

LATE QUATERNARY HYDROLOGICAL CHANGES IN NORTH
AFRICA BASED ON GEOCHEMICAL AND MICROFOSSIL
ANALYSES IN SEDIMENTS FROM THE EASTERN
MEDITERRANEAN SEA

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**LATE QUATERNARY HYDROLOGICAL CHANGES IN NORTH AFRICA
BASED ON GEOCHEMICAL AND MICROFOSSIL ANALYSES IN
SEDIMENTS FROM THE EASTERN MEDITERRANEAN SEA**

by

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Abstract

Aim of this thesis is to understand the hydrological cycle system effect of the North African monsoon since the Last Glacial Maximum (LGM) on terrestrial ecosystems and effect of humid periods on marine ecosystems of the Eastern Mediterranean Sea (EMS). In particular, the focus is placed on the drastic regime shift from arid conditions of LGM to the humid and vegetated conditions of the mid-Holocene in North Africa. The timing of this regime shift is investigated in order to determine the hydrological cycle and expansion of C4 plants in North Africa showed a covariance with precessional cycle or millennial scale. In order to achieve this objective, variations in compound-specific hydrogen and carbon isotopes of sedimentary n-alkanes of ODP site 967B are scrutinized. $\delta D_{n\text{-alkanes}}$, a proxy for precipitation, ranging from -199‰ to -127‰, co-varied with insolation change response to orbital forcing. Depleted $\delta D_{n\text{-alkanes}}$ were found from deglaciation to middle Holocene, suggesting increased precipitation during the African Humid Period (AHP) from 15 ka to 5 ka caused by northward migration of the Intertropical Convergence Zone (ITCZ). On the contrary, lower precipitation was inferred by enriched $\delta D_{n\text{-alkanes}}$ during LGM and late Holocene. $\delta^{13}C_{n\text{-alkanes}}$ at Site 967 did not show a trend in harmony with $\delta D_{n\text{-alkanes}}$ but exhibiting millennial-scale variations ranging from -25.9‰ to -33.2‰. These $\delta^{13}C_{n\text{-alkanes}}$ values are consistently C4 grass dominated environment in the watershed area of River Nile since LGM even during AHP. The greening of Sahara Desert was dominated by C4 plants during AHP coupled with formation of Sapropel layers in EMS fueled by African monsoon changes in North Africa. Discharge of freshwater into EMS via Nile River and Wadi connective system could alter marine ecosystems in EMS. Both planktic and benthic foraminiferal assemblages in sediment core from Nile deep-sea fan were examined together with *Globigerinoides ruber* (a planktic foraminiferal species living in surface water) $\delta^{13}C$ and $\delta^{18}O$ analysis. Isotopic excursions on both $\delta^{13}C$ and $\delta^{18}O$ of *Globigerinoides ruber* were observed during sapropel S3 and S4 layers. These isotopic excursions are interpreted as signature of enhanced freshwater discharge caused by increased precipitation and terrigenous input in watershed area of Nile River. Increased %*Globigerina bulloides*, a high productivity indicator, suggest nutrient rich condition during then. Benthic foraminiferal assemblages were employed to reconstruct oxygen (O_2) conditions in pore water. Notable species turnover to deep infauna species, dysoxic indicator, were observed in sapropel layers. Low species diversities of both planktic and benthic foraminifera are likely due to thermocline shallowing by enhanced freshwater discharge and dysoxic bottom water caused by high productivity during sapropel layer formations.

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Chapter 1. Introduction

1.1. The Eastern Mediterranean Sea

The Eastern Mediterranean-Levant region is located at the convergence of the Eurasian continent, the Saharan-Arabian desert and the Mediterranean Sea. The almost land locked Mediterranean Sea maintains its sole connection to the Atlantic Ocean via the Gibraltar Strait. As a result, sea surface conditions are diverse with west to east salinity and sea surface temperature (SST) increases and a corresponding productivity decrease (Antoine et al., 1995; Malanotte-Rizzoli et al., 1999; Pinardi and Mosetti, 2000). Precipitation over the Levantine Basin is mainly originated in the northeast Atlantic Ocean, passing over Europe and the Mediterranean Sea (Eshel, 2002; Rindsberger et al., 1983); sporadically, sub-tropic warm air over the southern Mediterranean resulted in precipitation over the Levantine basin (Dayan, 1986). Cold dry Arctic air that penetrates into the eastern Mediterranean region results in an increase in surface water density, leading to the formation of the Levantine Intermediate Water (LIW) off the island of Rhodes (Malanotte-Rizzoli et al., 1999; Pinardi and Mosetti, 2000). The African monsoonal system is associated with the low-latitude rainfall system (Rossignol-Strick, 1985) that directly influences the North Africa vegetation cover and indirectly influences the hydrography of the Levantine Basin. This system fluctuates in time, and is at its highest strength during periods of June maximum insolation in the Northern Hemisphere that coincide with elevated River Nile discharge (Haynes Jr, 1987; Rossignol-Strick, 1985; Rossignol-Strick et al., 1982). The River Nile was recognized as an important source of freshwater during Sapropel layer deposition in EMS (Kholeif, 2010; Scrivner et al., 2004) besides, rainfall on the entire Mediterranean Sea from Atlantic sources (Kallel et al., 1997; Bar-Matthews et al., 2000). Beside freshwater discharge from River Nile, several studies discussed rainfall effect over the entire Mediterranean Sea and the influx of Black Sea water during periods of sapropel formation (Almogi-Labin et al., 2009, reference are therein). The Nile deep-sea system is the largest sedimentary accumulation in EMS, and one of the largest modern deep-sea turbidite systems. It is more than 600 km wide and 300 km long, and consists of a mud-rich sediments delivered by Nile River (Reading and Richards, 1994). Since the late Miocene the accumulation of the Nile deep-sea sediments began to form above mobile Messinian evaporites (Gauillier et al., 2000; Loncke et al., 2006).

1.2. The Nile System

The Nile Delta is a delta located in the northern Egypt where the Nile River flowing into the EMS. The Nile Delta is formed where the supply of pluvial sediment has been abundant, and wave and current action have not been sufficient to disperse it. Of the numerous tributaries of the Nile that once existed, the Rosetta Branch to the west and the Damietta Branch to the east, are now present. The

Nile River crosses equatorial Africa (White Nile), tropical areas (Blue Nile and Atbara River) and areas with arid climates (Main Nile) to discharge into EMS through a large arcuate delta. Most of the discharge from the Nile River is originated from the Ethiopian Highlands and the Blue Nile system which influenced strongly by wet summer monsoon (seasonal flood) (Said, 1981; Williams et al., 2000). The steep Ethiopian Highlands generate abundant terrigenous particles and 70% of the present-day water discharge. Conversely, Sudd swamps (White Nile) act as a sediment filter. Fine-grained Nile sediment originate from alumina and iron-rich soil of Ethiopia, and have particular depositional features distinct from those of other soils of the Mediterranean region (Manohar, 1981). The main clay minerals are montmorillonite (smectite), illite, and kaolinite, which form most of the fluvial load and are spread on the outskirts of the Nile cone and in the south-eastern corner of the Levantine Basin. The coarse fraction, which is mostly composed of quartz, also originates in Ethiopia and in Sudan, mainly from eroded Nubian sandstones. These sands used to arrive mainly during the June to September Nile floods. Additional sands originate in the Eastern and Western Desert of Sudan and the numerous Egypt wadis but very irregularly. These sediments averaged about 80–160 million tons per year before completion of the Aswan High Dam in 1964 but were then reduced significantly. Reduction in sediment supply began with the building of the Delta Barrages, completed in 1881, and the Aswan Dam completed in 1902. The Aswan High Dam has a big impact on the reduction of sediment supply to the Nile Delta. These include severe erosion along the delta coastline and penetration of saline water from the sea into river mouths, lagoons, and groundwater. The Nile Deep Sea Fan is the largest deep-sea sedimentary basin of EMS, and it differs from most other large subsea fans as being developed in a relatively small, enclosed sea (Stanley and Maldonado, 1977). Deposited sediments in the Nile Deep Sea Fan are expected to be recorded not only EMS paleoceanographic changes but also North African climatic histories. Therefore, sedimentary data from the Nile Deep Sea Fan is important to understand a role of Nile River flow modulated by the African monsoon and corresponding changes in ocean circulation and stratification in EMS (Kholeif and Ibrahim, 2010).

1.3. Geology of the Nile

Average flow of the Nile River at its mouth is 2800 m^3 per second or $84 \times 10^6 \text{ m}^3$ per year, which is very low compared to its length (6825 km) or area of its watershed (2.87 million km^2). This deficit is due mainly to the fact that much of the basin is subjected to an arid climate and therefore that the water undergoes high evaporation (Ducassou et al., 2006). The Main Nile, north of 18°N and whose total load is $230 \pm 20 \times 10^6$ tons per year (Garzanti et al., 2006), receives its water from three main sources: The White Nile, which flows through a part of equatorial Africa, the Blue Nile and the Atbara River, which lie at the Ethiopian highlands. The White Nile, which rises in Lake Victoria contributes

nearly one third of the total load, but only for a minor proportion of sediment as the White Nile has a very low liquid flow. Indeed, its course through the bush and the Sudan savannah is with little slope and many marshes. Sediments of the White Nile found in the deep basin and the delta are almost devoid of pyroxene (3%). On the other hand, abundant amphibole (97%) are derived from erosion of land metamorphic granites (Foucault and Stanley, 1989). The Blue Nile, which originates at Lake Tana in the Ethiopian highlands, contributes more than half the total load the main Nile (56%) (Foucault and Stanley, 1989) and its sediment load is $140 \pm 20 \times 10^6$ tons per year (Garzanti et al., 2006). This tributary brings pyroxenes, but also alkali feldspar and hornblende (Ca amphibole). Proportion of the hornblende is 79% against 21% for pyroxenes (Foucault and Stanley, 1989). Water discharge of the Blue Nile is 1620 m^3 per second on annual average and increases up to 5000 to 6000 m^3 per second during floods. The Atbara River contributes a small portion of the total load of the Nile River ($82 \pm 10 \times 10^6$ tons per year), carrying numerous fragments of volcanic rocks as well as olivine and augite from basaltic rocks (Garzanti et al., 2006). Pyroxenes (91%) are more abundant than amphibole (9%) (Foucault and Stanley, 1989). Differential flow for the three tributaries is based on the difference of surface of their respective drainage area and the variation of precipitation. Indeed, the Blue Nile and the Atbara River have a term shorter than the White Nile, but with a slope gradient greater, and draining rain water in the Ethiopian highlands that are subject to intense rainfall at the monsoons summer. Therefore, the Blue Nile and the Atbara River contribute a significant role in sediment load of the main Nile.

1.4. Evolution of the Nile

During the Neogene, the Nile River has undergone various trips through the arid expanses of the Sahara. Since the incision of the valley in the late Miocene, the river has experienced four major episodes: the Eonile, the Paleonile, the Prenile, and Neonile (Said, 1993, 1981). The Neonile was set up during the Holocene. With increased equatorial African lake levels, caused the addition of Lakes Victoria and Albert in the drainage basin of the Nile River. During 12 to 10 ka, widened Nile River caused a realignment of silt deposited by previous Neonile. Since 10 ka, rainfall on the Ethiopian highlands and the south of Egypt had significantly increased for 6 kyrs. Because of increased flow from the Ethiopian highland and equatorial African lakes, the present Nile River regime has been established.

1.5. Present African Climate

As a part of the Hadley cell circulation, trade winds from both hemispheres blow from the subtropics toward the tropics. Because warm dry air carried by the trade winds passes over the tropical

ocean, water vapor continuously evaporates from the sea surface. The region near the equator where the trade winds from both hemispheres meet is called the intertropical convergence zone (ITCZ) (Meehl and van Loon, 1979). Water vapor carried by the trade winds rises and contributes abundant rainfall along the ITCZ. Position of the ITCZ is near the equator in winter whereas migrates northward in summer. Warm and moist winds blow from the Indian Ocean in summer. The westward deflection of wind due to Coriolis effect provides part of the moisture-laden air currents over the Ethiopia. Upon reaching the Ethiopian highlands, they are forced to rise and condense to form precipitation. As a result, the Ethiopian highland, a Nile River source, receives long rainy season from July to September (Nicholson, 1996).

