happens due to the addition of off-scraping sediments during subduction, and due to continental collision. End member scenario 2 gives a lower limit of paleodepth estimation (higher rate of uplift).



Previous models indicated that the sediments at a subduction zones undergo 3 main fates; 1) subduction and addition to the mantle, 2) offscraping followed by accretion near the accretionary wedge toe, 3) underplating onto the bottom of previously accreted sediments. Following ref.x, we assume that a two-third of the incoming sediments contribute to the increase of MR volume.

The change in MR volume per time step ($\frac{d}{dt}(H \times B)$) is given by,

$$\frac{d}{dt}(H \times B) = u \times f \times D$$

where H is the height and B is the breadth of the MR, u is the rate of plate convergence, f is the contribution factor (2/3) and D is the thickness of the incoming sediment column.

This equation can be solved to give,

$$H \times \frac{dB}{dt} + B \times \frac{dH}{dt} = u \times f \times D$$

For end member 1, the first term is zero. Therefore, the change in MR height per time step is,

$$\frac{dH}{dt} = \frac{(u \times f \times D)}{B}$$

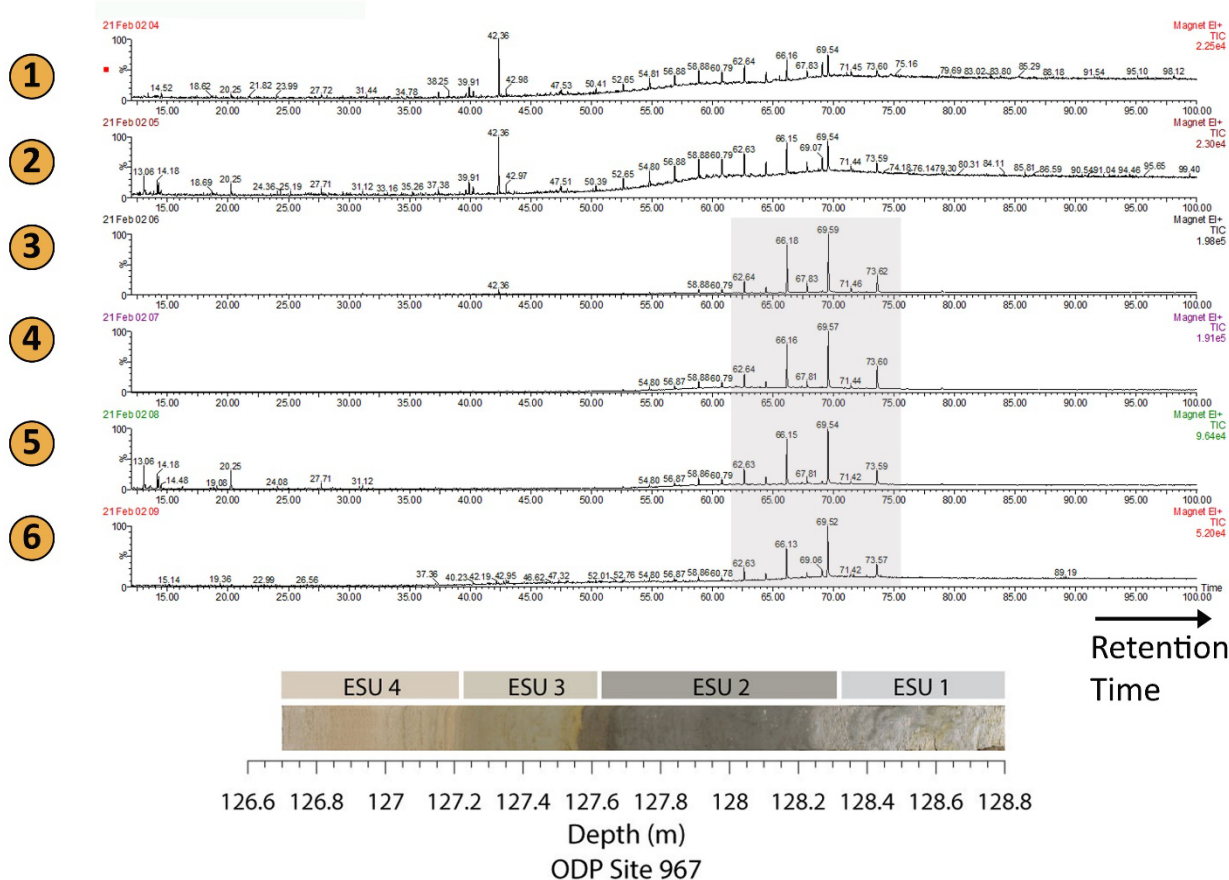
For end member 2, the MR breadth (B) is reduced by u per time step, due to continental collision.

$$\frac{dH}{dt} = \frac{(u \times f \times D) + (u \times H)}{B}$$

For both scenarios, MR height per time step (i) can be given by,

$$H[i] = H[i - 1] + \frac{dH}{dt} \times dt$$

We use the Pliocene plate convergence rates in ref.x for the calculations. The thickness of Messinian lower evaporite layer is used as the thickness of incoming sediment layer at 5.3 Myr. The thickness is updated per each time step, assuming a constant sedimentation rate of 0.02 m kyr⁻¹.