1.6. Monsoon and Astronomical Theory

Astronomical theory of paleoclimate explains the glacial-interglacial cycles during the Quaternary (e.g., Loutre and Berger, 2005). Climate is sensitive to both the total amount and the latitudinal and seasonal distribution of solar radiation onto the earth's surface. Three astronomical cycles are of relevance to these aspects: the eccentricity (cyclicity of 100 ka and 400 ka), the obliquity (cyclicity of 41 ka), and the precession (cyclicity of 19 and 23 ka), which are denoted as 'Milankovitch cycles'. Tüenter et al., (2003) suggests that both precession and obliquity mainly responsible for an intensity of the African summer monsoon and the signals are recorded in EMS sediments throughout the Pleistocene as a consequence of changes in Nile River discharge (Rossignol-Strick, 1985). Glacial-interglacial climatic oscillations had a large influence on the Mediterranean environments (Rose et al., 1999). Wet and dry periods are called 'pluvial' and 'arid' periods, respectively have been evidenced in Nile River (Said, 1993; Williams et al., 2000) and EMS (Weldeab et al., 2002) deposits. The Nile River floods in pluvial periods are responsible for supplying organic rich sediments (Kidd et al., 1978).

1.7. African Humid Period

North Africa was subjected to a wetter and warmer period between 15 ka and 5 ka known as African Humid Period (AHP, Barker et al., 2004; deMenocal et al., 2000; Junginger and Trauth, 2013). Numbers of marine core sediments (deMenocal et al., 2000; Ehrmann et al., 2017), lake core sediment (Berke et al., 2012; Tierney et al., 2008) and archaeological sites (Kuper and Kröpalin, 2006; Stanley et al., 2003) documented that AHP peaked between 9 ka and 6 ka when sapropel S1 deposited in EMS (Ritchie et al., 1985). Summer insolation paced by precessional cycle plays a principal role in greening and desertification of the Saharan Desert through precipitation in North Africa (deMenocal et al., 2000).

1.8. Sapropels

Sapropel is a dark-colored sediment with rich in organic matter. Numbers of sapropel layers are found in EMS sediments and have been the subject of numerous studies on the geographical distribution, age and formation (Casford et al., 2003; Cramp and O'Sullivan, 1999; Kallel et al., 2000a, b; Kroon et al., 1998). Sapropel layers in EMS may be laminated or bioturbated depending on their thickness and sedimentation rate: homogeneous (S1), color banded (S3, S5, S7 and S9) or composite (S4, S6 and S8). These black deposits may contain near the coast, macroscopic plant debris of continental origin. Sapropel layers contain planktic foraminifera, but are almost devoid of benthic foraminifera (Casford et al., 2003). The absence of benthos and excellent preservation of organic matter are strong evidences for anoxia bottom water. Sapropels formed both in interglacial periods and glacial periods, suggesting no direct relationship to glacial and interglacial cycle although most sapropels were formed during interglacial periods except for sapropel S6 during marine isotope stage (MIS) 6. Quantitative estimation for each sapropel duration is difficult because organic matter on sediment surface is oxidized when anoxia conditions cease. In addition, bacterial activity may degrade in situ organic matter in sapropel deposited 200 kyrs ago (Coolen et al., 2002). Two major hypotheses to form sapropels: (1) biological process by enhanced biological productivity linked to riverine nutrient supply (Calvert et al., 1992); and (2) physical process by water stagnation and oxygen deficiency in bottom water leading to organic matter preservation. Enhanced freshwater discharge leads to a reduction of surface water density, which hampers intermediate and deep water ventilation (Ducassou, 2006). Sapropels in EMS have been correlated across the basins and their timings are well dated based on radiocarbon dating for sapropel S1 (6.1-10.2 ka) (De Lange et al., 2008) and astronomical tuning dating for the rest of the sapropels (Cita et al., 1977; Emeis and Sakamoto, 1998). However, existence of sapropel 2 is not certain (Cita et al., 1977).

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Chapter 2

Hydrological and vegetation changes in Northeast Africa over the past 23,000 years based on compound-specific δD and $\delta^{13}C$ variations of n-alkanes in sediments from the eastern Mediterranean Sea

Abstract

Hydroclimate variation and vegetation changes of the Nile River watershed area in northeast Africa since the Last Glacial Maximum (LGM) were reconstructed based on *n*-alkane molecular distributions and their carbon isotope ratios ($\delta^{13}C_{n\text{-alkanes}}$) and their hydrogen isotope ratios ($\delta D_{n\text{-alkanes}}$) in sediments from Ocean Drilling Program (ODP) Site 967 in the Eastern Mediterranean Sea (EMS). $\delta D_{n\text{-alkanes}}$, a proxy for precipitation, ranging from -199‰ to -127‰, co-varied with insolation change response to orbital forcing. Depleted $\delta D_{n\text{-alkanes}}$ were found from deglaciation to middle Holocene, suggesting increased precipitation during the African Humid Period (AHP) from 15 ka to 5 ka caused by northward migration of the Intertropical Convergence Zone (ITCZ). On the contrary, lower precipitation was inferred by enriched $\delta D_{n\text{-alkanes}}$ during LGM and late Holocene. $\delta^{13}C_{n\text{-alkanes}}$ at Site 967 did not show a trend in harmony with $\delta D_{n\text{-alkanes}}$ but exhibiting millennial-scale variations ranging from -25.9‰ to -33.2‰. These $\delta^{13}C_{n\text{-alkanes}}$ values are consistently C4 grass dominated environment in the watershed area of River Nile since LGM even during AHP.

2.1. Introduction

Present hyperarid Sahara Desert is the largest dust source of the Earth surface (Ginoux et al., 2012) transported over the Atlantic Ocean by easterly trade wind and over the Mediterranean Sea by cyclones mainly during Spring and Summer (e.g., Moulin et al., 1997, and references therein). The Sahara Desert is subjected to significant paleohydrological variations between 15-5 ka BP (Barker et al., 2004; Junginger and Trauth, 2013). This period is known as the African Humid Period (AHP) characterized by almost complete vegetation cover with annual grasses and shrubs in the present Sahara Desert so-called Green Sahara (e.g., COHMAP MEMBERS, 1988; deMenocal et al., 2000; DeMenocal and Tierney, 2012). AHP peaked between 9 ka and 6 ka when sapropel S1 deposited in the Mediterranean Sea (Ritchie et al., 1985). Summer insolation paced by precessional cycles plays a principal role in greening and desertification of Saharan Desert through precipitation in North Africa (deMenocal et al., 2000).

Stable hydrogen isotope (δD) of sedimentary *n*-alkanes biomarkers are employed to reconstruct past hydroclimate variations (Eglinton and Eglinton, 2008; Sachse et al., 2012) which, the δD of lipids track the δD of environmental waters (Sauer et al., 2001) and hence, it reflects the local precipitation

(Sachse et al., 2012 and references therein). Accordingly, the δD of lipids are potentially quantitative proxy for δD precipitation. $\delta D_{n\text{-alkanes}}$ values are significantly correlated with the δD signature of source water (leaf and xylem water) originated from precipitation (Sachse et al., 2012 and references therein). In the tropics, the “amount effect” is main controlling factor for δD in rain water and n-alkanes of terrestrial plants, δD values decreased with precipitation intensities (Dansgaard, 1964; Feakins and Sessions, 2010; Kahmen et al., 2013).

Compound-specific carbon isotope of n-alkanes reflect carbon fixation pathway during photosynthesis (Huang et al., 2001; Street-Perrott et al., 1997). During photosynthesis, plants discriminate against the carbon-13 isotope (^{13}C) and preferentially fix the carbon-12 isotope (^{12}C) of carbon dioxide (CO_2) to an extent that is correlated with the stomatal conductance of plant cells (Delucia et al., 1988). This discrimination against ^{13}C is more pronounced in C3 plants (Farquhar et al., 1989). Basically, 90% of plant species, including all trees, most shrubs, and cool-season grasses and sedges, use a photosynthetic pathway to produce a three-carbon molecule, 3-phosphoglyceric acid, in a process called carboxylation that is catalyzed by the enzyme ribulose 1,5-bisphosphate carboxylase-oxygenase (Rubisco). In the carboxylation reaction, CO_2 is fixed by combining it with ribulose-1,5-bisphosphate (RuBP) (Jensen and Bhar, 1977; Sage, 2001, 2004). $\delta^{13}\text{C}$ records in C3 plants range from -30‰ to -42‰ (Rommerskirchen et al., 2006; Vogts et al., 2009). C4 plants (including hot-region grasses) use the Hatch-Slack cycle, in which CO_2 is initially fixed in a compound that contains four carbon molecules (Hatch and Slack, 1966). In C4 plants photosynthetic processes occur in two types of cells: mesophyll cells and bundle-sheath cells (Brown, 1975; Kadereit et al., 2003; Muhaidat et al., 2007). In bundle-sheath cells, CO_2 is concentrated before being fixed by Rubisco. Consequently, the organic carbon of C4 plants is less depleted in ^{13}C , and their $\delta^{13}\text{C}$ values range between -18‰ and -26‰ (Rommerskirchen et al., 2006; Vogts et al., 2009). The contribution of CAM plants to the n-alkanes in sediments is negligible because of the low contribution of CAM plants to biomass production (Lüttge, 2004).

Present distribution of vegetation in North Africa (Figure 2.1) is determined by climate, mainly precipitation and temperature (White, 1983). Evergreen rainforest occurs in the most humid regions of West Africa around the equator, where woody plants account for most of the vegetation structure and phytomass (White, 1983), with $>80\%$ of the cover being woody (Good and Caylor, 2011). Woodlands characterized by open stands of trees (deciduous and semi-deciduous forests) are confined to tropical and subtropical regions on the periphery of the evergreen rainforest and extend from the Atlantic Ocean coastline toward the African Great Lakes. The dominance of woody cover (40–80%, Good and Caylor, 2011), with heliophilous grasses as a secondary constituent, distinguish the woodlands from other types of vegetation (White, 1983). A grassland ecosystem with $<10\%$ woody cover (Good and Caylor,

2011) occurs on the periphery of the Sahara Desert (White, 1983), and wooded-grasslands are confined to the woodland and grassland ecosystems with 10–40% woody cover (Good and Caylor, 2011). In the Sahara Desert ecosystem, which occupies most of North Africa, plants suffer from water scarcity owing to very small precipitation and high evaporation rates (White, 1983).

Several studies have reported origins of sedimentary n-alkanes in terms of plant species and types (e.g., Cranwell, 1973; Ficken et al., 2000; Michener and Lajtha, 2007; Nott et al., 2000; Zech et al., 2009). Submerged aquatic plants primarily produce n-alkanes shorter than n-C₂₃; n-C₂₃ to n-C₂₅ are indicative of floating aquatic plants (Ficken et al., 2000; Nott et al., 2000; Zech et al., 2009); n-C₂₇ to n-C₂₉ are generally derived from trees and shrubs; and n-C₃₁ to n-C₃₃ are major constituents of grasses (Cranwell, 1973; Michener and Lajtha, 2007; Zech et al., 2009). Previous studies have reconstructed paleovegetation and paleohydrological variations of Africa by using $\delta^{13}\text{C}_{\text{n-alkanes}}$ and $\delta\text{D}_{\text{n-alkanes}}$ obtained from the Atlantic Ocean (Dupont et al., 2013; Kuechler et al., 2013; Maslin et al., 2012; Niedermeyer et al., 2010; Vogts et al., 2012; Zhao et al., 2003), and the Gulf of Aden (Feakins et al., 2007). However, hydroclimate studies based on $\delta^{13}\text{C}_{\text{n-alkanes}}$ and $\delta\text{D}_{\text{n-alkanes}}$ in EMS, the catchment areas of Nile River, are still limited. Menzel et al. (2004) reconstructed vegetation cover in North Africa during Sapropel S5. At ODP Site 967, Rose et al. (2016) reconstructed changes in northeast African vegetation between 3.05 and 1.75 Ma during Plio-Pleistocene sapropel cycles. Castañeda et al. (2016) reported significant hydroclimate variability in EMS for past 28 kyrs multi-proxy records including $\delta^{13}\text{C}_{\text{n-alkanes}}$ and $\delta\text{D}_{\text{n-alkanes}}$. Because the sediment sample core GeoB7702-3 was obtained from the continental slope off Israel, Mediterranean vegetation and precipitation also might have influence on the sedimentary $\delta^{13}\text{C}_{\text{n-alkanes}}$ and $\delta\text{D}_{\text{n-alkanes}}$. Therefore, it is worth investigating hydroclimate change in Nile Basin in offshore region. Site ODP 967 is located on a seamount south of Cyprus where less influenced by direct terrigenous input from the Mediterranean Basin. Paleoceanographic studies at Site ODP 967 have been performed to reconstruct sea-surface temperature (Emeis et al., 1998; Kroon et al., 1998), aeolian dust input (Larrasoana et al., 2003) and redox condition (Azrieli-Tal et al., 2014) since LGM. However, hydroclimate change has not yet been revealed. Here we present n-alkane molecular distributions and their compound-specific isotope records in sediments from Site ODP 967 to reconstruct hydroclimate and vegetation variabilities in North Africa, watershed area of River Nile.

2.2. Material and Methods

2.2.1. Samples

Marine sediment cores used in our study were obtained at Site 967 from EMS during ODP Leg 160 (Emeis et al., 1996). Site 967 is located on the northern slope of the Eratosthenes Seamount south of Cyprus (34° 04' N, 32° 43' E, water depth: 2555 m, Fig. 2.2). Sediment samples taken from the top

2 m of Hole 967B (Core 1H-1 and 1H-2) were used to measure n-alkane concentrations and its carbon and hydrogen isotopes. The sediments from Core 1H-1 and 1H-2 were hemipelagic bioturbated nannofossil oozes and nannofossil clays with a 21-cm-thick sapropel S1 layer (Emeis et al., 1996). The measured intervals were converted to a revised meters composite depth scale (Sakamoto et al., 1998). **2.2.2. Age Model**

Age model for the uppermost part of sediment cores at Site 967 was established by Larrasoana et al. (2003) based on linear interpolation of Ba/Al ratios data versus sapropel layer S1, together with planktic foraminiferal oxygen isotope stratigraphy (Emeis et al., 2000; Kroon et al., 1998). In addition, top and bottom ages of sapropel layer S1 were well constrained by radiocarbon dating of planktic foraminifera from a number of sediment cores in EMS (10.8 ± 0.4 to 6.1 ± 0.5 cal. kyr BP; De Lange et al., 2008). The top 2 m of Hole 967B are corresponding to the past 30 kyrs.

2.2.3. n-Alkane Analyses

Ninety-eight consecutive samples (10 cc) were taken from top 2 m cores of Hole 967B at depth intervals of 2.0 cm (Table 2.1). The samples were freeze-dried with an EYELA FDU-1200 freeze dryer combined with a ULVAC GLD-051 oil-sealed rotary vacuum pump. The fore-line trap of the ULVAC OFI-200 suction filter was equipped to prevent the counter flow of diffusion oil into the freeze dryer. The freeze-dried samples were weighed and homogenized with a porcelain mortar and ultrasonically extracted with 15 ml of dichloromethane/methanol (2/1 by volume) three times for 20 min each time. The combined extracts were rotary evaporated and dried with a gentle stream of N₂. The total extract was re-dissolved in a small amount of hexane and separated by silica gel column chromatography. Glass columns (50 mm × 7 mm i.d.) were filled with silica gel that had been previously heated at 450°C for 3 hours followed by deactivation with 5 wt% H₂O. The extract was eluted with n-hexane to separate alkane fraction from polar fraction. n-Alkanes were identified and quantified by gas chromatography/mass spectrometry (GC/MS) using a Hewlett Packard model HP6890 GC/MSD5972A system. A DB-5MS capillary column (30 m × 0.25 mm i.d. film thickness 0.25 μm) was held at 50°C for 2 minutes, programmed to 120°C at 30°C/minutes, then to 310°C at 5°C/minutes, and finally held at 310°C for 17.67 minutes. Helium was used as the carrier gas.

Stable carbon isotope ($\delta^{13}\text{C}$) measurements of n-alkanes were conducted following to Seki et al. (2010) on 48 samples taken from the top 2 m of Hole 967B (Table 2.3). The $\delta^{13}\text{C}$ analyses were carried out by gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) using a HP 6890 GC equipped with a DB-5 fused silica capillary column (30 m × 0.32 mm i.d., film thickness 0.25 μm) and an on-column injector, a combustion interface (Finnigan GC combustion III), and a

Finnigan MAT Delta Plus mass spectrometer. The combustion was performed in a microvolume furnace with CuO and Pt at 840°C (Hayes et al., 1990). The GC-IRMS equipment was calibrated daily by a mixture of C₁₅ to C₃₆ n-alkanes standards with known isotopic values (Vienna Pee Dee Belemnite, VPDB).

Compound-specific hydrogen isotope (δD) of n-alkanes were determined following to Seki et al. (2010) using a GC/thermal conversion/ IRMS system consisting of a HP 6890 GC connected to a Finnigan MAT Delta Plus XL mass spectrometer. Capillary GC column conditions are (30 m \times 0.32 mm i.d., film thickness 0.25 μ m). Pyrolysis (thermal conversion) of n-alkanes to H₂ was achieved at 1450°C in a microvolume ceramic tube. C₂₁ n-fatty acid methyl ester, as an internal isotopic standard with isotopic values $\delta^{13}C = -26.2\%$ and $\delta D = -227\%$ for carbon and hydrogen compound specific isotopes were injected between measurements to check instrumental condition. A laboratory standard containing C₁₆–C₃₀ n-alkanes was analyzed daily with analytical error 5%. δD values are given in per mil (‰) notation relative to Standard Mean Ocean Water (SMOW).

A binary mixing equation was used to calculate relative contribution of C3 and C4 plants from $\delta^{13}C_{n\text{-alkanes}}$ in sediments from Hole 967B:

$$\%C4 = (Xs - Xc3) / (Xc4 - Xc3) \times 100$$

Where Xs is $\delta^{13}C_{n\text{-alkanes}}$ of sediment samples in Hole 967B. Xc3 and Xc4 are end member data for $\delta^{13}C_{n\text{-alkanes}}$ of C3 and C4 plants, respectively: Xc3 for $\delta^{13}C_{n\text{-C31}}$ is $-35.7 \pm 2.8\%$ and Xc4 for $\delta^{13}C_{n\text{-C31}}$ is $-22.1 \pm 2.1\%$ (Rommerskirchen et al., 2006; Vogts et al., 2009).

2.3. Results

2.3.1. Molecular Distribution of n-Alkanes

In Site 967 sediments, high-molecular-weight n-alkanes were characterized by a predominance of C₂₇, C₂₉, and C₃₁ homologues, and weight of the n-alkanes ranged from 2.5 to 728.7 ng/g dry-sediment (Fig. 2.3; Table 2.2). In general, n-alkane concentrations at Site 967 were relatively low (<10 ng/g) at samples below 160 cm core depth and high (>10 ng/g) at samples above 160 cm core depth (Fig. 3). Significantly high n-alkane concentrations (>100 ng/g) were observed in sapropel S1 layer.

2.3.2. Compound-specific carbon and hydrogen isotope compositions of n-alkanes

$\delta^{13}C$ values of C₂₃–C₃₁ n-alkanes in the top 2 m of Hole 967B were shown in Figure 2.4. For the past 23 kyrs, $\delta^{13}C$ values of n-C₂₃, n-C₂₅, n-C₂₇, n-C₂₉ and n-C₃₁ showed millennial-scale fluctuation within a range between -31.2% and -26.1% , -31.2% and -27% , -32.9% and -29.6% , -33.2% and -28.5% and -32.1% and -25.9% , respectively. Among them, $\delta^{13}C_{n\text{-C27}}$ values generally more

depleted than the other n-alkanes homologues (Fig. 2.4). No clear long-term trend in $\delta^{13}\text{C}_{\text{n-alkanes}}$ was observed from LGM to Holocene. In addition, $\delta^{13}\text{C}_{\text{n-alkanes}}$ did not show notable change during sapropel S1 layer where significantly high n-alkane concentrations were found.

δD values of $\text{C}_{27}\text{-C}_{31}$ n-alkanes in the top 2 m of Hole 967B were shown in Figure 2.4. The $\delta\text{D}_{\text{n-alkanes}}$ showed similar pattern co-varied with summer insolation change at 20°N (Fig. 2.4). $\delta\text{D}_{\text{n-alkanes}}$ ranged from -199‰ to -127‰ for the past 23 kyrs with negative shift during AHP including sapropel S1 layer.

The $\delta^{13}\text{C}_{\text{n-C}_{31}}$ data showed a large range in values (-32.1 to -25.9‰). These signatures are mainly controlled by the relative contribution of C3 and C4 plant waxes. Time-series changes in relative contribution of C4 plants are shown in Fig. 2.5. The relative contributions of %C4 plant ranged from 26 to 72%. The expansion of C4 plants showed millennial scale variations and no harmony with precessional orbital forcing.

2.4. Discussion

2.4.1. n-Alkane Transport and Source

The Sahara Desert is a present dust source of EMS. Sedimentary hematite content derived from magnetic properties and Ti/Al ratios in EMS are proxies for aeolian dust supply from the Sahara Desert (Azrieli-Tal et al., 2014; Larrasoana et al., 2003). Larrasoana et al., (2003) have suggested that titanium is transported as aeolian dust to marine sediment, whereas aluminum is derived from both aeolian (kaolinite) and fluvial sources (smectite). Hence, the Ti/Al ratio in sediments at Site 967 is interpreted as an indicator of relative contribution of aeolian (Saharan dust) and fluvial (Nile discharge) sources. Both temporal changes in Ti/Al ratios and hematite content at Site 967 co-varied with Northern Hemisphere insolation at 20°N , suggesting distinct dust minima coincided with Northern Hemisphere insolation maxima during AHP (Larrasoana et al., 2003). African monsoon strength driven by summer insolation change are closely linked to the changes in humidity in North Africa (COHMAP MEMBERS, 1988; deMenocal et al., 2000). Summer insolation change is modulated by precession cycle (Fontugne and Calvert, 1992; Rohling, 1994; Rossignol-Strick, 1985). During pluvial/wet periods, summer African monsoon penetrates more northward beyond the central Saharan watershed. This leads to a greening of the Sahara and reduces input of Saharan aeolian dust into EMS. On the contrary during arid/dry periods, summer African monsoon shifts southward. This converts the Saharan region to a barren ecosystem and increases input of aeolian dust into EMS (Brovkin et al., 1998; Claussen et al., 1998).

Mechanisms that transport terrestrial biomarkers (e.g., $\text{C}_{23}\text{-C}_{33}$ n-alkanes) into marine sediments are primarily fluvial inputs in coastal regions (Hinrichs and Rullkotter, 1997) and aeolian

fallout in the open ocean (Pagani et al., 2000). The Nile deep-sea fan system plays a major role in sediment accumulation in EMS (Reading and Richards, 1974). Contribution of Nile particulate matter to the surface sediment south of Cyprus in EMS is inferred to be 40–50% based on $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios (Krom et al., 1999). At Site 967, the maxima in n-alkanes concentrations coupled with aeolian dust minima during sapropel S1 deposition in AHP (Larrasoana et al., 2003). Subsequently, at Site 967, mechanism of n-alkane transport is assumed to be fluvial during pluvial period whereas aeolian during dry period. Negative shift of $\delta\text{D}_{\text{n-alkanes}}$ suggests enhanced freshwater discharge by high rainfall in North Africa and Mediterranean region during AHP (Fig 2.4). The Mediterranean region also experienced increasing precipitation during sapropel deposition (Bar-Matthews et al., 2003, 2000, Kallel et al., 2000, 1997; Magny et al., 2002; Rossignol-Strick, 1999). Wu et al. (2016) measured Sr-Nd isotopes of detritus in sediment core CP10BC obtained off western Libya in EMS and concluded that origin of the detritus in sapropel S1 during AHP was mainly from fossil river/wadi systems along the Libyan-Tunisian margin. In contrast, during LGM and late Holocene, minima in n-alkanes concentrations at Site 967 coincided with aeolian dust maxima. This suggests an enhanced contribution by aeolian transport of n-alkanes and weaken riverine input during LGM and late Holocene. This scenario is consistent with low precipitation based on positive $\delta\text{D}_{\text{n-alkanes}}$ and abundant hematite content (Larrasoana et al., 2003) at Site 967 during LGM and late Holocene.