Supplementary Figure 1 | Results from the saturated hydrocarbon analysis of ODP site 967 samples across the M/P boundary. Samples 1 and 2 come from ESU (Eratosthenes Seamount Unit) 3, whereas samples 3-6 come from ESU 2. The combination of ESU2 and ESU3 was proposed as site 967 mystery sapropel. Previously proposed M/P boundary is at the ESU1-2 transition. Peaks in the shaded interval correspond to long-chain n-alkyl compounds derived from terrestrial plant material. Any sign of significant algae/ cyanobacterial blooms is absent.

Supplementary Table 1 | Organic matter contents at the Miocene/Pliocene boundary for ODP sites 969 and 967

ODP site, Hole	Core, Section	Interval (cm)	Core depth (m)	Age (kyr)	Organic matter (%)
ODP 969 B	11H, 6	5-6	95.95	5294.841	0.52
ODP 969 B	11H, 6	20-21	96.1	5298.319	0.36
ODP 969 B	11H, 6	35-36	96.25	5301.797	0.9
ODP 969 B	11H, 6	50-51	96.4	5305.275	1.75
ODP 969 B	11H, 6	65-67	96.56	5313.328	2.73
ODP 969 B	11H, 6	80-82	96.71	5318.246	1.5
ODP 969 B	11H, 6	110-111	97	5327.754	1.06
ODP 969 B	11H, 6	120-122	97.11	5331.361	1.85
ODP 969 B	11H, 6	145-147	97.36	5340.541	0.56
ODP 969 B	11H, 7	50-52	97.91	5358.574	0.52
ODP 969 B	11H, cc	15-17	98.17	5367.098	0.47
ODP 967 C	12H, 3	26-27	126.94	5294.864	0.27
ODP 967 C	12H, 3	42-43	127.1	5304.318	0.4
ODP 967 C	12H, 3	57-58	127.25	5312.375	0.29
ODP 967 C	12H, 3	75-76	127.43	5315.75	0.3
ODP 967 C	12H, 3	102-103	127.7	5320.813	0.37
ODP 967 C	12H, 3	124-125	127.92	5324.938	0.35
ODP 967 C	12H, 3	138-139	128.06	5327.563	0.3
ODP 967 C	12H, 4	14-16	128.33	5332.625	0.35
ODP 967 C	12H, 4	27-30.5	128.46	5339.079	0.2
ODP 967 C	12H, 4	47-49	128.66	5350.132	0.18

Supplementary Table 2 | XRD results across the Miocene/Pliocene boundary for ODP sites 969 and 967.

Site	Core depth (m)	Age (kyr)	Amorphous	Quartz	Plagioclase	K-Felds.	Calcite	Dolo.	Gypsum	Pyrite
ODP969	95.95	5294.84	7.6	3.3	0.8	0.6	68.1	1.5	2.1	0.3
	96.25	5301.80	12.6	3.7	1	0.6	65.3	1.2	1.9	0.4
	96.56	5313.33	8.8	2.4	0.6	0.6	71	1.1	1.5	0.3
	96.85	5322.84	11	3.6	1.1	0.8	58.6	1.5	11.7	0.1
	97.11	5331.36	9.3	2.3	0.4	0.5	56.2	1.1	18.7	0
	97.2	5335.30	21.2	8.3	1.4	1.1	21.6	2.6	4.8	0.2
	97.66	5350.38	11.3	11.7	2.2	1.4	15.9	4	3.1	0.3
	98.17	5367.10	12.9	12.5	2.6	1.7	14.2	3.9	2.7	0.1
ODP 967										
	126.86	16	3	1.1	0.7	61.2	5.7	16	0.6	ND
	127.1	15.3	5.2	3.8	1.1	42.4	9.9	15.3	0.5	ND
	127.26	7.8	12.8	2.8	0.4	9.4	19.1	7.8	0.6	ND
	127.42	10.3	12.4	2.8	0.4	10.8	12.8	10.3	0.5	ND
	127.62	9.1	13.6	5.2	2.6	20.5	0.5	9.1	0.3	ND
	127.9	10.2	12.3	4.1	1.2	21.6	0.7	10.2	0.2	ND
	128.14	16.6	10.1	4.6	0.3	33.9	0.4	16.6	0.1	ND
	128.27	14.6	5.7	2.9	0.8	54.4	0.7	14.6	0.6	ND
	128.49	16.1	9.3	2.7	1.1	40	1.4	16.1	0.9	ND
	128.71	15.7	8.3	3.2	0.5	38.7	0.9	15.7	1	ND

K-Felds., K-feldspar; Dolo, Dolomite; ND, not detected or below detection limit.

Supplementary references

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