Origins of sedimentary n-alkanes are related to plant species and plant habitats: C_{23} , submerged aquatic plants; C_{23} to C_{25} , floating aquatic plants; C_{27} to C_{29} , trees and shrubs; and C_{31} to C_{33} , grasses (Cranwell, 1973; Ficken et al., 2000; Michener and Lajtha, 2007; Nott et al., 2000; Zech et al., 2009). Sinninghe Damsté et al. (2011) have reported that rainforest (mostly C_3) n-alkanes are dominated by C_{29} . C_3 savanna trees and shrubs and annual C_4 grasses have a maximum at C_{31} , whereas annual C_4 grasses also tend to produce higher amounts of C_{33} . In Site 967 sediments, carbon chain lengths of n-alkanes ranged from C_{23} to C_{33} (Fig. 2.3). Among the n-alkane homologues, C_{27} , C_{29} and C_{31} were relatively abundant at Site 967. Lignin analyses at Site 967 revealed that plant wax vegetation source was grass-dominated vegetation in both wet (sapropel) and dry (nannofossil ooze) periods and mainly originated from North Africa (Rose et al., 2016).

2.4.2. Relationship between Vegetation and Precipitation

Change in $\delta^{13}\text{C}_{\text{n-alkanes}}$ at Site 967 showed a different trend from the $\delta\text{D}_{\text{n-alkanes}}$. The $\delta^{13}\text{C}_{\text{n-alkanes}}$ fluctuated at millennial scale whereas $\delta\text{D}_{\text{n-alkanes}}$ exhibited clear long-term trend at orbital scale. Relative contribution of C_4 plants based on the $\delta^{13}\text{C}_{\text{n-alkanes}}$ at Site 967 were 26% - 72%, suggesting considerable C_4 plants cover throughout the past 23 kyrs including AHP. $\delta\text{D}_{\text{n-alkanes}}$ at Site 967 co-varied with summer insolation change at 20°N , exhibiting negative shift during AHP. Such trend is

common in North and Central Africa: EMS off Israel (Castañeda et al., 2016); Congo Basin (Scheffuß et al., 2005); Gulf of Aden (Tierney and de Menocal, 2013); Lake Tanganyika (Tierney et al., 2008); and Lake Victoria (Berke et al., 2012). All of these $\delta D_{n\text{-alkanes}}$ data suggest high precipitation and strong moisture advection in the regions of watershed area of Nile River during AHP. Vegetation influences on available amount of precipitation by modulating surface evaporation so called vegetation-precipitation feedback (e.g., Ruddiman, 2001). For instance, surface evaporation increases when vegetation replaces grasses with trees (Liu et al., 2010). During AHP, less negative $\delta^{13}C_{n\text{-alkanes}}$ and highly depleted $\delta D_{n\text{-alkanes}}$ at Site 967 suggest an expansion of vegetation cover in watershed areas of Nile River with predominant C4 annual grasses. Savanna-like ecosystem with annual grasses and shrubs is a feature of “Green Sahara” during AHP (Hoelzmann et al., 1998; van Helmond et al., 2015). This implies weak vegetation-precipitation feedback in watershed areas of Nile River even during AHP.

2.4.3. Paleovegetation and Hydroclimate Changes during the Last 23 kyr

2.4.3.1. LGM (23 - 19 ka)

Enriched $\delta D_{n\text{-alkanes}}$ at Site 967 and many places in and around North Africa (Castañeda et al., 2016) indicated aridity and low precipitation in the watershed areas of Nile River during LGM. Under arid environment with weak precipitation, atmospheric moisture source is depending on local evaporation (Trenberth, 1999). Ancient sand dune distributions suggest that the Sahara Desert extended hundreds of kilometers further south than at present, the result being an equatorward contraction of vegetation zones (Hooghiemstra et al., 1992) because of southward migration of ITCZ by weakened summer monsoon (Brovkin et al., 1998). Increased aeolian dust transport from the Sahara Desert into the eastern Mediterranean Sea is also suggested by the abundant hematite content at Site 967 (Larrasoña et al., 2003). A major retreat of rainforest during the LGM occurred; during that time, the rainforest was replaced by savanna and grassland vegetation (Runge, 1996). Annual precipitation in the eastern Congo Basin during the LGM is estimated to be 1000 mm, significantly lower than the current annual precipitation of 2000–2400 mm (Runge, 1996). Lakes Victoria and Albert, sources of the Nile River, recorded low lake levels due to extreme aridification during the LGM (Talbot and Laerdal, 2000; Williams et al., 2006). Pollen records at Core 9509 from EMS imply low arboreal pollen and abundance of C4 grasses, mainly Chenopodiaceae, Amaranthaceae (*Artemisia monosperma*), and *Ephedra distachya*, which represent steppe, saline desert, littoral sand belt, and marshy ecosystems (Langgut et al., 2011). These results suggest that the desert and semi-arid savanna ecosystems expanded during the LGM (Rommerskirchen et al., 2006).

On the contrary, glacial $\delta^{13}\text{C}_{\text{n-alkanes}}$ at Site 967 showed relatively negative values compared to the other period and estimated C4 plants contribution were ranging from 44% to 53% (Fig. 2.5). These data suggest a significant contribution of C3 plants for n-alkanes in sediments at Site 967 during LGM. A possible explanation is that considerable portion of n-alkanes were transported from the upstream region of the Nile River.

Last glacial termination is characterized by millennial-scale abrupt climate events such as Heinrich event I, Bølling-Allerød warming, and Younger Dryas event. Castañeda et al. (2016) summarized $\delta\text{D}_{\text{n-alkanes}}$ records in and around North Africa since LGM and indicated aridity during Heinrich Stadial I (HS1) and Younger Dryas (YD) based on pronounced positive shifts of $\delta\text{D}_{\text{n-alkanes}}$. Our Site 967 data also indicates the pronounced two $\delta\text{D}_{\text{n-alkanes}}$ peaks (Fig. 2.4 and 2.5), likely to be corresponding to HS1 and YD regardless of lack of age control point.

2.4.3.2. AHP (15 - 5 ka)

As the monsoon intensified during the early Holocene insolation maximum, precipitation in North Africa increased with northward migration of ITCZ after HS1. This period is known as AHP (deMenocal et al., 2000) and was characterized by almost complete vegetation cover with annual grasses and shrubs in the present Saharan Desert (e.g., COHMAP Members, 1988; deMenocal et al., 2000; deMenocal and Tierney, 2012). The transition from dry to humid conditions archived in lake level in Lake Tana (Lamb et al., 2007) and Lake Victoria (Talbot and Laerdal, 2000). Drastic negative shift of $\delta\text{D}_{\text{n-alkanes}}$ ($>40\text{‰}$) were observed at Site 967 after YD, marking AHP peak when Sahara Desert was greening under humid condition (i.e., increasing of rainfall amount and migration of ITCZ more northward). Such large negative shift of $\delta\text{D}_{\text{n-alkanes}}$ denotes strong precipitation and moisture advection from far distance.

AHP peak from 11 ka to 7 ka identified by the most depleted $\delta\text{D}_{\text{n-alkanes}}$ is coincident with sapropel S1 layer formation. Sapropels (organic carbon-rich sediments) deposited periodically within Plio-Pleistocene sediments of the Mediterranean Sea are paced by the precessional cycle of Earth (e.g., Cramp and O'Sullivan, 1999). Freshwater discharge from North Africa into the Mediterranean Sea, fueled by an intensified monsoon, plays a crucial role in sapropel formation (Rohling et al., 2015). Sapropel S1 is the most recent sapropel layer deposited during the early-to-middle Holocene. The age of the top and bottom of the sapropel S1 layer is well determined (10.8 ± 0.4 to 6.1 ± 0.5 ka; De Lange et al., 2008). At Site 967, n-alkane concentrations were notably high during the sapropel S1 interval, and there were two concentration peaks (Fig. 2.3). Onset of the sapropel S1 layer formation started at 135 cm at Site 967, followed by the first n-alkane concentration peak at 130 cm. Significantly high

sedimentary concentrations of n-alkanes suggest optimal preservation of biomarkers (Menzel et al., 2003).

During AHP peak, $\delta^{13}\text{C}_{\text{n-alkanes}}$ at Site 967 showed relatively positive values and estimated C4 plants contribution were ranging from 55 to 72% (Fig. 2.5), suggesting flourishing of C4 plants. Pollen assemblage at Core 9509 indicated that total trees increased since 15 ka, reaching a maximum of 20% from several percent (Langgut et al., 2011). Regardless of the increase in tree pollens, majority of pollen assemblages at Core 9509 was grasses such as Cyperaceae. Pollen records at core PS009PC also suggest abundant annual C4 grasses during AHP (van Helmond et al., 2015). The predominant C4 plants during AHP peak indicates an expansion of savanna grassland ecosystems in North Africa and suppresses a mobilization of Saharan dust. Low Ti/Al ratio and hematite contents (Larrasoña et al., 2003) as well as elevated Ba/Al ratio (Azrieli-Tal et al., 2014) at Site 967 support a deflation of aeolian dust during AHP peak due to migration of ITCZ more northward.

During the termination of AHP since 7 ka, $\delta\text{D}_{\text{n-alkanes}}$ signature gradually enriched, suggesting onset of aridification in North Africa as a result of southward migration of ITCZ and decreasing of rainfall amount. Pollen records (van Helmond et al., 2015) and increases in Ti/Al ratios and hematite contents (Larrasoña et al., 2003) also indicate less wet environments. Compared to AHP peak, contribution of C4 plants decreased, suggesting shrink of green Sahara with flourished C4 grasses. This leads to a formation of today's arid Sahara Desert (Gasse, 2000).

2.4.3.3. Middle to Late Holocene (Last 5 kyrs)

Gradually enriched $\delta\text{D}_{\text{n-alkanes}}$ at Site 967 suggest progressive aridification in catchment areas of Nile River since 5 ka. Decline of lake level and long-term drying were reported in Lake Tana (Marshall et al., 2009), African Sahel (Said, 1993), and East Africa rift valley lakes (Grasse and Van Campo, 1994). Majority of tropical and subtropical African regions were shifted to a drier condition owing to the change of precipitation regimes and increase of evaporation (Marchant et al., 2004). In Kenya, pollen assemblages in sediments from Lake Bogoria, Mount Kenya, and Mount Elgon since ~5 ka have been more drought-adapted species than high-altitude forest species (Hamilton, 1982; Street-Perrott and Robert, 1983; Vincens, 1986). Slightly increased *Artemisia* (Langgut et al., 2011) and increased Ti/Al ratios and hematite contents (Larrasoña et al., 2003; Konijnendijk et al., 2014) are consistent with dryer conditions in North Africa by comparing with AHP.

$\delta^{13}\text{C}_{\text{n-alkanes}}$ at Site 967 fluctuated at millennial timescale during the last 5 kyrs. The $\delta^{13}\text{C}_{\text{n-alkanes}}$ record was inconsistent with progressive aridification suggested by enriched $\delta\text{D}_{\text{n-alkanes}}$. Estimated C4 plants contribution was ranging from 42 to 70% (Fig. 2.5), suggesting that an origin of n-alkanes in sediments at Site 967 were approximately equally contributed by C3 and C4 plants. With prevailing

desertification in North Africa, transition of vegetation from green Sahara with C4 annual grasses (i.e. savannah-like ecosystem) to present barren Sahara Desert has been occurred. Since Middle-Holocene, ITCZ shifted southward with millennial and sub-millennial-scale oscillations (Haug et al., 2001; Fleitmann et al., 2007). Marriner et al. (2012) demonstrated that development of the Nile's catchment has been controlled by a precipitation change in East Africa driven by a millennial-scale southern displacement of the ITCZ. Although our age model for sediment core at Site 967 is unable to constrain the detailed timings, source of the $\delta^{13}\text{C}_{\text{n-alkanes}}$ must have been influenced by the latitudinal shift of ITCZ. When desertification proceeds in North Africa, upstream region of the Nile watershed area such as the Ethiopian Highland becomes an important source of n-alkanes source. Consequently, $\delta^{13}\text{C}_{\text{n-alkanes}}$ change at Site 967 was not in harmony with the $\delta\text{D}_{\text{n-alkanes}}$.

2.5. Conclusions

Hydroclimatic and vegetation changes of watershed areas of the Nile River in northeast Africa during the past 23 kyr BP were reconstructed based on n-alkane molecular distributions and their hydrogen and carbon isotopes in ODP 967 sediments from the EMS. $\delta\text{D}_{\text{n-alkanes}}$, a proxy for precipitation co-varied with precessional orbital forcing, while the $\delta^{13}\text{C}_{\text{n-alkanes}}$ showed millennial-scale variation and no harmony with orbital forcing. During LGM, the watershed areas of Nile River were arid but considerable portion of n-alkanes in sediments at Site ODP 967 was derived from C3 plants. This suggests that the major source of the n-alkanes was in the up-stream region of the Nile River. During AHP peak, $\delta^{13}\text{C}_{\text{n-alkanes}}$ at Site 967 showed relatively positive values suggesting greening of Sahara Desert prevailed by C4 plants as a result of increased rainfall by northward migration of ITCZ. Since AHP termination at ~ 7 ka, gradually enriched $\delta\text{D}_{\text{n-alkanes}}$ signature indicated progressive aridification in North Africa. The $\delta^{13}\text{C}_{\text{n-alkanes}}$ record during the last 5 kyrs fluctuated at millennial and sub-millennial timescale, inconsistent with enriched $\delta\text{D}_{\text{n-alkanes}}$. When desertification proceeds in North Africa, upstream region of the Nile watershed area such as the Ethiopian Highland becomes an important source of n-alkanes source. Consequently, $\delta^{13}\text{C}_{\text{n-alkanes}}$ change at Site 967 was not in harmony with the $\delta\text{D}_{\text{n-alkanes}}$.

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Table 2.1. Core ID, onboard core composite depth (mbsf, Shipboard Science Party, 1996), revised meter composite depth (rmcd, Sakamoto et al., 1998), age model (cal. kyr BP), Ba/Al ratio (Azrieli-Tal et al., 2014) and Ti/Al ratio (Azrieli-Tal et al., 2014) at ODP 967.

Core	Type	Section	W/A	Depth	Onboard core composite depth (mbsf)		Revised meter composite depth (rmcd)	Age (cal kyr BP)	Ba/Al*10 ⁴	Ti/Al
					Top	Bottom				
1	H	1	A	0-2	0	2	3	0.2		
1	H	1	A	2-4	2	4	5	0.3		
1	H	1	A	4-6	4	6	7	0.4		
1	H	1	A	6-8	6	8	9	0.5		
1	H	1	A	8-10	8	10	11	0.7		
1	H	1	A	10-12	10	12	13	0.8		
1	H	1	A	12-14	12	14	15	0.9		
1	H	1	A	14-16	14	16	17	1		
1	H	1	A	16-18	16	18	19	1.2		
1	H	1	A	18-20	18	20	21	1.3		
1	H	1	A	20-22	20	22	23	1.4		
1	H	1	A	22-24	22	24	25	1.5		
1	H	1	A	24-26	24	26	27	1.6		
1	H	1	A	26-28	26	28	29	1.8		
1	H	1	A	28-30	28	30	31	1.9		
1	H	1	A	30-32	30	32	33	2		
1	H	1	A	32-34	32	34	35	2.1		
1	H	1	A	34-36	34	36	37	2.3		
1	H	1	A	36-38	36	38	39	2.4		
1	H	1	A	38-40	38	40	41	2.5		
1	H	1	A	40-42	40	42	43	2.6		
1	H	1	A	42-44	42	44	45	2.7		
1	H	1	A	44-46	44	46	47	2.9		
1	H	1	A	46-48	46	48	49	3		
1	H	1	A	48-50	48	50	51	3.1		
1	H	1	A	50-52	50	52	53	3.2		
1	H	1	A	52-54	52	54	55	3.4		
1	H	1	A	54-56	54	56	57	3.5		
1	H	1	A	56-58	56	58	59	3.6		
1	H	1	A	58-60	58	60	61	3.7		
1	H	1	A	60-62	60	62	63	3.8		
1	H	1	A	62-64	62	64	65	4		
1	H	1	A	64-66	64	66	67	4.1		
1	H	1	A	66-68	66	68	69	4.2		
1	H	1	A	68-70	68	70	71	4.3		
1	H	1	A	70-72	70	72	73	4.5		
1	H	1	A	72-74	72	74	75	4.6		
1	H	1	A	74-76	74	76	77	4.7		
1	H	1	A	76-78	76	78	79	4.8		
1	H	1	A	78-80	78	80	81	4.9		
1	H	1	A	80-82	80	82	83	5.1		
1	H	1	A	82-84	82	84	85	5.2	20	0.085
1	H	1	A	84-86	84	86	87	5.3		
1	H	1	A	86-88	86	88	89	5.4		
1	H	1	A	88-90	88	90	91	5.6		
1	H	1	A	90-92	92	94	95	5.7		
1	H	1	A	92-94	92	94	95	5.8		
1	H	1	A	94-96	94	96	97	5.9		
1	H	1	A	96-98	96	98	99	6		
1	H	1	A	98-100	98	100	101	6.2	24	0.106
1	H	1	A	100-102	100	102	103	6.5	24	0.074

Table 2.1. cont.

Core	Type	Section	W/A	Depth	Onboard core composite depth (mbsf)		Revised meter composite depth (rmcd)	Age (cal kyr BP)	Ba/Al*10 ⁴	Ti/Al
					Top	Bottom				
1	H	1	A	102-104	102	104	105	6.8	24	0.073
1	H	1	A	104-106	104	106	107	7	51	0.07
1	H	1	A	106-108	106	108	109	7.3	109	0.071
1	H	1	A	108-110	108	110	111	7.6	172	0.07
1	H	1	A	110-112	110	112	113	7.8	74	0.087
1	H	1	A	112-114	112	114	115	8.1	39	0.102
1	H	1	A	114-116	114	116	117	8.4	144	0.79
1	H	1	A	116-118	116	118	119	8.7	210	0.069
1	H	1	A	118-120	118	120	121	8.9	204	0.072
1	H	1	A	120-122	120	122	123	9.2	127	0.065
1	H	1	A	122-124	122	124	125	9.5	171	0.065
1	H	1	A	124-126	124	126	127	9.7	161	0.068
1	H	1	A	126-128	126	128	129	10	92	0.073
1	H	1	A	128-130	128	130	131	10.3	50	0.075
1	H	1	A	130-132	130	132	133	10.5		
1	H	1	A	132-134	132	134	135	10.8		
1	H	1	A	134-136	134	136	137	11		
1	H	1	A	136-138	136	138	139	11.3		
1	H	1	A	138-140	138	140	141	11.5		
1	H	1	A	140-142	140	142	143	11.8		
1	H	1	A	142-144	142	144	145	12	29	0.077
1	H	1	A	144-146	144	146	147	12.2		
1	H	1	A	146-148	146	148	149	12.5	32	0.075
1	H	1	A	148-150	148	150	151	12.7		
1	H	2	A	0-2	150	152	153	13		
1	H	2	A	2-4	152	154	155	13.2		
1	H	2	A	4-6	154	156	157	13.5		
1	H	2	A	6-8	156	158	159	13.7		
1	H	2	A	8-10	158	160	161	13.9		
1	H	2	A	10-12	160	162	163	14.2		
1	H	2	A	12-14	162	164	165	14.4		
1	H	2	A	14-16	164	166	167	14.7		
1	H	2	A	16-18	166	168	169	14.9		
1	H	2	A	18-20	168	170	171	15.1		
1	H	2	A	20-22	170	172	173	15.4		
1	H	2	A	22-24	172	174	175	15.6		
1	H	2	A	24-26	174	176	177	15.9		
1	H	2	A	26-28	176	178	179	16.4		
1	H	2	A	28-30	178	180	181	17.1		
1	H	2	A	30-32	180	182	183	17.8		
1	H	2	A	32-34	182	184	185	18.6		
1	H	2	A	34-36	184	186	187	19.3		
1	H	2	A	36-38	186	188	189	20		
1	H	2	A	38-40	188	190	191	20.7		
1	H	2	A	40-42	190	192	193	21.5		
1	H	2	A	42-44	192	194	195	22.2		
1	H	2	A	44-46	194	196	197	22.9		
1	H	2	A	46-48	196	198	199	23.7		
1	H	2	A	48-50	198	200	201	24.4		

Table 2. 2. n-Alkane concentrations (ng g⁻¹) at ODP 967. Revised meter composite depth (rmcd) is by Sakamoto et al. (1998).

Revised meter composite depth (rmcd)	C24	C26	C28	C30	C32	C23	C25	C27	C29	C31	C33
3	0	5	2.8	0	0	4.8	15.8	32.7	53.7	16.6	0
5	6.4	7.5	14	3.3	0	10.6	26.7	58.6	92.9	34.8	0
7	0	5.2	2.8	0	0	4.8	14.2	33.8	44.1	8.5	0
9	0	3.4	6	4.6	4.2	0	7.8	18.1	35.2	19	0
11	0	0.9	3.4	1.3	0	0	2.4	11.4	17.3	5.4	0
13	0	0.5	3.1	1.1	0	0	0	5	9.1	0	0
15	1.7	3.2	2.5	0	0	6.8	13.1	37	55.2	4.3	0
17	4.8	3.1	2.4	0	0	14.6	11.6	24.1	30.8	4.5	0
19	3.1	3.3	2.5	0	0	6.4	10.2	16.4	23.2	3.6	0
21	3.4	3.2	2.4	0	0	4.4	8.2	10.2	12.2	3.3	0
23	2.1	2.3	2.1	0	0	4.7	8.9	14.6	17.2	0	0
25	3.4	3.8	1.8	0	0	5.5	11.3	21.8	20.1	6.8	0
27	0.5	0.5	0	0	0	1.3	3.2	6.3	3.6	1.6	0
29	1.9	2.1	0.6	0	0	3.6	6.8	9.8	7.8	0	0
31	2.5	2.6	1.1	0	0	7.7	11.1	16.3	9.5	0	0
33	0	0.8	0.1	0	0	0	1.9	4.2	2.5	0	0
35	2	2.7	3.1	0	0	8.3	12	28.9	40.7	12.3	0
37	1.6	3.2	4.6	0.7	0	3.5	13.4	40.9	84.1	35.1	0
39	2.4	2.9	3.4	0	0	5.7	11.5	31.8	60.4	25.1	0
41	7.2	8.8	10.8	4.8	0	15.8	27.9	77.6	148.4	74.2	0
43	0	0.8	0.6	0	0	2.2	4.3	14.8	29.2	7.3	0
45	0	0.3	0.7	0	0	0	7	19.7	28.4	4.3	0
47	4	4.7	3.9	0	0	6.2	20.9	37.6	53.6	8.1	0
49	0.7	1.3	1.5	0	0	4.4	5.8	16.9	32.2	5.7	0
51	0.4	1.2	2.1	0	0	1	1.9	6.9	9.6	2.8	0
53	3.5	2.7	1.9	0	0	10.7	10.3	23.7	25.5	0	0
55	1.8	2.3	1.7	0	0	5.2	9	24.8	25.5	3.6	0
57	1	2.3	2	0	0	2.2	8.9	30.9	35.4	7.8	0
59	0	0.5	0.8	0	0	0	0	4.6	6.3	0	0
61	9.1	8.9	7.3	2.5	0	8.2	24.2	60	68.6	36.3	0
63	4.9	6.8	6.4	1.9	0	10.2	25.7	63.4	69.6	22.1	0
65	3.7	5.7	5.9	2.2	0	8.1	21.9	54	66.9	27.9	0
67	4.2	4.7	4.9	1.3	0	8.1	16.8	36.9	65.9	26.7	0
69	6.3	5.4	4.1	0	0	14.8	18.6	36.1	55.8	20.1	0
71	7.2	5.3	4.8	1	0	6.8	17.5	38.2	72.8	29.5	0
73	4.1	6.2	6.4	2	0	8.4	19.5	43.8	80.4	36.4	0
75	4	5.3	5	1.1	0	9.4	18.9	41.7	68.3	21.9	0
77	2.1	2.6	2.5	0	0	4	10.4	25.6	42.7	10.7	0
79	11.3	11.8	9.6	2.2	0	15.7	34.6	65.6	109	45.5	0
81	8.4	6.4	4.6	0	0	11.2	23.8	39.4	69	27.9	0
83	2.8	2.9	2.7	0	0	5.6	13.2	28.8	45	11.2	0
85	0.5	0.9	0.3	0	0	0	5.2	12.5	12.9	2.3	0
87	2.3	2.6	2.6	0	0	5	9.2	21.9	29.1	9.4	0
89	0	0.5	0.2	0	0	0	3.1	9.3	12.7	1.4	0
91	2.2	3.1	2.7	0	0	4	12	25.3	30.6	8.4	0
95											
95	7.4	11.7	13.5	6.4	0	13.1	36.8	85	127.7	69.4	6.7
97	5.1	9.5	13.4	6.4	0	8.9	30.5	87.5	187.5	96.3	5
99	2.4	3.3	4.2	1.1	0	4.5	14.7	39.6	87.9	32.7	0
101	11.2	42.3	24.1	11.7	0	16.1	51.4	120.5	204.8	121.2	8.9
103	9	15.3	14.7	7.5	0	10.5	41.4	90.5	160.6	93.3	3.4
105	7.7	25.7	11.2	4.7	0	8.9	31.1	70.4	125.7	71.2	0
107	6.9	8.7	6.2	1.4	0	6.3	24	51	80.4	32.1	0
109	0	26	33	16.2	2.6	24.6	69.3	156.3	277.6	195.6	15
111	0	69	95.6	65.8	15.5	67.8	173.2	377.2	642.8	515.1	83.6

Table 2. 2. cont.

Revised meter composite depth (rmcd)	C24	C26	C28	C30	C32	C23	C25	C27	C29	C31	C33
113	0	34.1	50.7	31.8	7.1	36	95.8	240.5	480.5	318.6	42.6
115	0	12.2	13.3	7.6	2.2	90.5	214.7	463.8	728.7	587.5	95.1
117	0	43.1	45.9	19	3.8	45.5	100.4	231	326.7	209.1	18.6
119	0	17.7	18.6	6.4	0	24.8	56.9	111.7	179.8	94.6	2.6
121	0	3.3	3.8	1.5	0	4.8	11.7	31.7	55.5	33.7	0
123	0	62.4	70.4	37.8	6.3	59	122.6	263.6	406.6	276.1	27.9
125	0	42.5	53.7	25	4.5	46.6	96.4	219.6	357	248.9	23.9
127	0	49.1	51.7	23.9	0	56.5	104.8	259.3	337.8	211.1	20.6
129	0	51.6	58.7	29.4	6	55.6	110.2	292.1	424	296.8	40
131	0	3.6	3.4	1	0	4.9	12.8	29	48	18.8	0
133	0	7.6	8.5	3.1	0	5.3	22.1	48.7	88.9	40.8	0
135	0	1.6	1.2	0	0	2.2	6.4	17	29.3	8	0
137	0	2	1.6	0	0	3.1	7.6	16.3	22.1	4.7	0
139	0	6.2	6.1	2.4	0	6.6	17.3	42.9	69	22.3	0
141	0	1.1	1.1	0	0	0	3.9	13.1	25.5	4.5	0
143	0	0.9	2.6	0	0	0.4	3.6	12.3	20.4	3.8	0
145	0.5	0.9	0.8	0	0	0	3.8	11.5	19.9	4.2	0
147	4.3	3.6	4.3	1.5	0	4.2	13	32.8	67.1	25.4	0
149	2.4	4.3	4.3	1.4	0	4.1	12.3	27.6	54.9	17.5	0
151	1.7	4.3	3.9	0	0	2.6	5.6	21.9	48.3	11.8	0
153	0.3	1	1.5	0	0	1.2	3.7	16	39.3	10.2	0
155	5.8	9.1	9.9	2.9	0	9.4	26.9	68.9	117.5	40.9	0
157	0.3	1.3	1.2	0	0	1.3	7.3	19	24.1	9.3	0
159	0.8	2	2.5	0	0	1	8.2	26.8	52	22.7	0
161	2.4	3.4	4	1.6	0	4.3	11.5	36.4	82.3	29.3	0
163	0	1.1	2.5	0	0	2.2	3.3	17.8	49.6	9.9	0
165	5.8	6.7	2.5	2.5	0	7.4	21.3	48.2	76.4	30	2.3
167	1.8	2.3	2.8	1.4	0	2.6	7.2	20.6	44.8	13.8	0
169	1.6	3.3	3.8	1.4	0	3.9	10.1	25.4	42	13.7	0
171	0.2	0.3	0.3	0	0	0.7	1.9	4.1	7.3	1	0
173	1.2	2	1.8	0.6	0	2.1	5.3	11.4	19.1	6.5	0.5
175											
177	0	0.2	0.2	0	0	0.2	1.5	4	10.1	2.2	0
179	3	5.1	5.1	9	0	5.3	12.9	29.4	65.3	32.45	2.4
181	0	0.6	0.4	0	0	0.6	2.6	7.7	17.4	0	0
183	2.4	3.7	2.8	0	0	4.3	8.3	15.7	30.8	12.3	0
185	2.8	3.1	3.1	0.9	0	4.8	9.7	23.8	57.5	15.6	0
187	0.4	0.4	0.4	0	0	1.6	2	6.1	18.5	3.3	0
189	0.1	0.4	0.6	0	0	0.3	3.1	8.1	21.3	4.4	0
191	0	0.5	1.4	0	0	0.4	3.7	9.8	23.6	6.6	0.5
193	0	0	2.2	0	0	0	4.4	11.5	25.8	8.7	0
195	4.3	7.9	6.8	0	0	6.6	21.9	44.1	73.5	21.5	0
197	3.4	4.6	3.4	0	0	5.1	15.8	31.6	67.7	25.7	0
199	2.5	4.1	5.5	3.1	0	3.7	10	25.6	54.1	36.2	6.3
201	4.7	8.8	10.4	6.6	0	7.4	21.9	50.8	107.2	71	12.1

Table 2. 3. Carbon and hydrogen isotope ratio of n-alkanes at ODP 967. Revised meter composite depth (rmcd) is by Sakamoto et al. (1998).

Revised meter composite depth (rmcd)	Carbon isotope ratio (‰ VPDB)						Hydrogen isotope ratio (‰ VSMOW)		
	C23	C25	C27	C29	C31	C33	C27	C29	C31
3	-26.9	-27.9	-30.4	-29.9	-28.1				
5	-27.7	-28.9	-30.7	-31.0	-28.2		-127	-135	-138
7	-26.9	-27.5	-30.2	-29.4	-27.9	-26.4			
9									
11	-26.4	-27.7	-29.8	-29.0	-27.6				
13									
15									
17	-26.9	-28.9	-30.4	-29.4	-28.2				
19									
21									
23									
25	-27.8	-28.0	-30.2	-29.2	-29.5				
27	-29.2	-27.0	-29.1	-28.0					
29									
31									
33									
35	-28.5	-29.4	-31.8	-31.5	-30.1				
37							-146	-142	-150
39	-28.7	-29.2	-32.0	-31.5	-29.7				
41							-147	-156	-153
43	-28.4	-29.3	-31.8	-31.2	-29.2				
45									
47	-29.2	-28.9	-31.5	-30.7	-28.6				
49							-139	-133	-136
51	-28.5	-29.0	-30.5	-29.0	-26.7				
53									
55	-26.3	-28.1	-30.3	-29.0	-27.0				
57									
59									
61							-152	-149	-154
63	-26.9	-28.0	-30.3	-29.4	-26.2				
65							-153	-155	-164
67	-27.5	-28.8	-31.6	-31.2	-29.2			-141	-159
69									
71	-29.7	-29.6	-32.2	-31.4	-29.7				
73							-149	-149	-150
75	-27.1	-29.2	-31.1	-30.4	-29.0				
77									
79	-30.7	-29.4	-31.9	-30.9	-29.9				
81									
83	-27.1	-28.5	-30.3	-30.2	-27.7				
85									
87	-28.6	-28.0	-30.7	-32.0	-27.6				
89									
91	-27.6	-31.1	-30.4	-29.9	-28.0				
95									
95	-27.3	-28.9	-30.9	-30.2	-27.5		-165	-162	-168
97									
99	-31.2	-30.1	-31.8	-32.1	-30.4				
101							-156	-161	
103	-27.9	-28.4	-31.2	-30.0	-28.9		-159	-164	-179
105									
107	-26.5	-28.2	-30.9	-29.6	-31.0		-163	-164	-186

Table 2. 3. cont.

Revised meter composite depth (rncd)	Carbon isotope ratio (‰ VPDB)						Hydrogen isotope ratio (‰ VSMOW)		
	C23	C25	C27	C29	C31	C33	C27	C29	C31
109							-168	-167	-177
111	-28.6	-28.5	-31.1	-30.2	-28.0		-164	-165	-170
113							-169	-171	-180
115	-29.0	-30.7	-29.7	-31.3			-162	-163	-172
117							-174	-172	-181
119	-26.8	-27.0	-29.9	-28.8	-26.9	-27.4	-184	-178	-199
121									
123	-26.0	-27.5	-29.9	-28.5	-26.3	-26.2	-177	-174	-190
125									
127	-26.5	-27.8	-29.6	-28.7	-25.9	-26.3	-169	-163	-190
129									
131	-27.8	-29.1	-30.9	-30.1	-27.6	-28.1		-164	-175
133									
135	-26.9	-28.6	-31.3	-30.4	-28.4			-164	-173
137									
139	-28.6	-29.6	-31.6	-31.4	-31.5				
141									
143	-27.2	-29.2	-31.8	-31.1	-30.2				
145									
147	-28.9	-29.8	-32.2	-31.4	-30.6		-162	-170	-171
149									
151	-29.8	-29.8	-31.8	-31.7	-31.0				
153							-140	-142	-146
155		-28.2	-30.7	-30.2			-135	-135	-135
157									
159	-26.9	-28.0	-31.2	-30.0	-28.1	-27.2	-140	-138	-143
161									
163	-28.3	-29.6	-32.0	-31.2	-29.8		-153	-154	-153
165									
167		-28.5	-31.0	-31.2	-29.2		-146	-147	-152
169									
171	-30.2	-29.5	-31.2	-30.5	-29.0				
173									
175									
177	-29.4	-30.6	-32.4	-31.7	-30.2				
179	-30.2	-30.8	-32.6	-33.2	-32.1	-30.3		-140	-139
181	-30.3	-31.2	-32.9	-32.3	-30.9				
183									
185			-30.9	-29.7				-138	-143
187									
189			-32.0	-31.6	-29.7		-151	-154	-156
191									
193		-28.3	-31.7	-30.9	-28.5				
195							-147	-148	-151
197		-29.0	-32.2	-30.8	-29.4			-160	-165
199									
201							-131	-148	-144

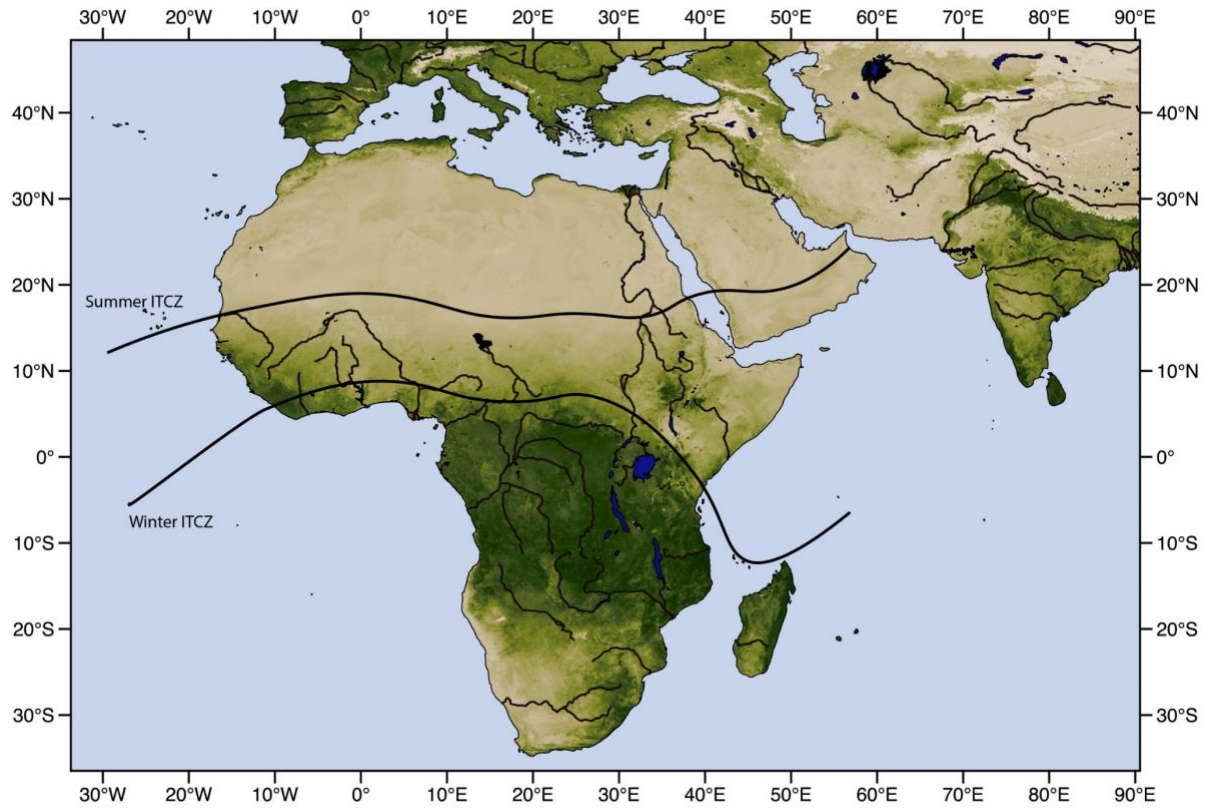


Figure 2. 1: Modern vegetation transitions and precipitation of present Africa with present hydrological system. Black lines indicate the Intertropical Convergence Zone (ITCZ) during July-August and January (Nicholson, 1996).

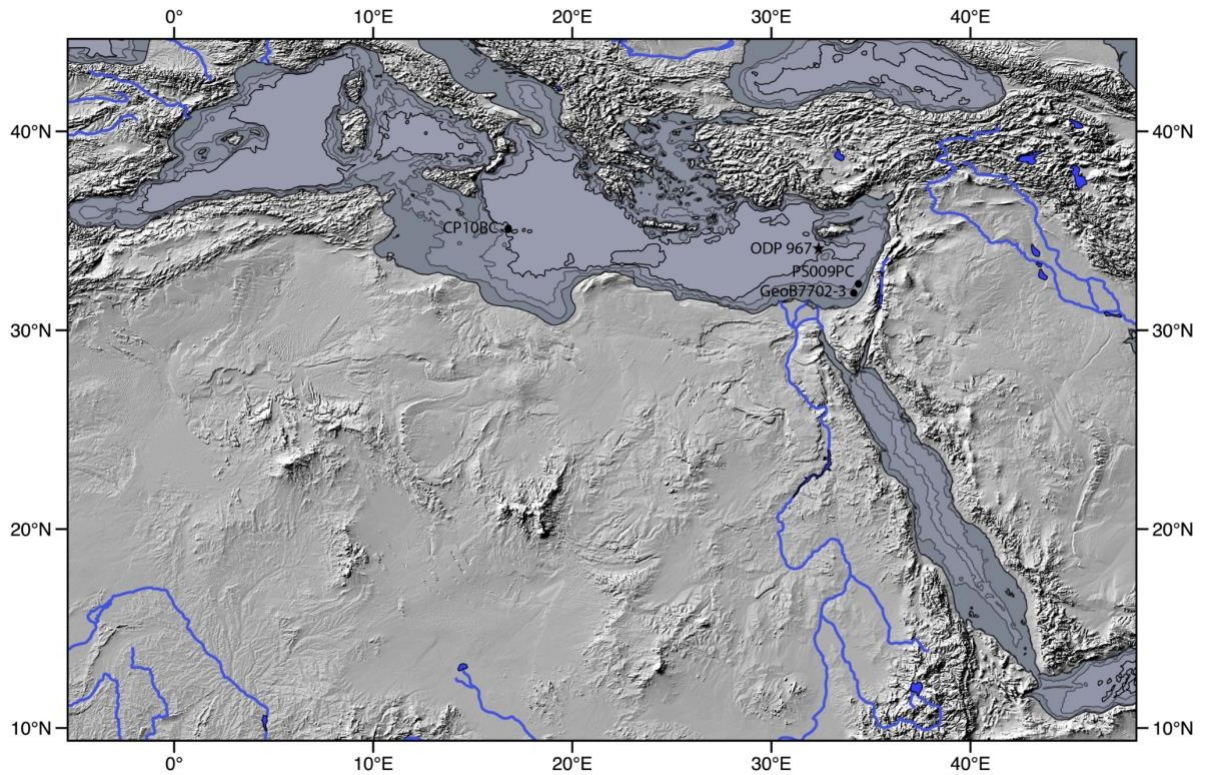


Figure 2. 2: Shaded relief map of North Africa and ODP Site 967 location with black star in the eastern Mediterranean Sea (black star) in the path of the Nile River outflow. The approximate locations of cores GeoB7702-3 (Castañeda et al., 2016), CP10BC (Wu et al. 2016) and PS009PC (van Helmond et al., 2015).

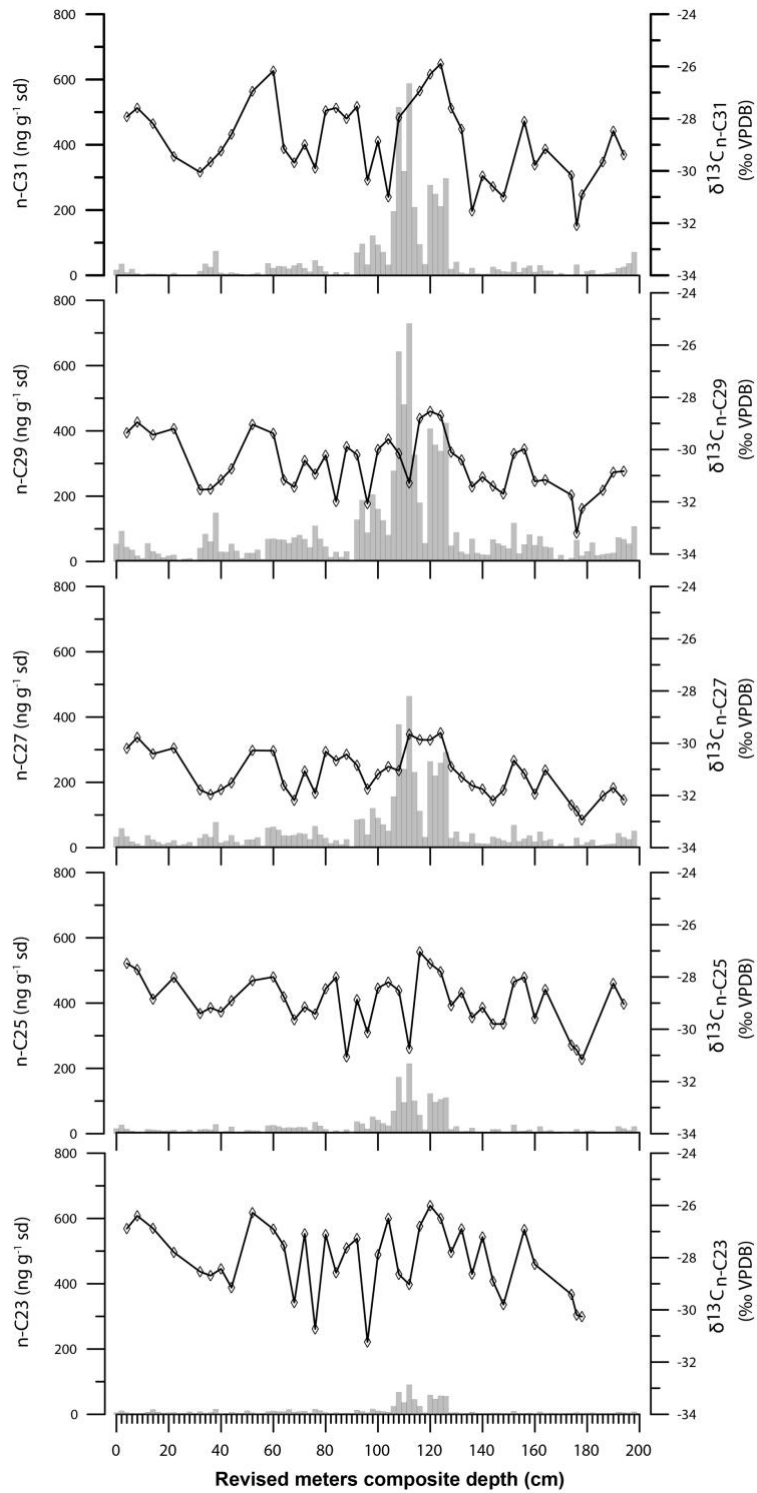


Figure 2. 3: Histograms showing the concentrations of n-alkanes (ng g^{-1} of sediment; left axis). The line graphs show stable carbon isotope ratios of n-alkanes (in ‰ VPDP, right axis) versus the revised meters composite depth for ODP site 967 in the Eastern Mediterranean Sea.

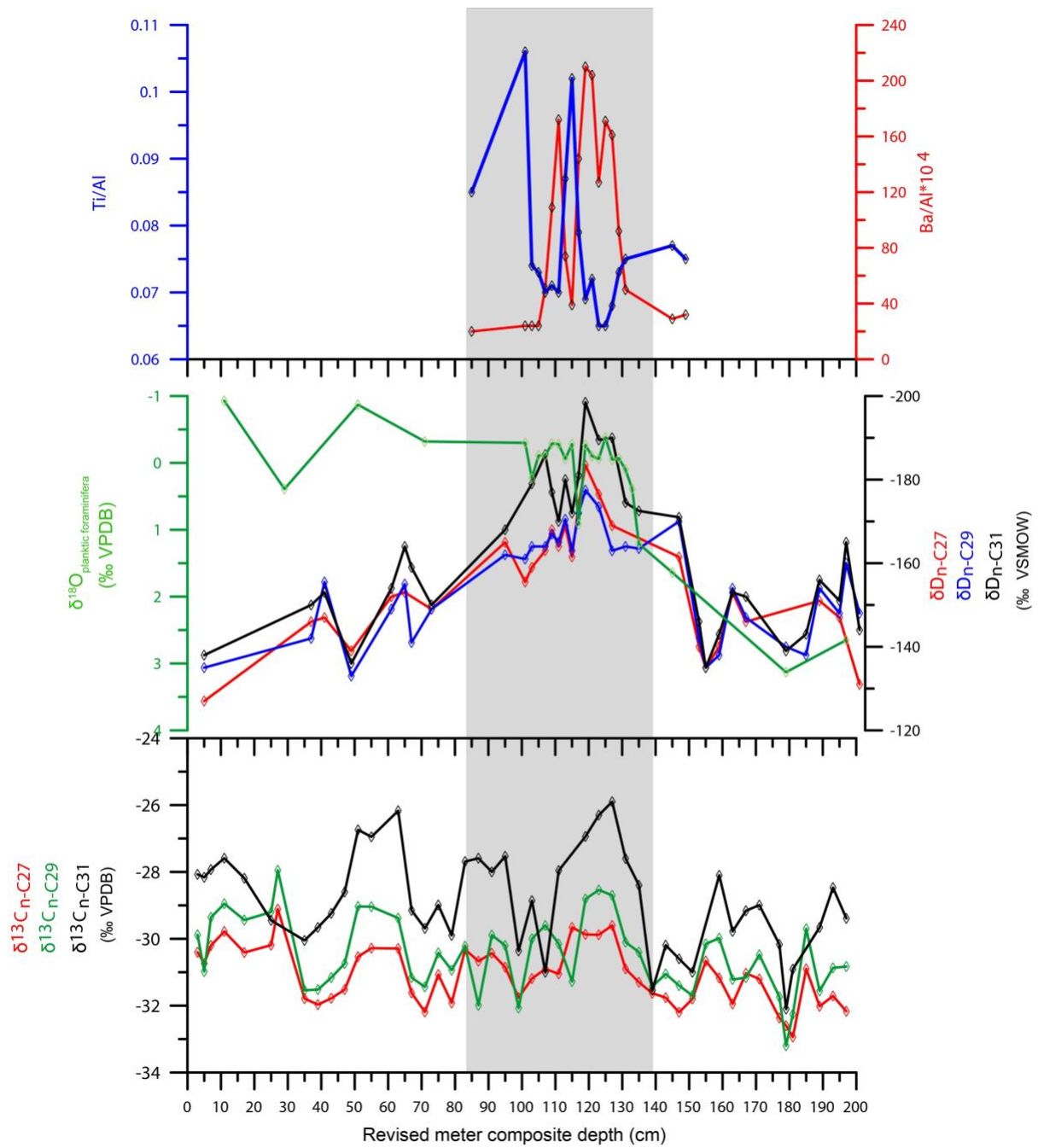


Figure 2. 4: Downcore profiles versus depth of compound specific isotopes of: A) Ti/Al ratio and B) Ba/Al ratio (Azrieli-Tal et al., 2014), C) $\delta^{18}\text{O}$ (‰ VPDB) (Emeis et al., 1998), D) Hydrogen (δD) (‰, VSMOW) and E) Carbon ($\delta^{13}\text{C}$) (‰, VPDB) of individual n-alkanes n-C₂₇, n-C₂₉, n-C₃₁.

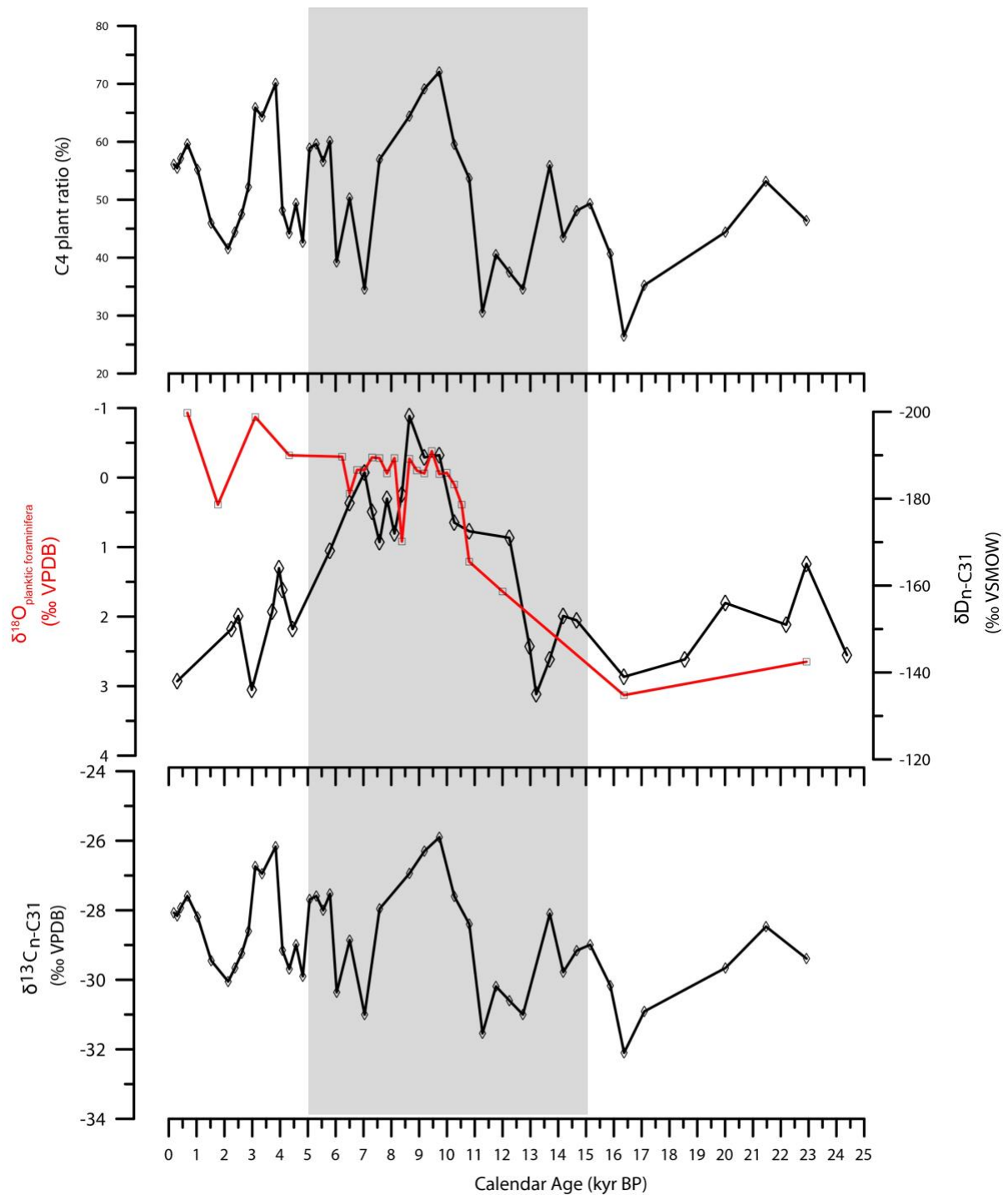


Figure 2. 5: Downcore profiles versus calendar age (kyr) of compound specific isotopes of: A) Percent pf C4 annual grasses, B) $\delta^{18}\text{O}$ (‰ VPDB) (Emeiset al., 1998), C) Hydrogen (δD)(‰ VSMOW) and D) Carbon ($\delta^{13}\text{C}$)(‰ VPDB) of individual n-alkanes n-C₃₁.

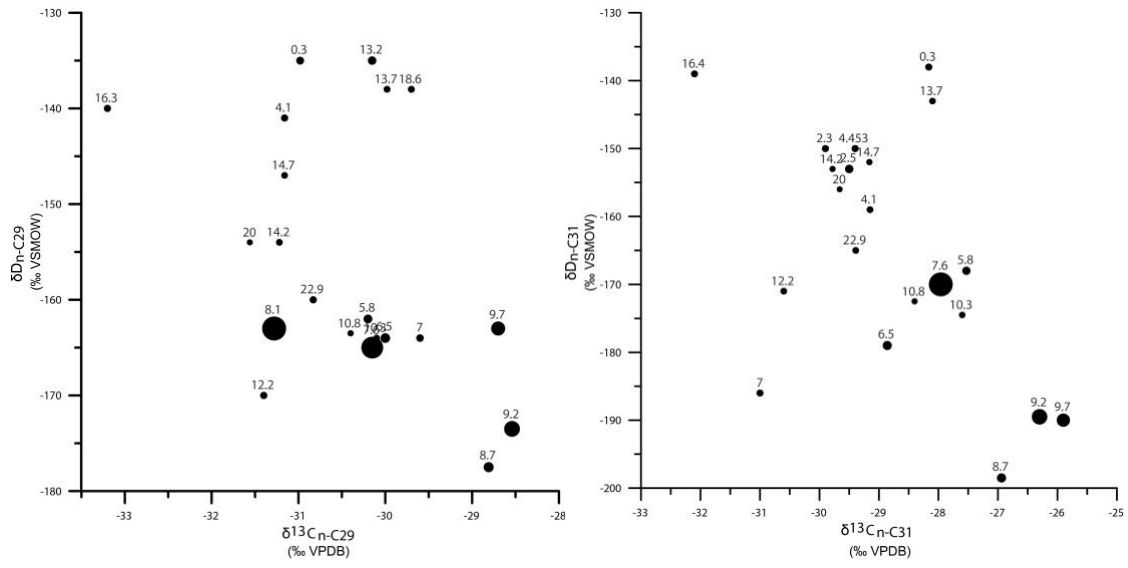


Figure 2. 6: Relationship between $\delta^{13}\text{C}$ (‰ VPDB) and δD (‰ VSMOW) of individual n-alkanes n-C₂₉ and n-C₃₁ since the past 23 ka. The volume of circles related to the concentration n-alkanes n-C₂₉ and n-C₃₁.

Chapter 3

North African paleo-hydrological variations influence on paleoecology and microhabitat of foraminifera in eastern Mediterranean sediments during sapropel depositions

Abstract

Planktic and benthic foraminiferal assemblages in sediment core from the Nile deep sea fan in the Eastern Mediterranean Sea (EMS) were analyzed in order to understand how foraminifera respond to environmental changes during sapropel deposition. For the past 100 kyrs, three sapropel layers S1, S3, and S4 were observed at Core M70b-St#822. Total organic carbon contents showed pronounced peaks at the three sapropel layers. Negative shifts of both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of *Globigerinoides ruber*, a planktic foraminiferal species living in surface water, were observed at sapropel layers S3 and S4. This indicates enhanced freshwater discharge from Nile River due to increased precipitation in North Africa caused by northward migration of the intertropical convergence zone (ITCZ). During sapropel S3 and S4, planktic foraminiferal species diversity were significantly low, possibly due to intensified halocline. Intensified halocline leads to stagnant ocean ventilation and decreases bottom water oxygen content. Benthic foraminiferal assemblages were sensitively responded to the events. During sapropel layers S4, benthic foraminifera was nearly barren, indicating anoxic bottom water. During sapropel layers S3, benthic foraminiferal species diversity was low but several infaunal species were observed. This suggests a dysoxic bottom water during sapropel S3. On the other hand, during sapropel S1, no major changes in benthic foraminiferal assemblage was found. This suggests that bottom water oxygen level did not critically decrease.

3.1. Introduction

The Eastern Mediterranean Sea (EMS) sediment is characterized by numerous brownish to black colored intercalated beds. These beds are relatively enriched in organic carbon and often well laminated, and are named sapropels (Rohling and Hilgen, 1991). Changes in the latitudinal position, timing and intensity of the African monsoon rains have had profound effects on the sedimentological characteristics of EMS. Sapropels deposited in dysoxic to anoxic bottom waters (Daux et al., 2006; Meyers, 2006) when summer monsoon was intensified (Rossignol-Strick, 1983). This allows good preservation of organic matter in the sediments and less or no bioturbation (Jorissen, 1999; Kuhnt et al., 2007; Nolet and Corliss, 1990). Increased freshwater flux from North Africa into EMS during sapropel formations have been recorded as negative planktic foraminiferal $\delta^{18}\text{O}$ values (Cita *et al.*, 1977; Cramp et al., 1988; Mangini and Schlosser, 1986; Rohling and Hilgen, 1991; Rossignol-Strick *et al.*, 1982; Rossignol-Strick, 1985; Vergnaud-Grazzini *et al.*, 1977; Williams *et al.*, 1978). Increased

riverain input provides not only freshwater but also nutrients and continental organic matter into EMS (Rohling and Hilgen, 1991).

The Nile deep-sea fan is one of the largest modern deep-sea turbidite and plays an important role in sedimentary accumulation in EMS. This post-Miocene deposit has approximately 10 km thickness above mobile Messinian evaporites formed by the Messinian salinity crisis from 5.96 to 5.33 Ma (Gauillier et al., 2000; Loncke et al., 2006). Therefore, the initial distribution and thickness of Messinian evaporites have strongly influenced on the present sea-floor shape and processes of sediment dispersal (Loncke et al., 2006). Mediterranean climate is characterized by hot, dry summers and cool, wet winters. Deserts of North Africa lies within a zone of the subtropical high-pressure belt (Boucher, 1975). In summer, most of the Mediterranean region particularly the southeastern part experiences drought by northward migration of the subtropical high-pressure belt (Rohling and Hilgen, 1991). Although there is no precipitation on the African Mediterranean coast in summer, there is heavy rainfall on catchment areas of the Nile River with northward migration of ITCZ. As a result, the Nile River discharges large amount of freshwater as well as numerous terrigenous inputs into EMS during summer. This process had happened naturally before building the Aswan High Dam in 1964. Since the Aswan High Dam completion, decrease in discharge of fresh water and sediment have been occurred and erosion of the Nile River delta progressed.

Aim of this study is to understand how planktic and benthic foraminifera respond to environmental changes in EMS, particularly sapropel events during the past 100 kyrs. Planktic and foraminiferal assemblages as well as their carbon and oxygen stable isotopes in sediments from the Nile deep sea fan are investigate.

3.2. Material and Methods

M70b-St#822 gravity core (32°20.92'N; 31°48.02'E; 1089 m water depth; 4.5 m long) was used in this study obtained from the Nile deep sea fan in EMS during M70b cruise of R/V Meteor in October 2006 (Fig. 3-1). Major lithology of M70b-St#822 core is homogenous clay with calcareous ooze.

3.2.1. Age Model

Age model of M70b-St#822 gravity core was established based on the astronomical tuning by comparison of sapropel midpoints with inferred 65° N summer insolation maxima with a fixed 3-kyr time lag (Lourens, 2004). The lag estimation was corrected to 2.7 ± 1.1 kyrs (Konijnendijk *et al.*, 2014). For M70b-St#82 core samples, thickness of sapropel layers was determined by total organic carbon contents (wt%). In addition, top and bottom ages of sapropel layer S1 are well constrained

based on radiocarbon dating of planktic foraminifera from the numbers of sediment cores in EMS (10.8 ± 0.4 to 6.1 ± 0.5 cal. kyr BP; De Lange *et al.*, 2008). The established age model shows top 4.5 m of M70b-St#822 is corresponding to for the past 100 kyrs. Due to a few age control points, discussions on detailed timings beyond millennial time-scales are limited.

3.2.2. Sediment Samples Analyses

Selected 46 samples of core M70b-St#822 were used for analyses on total organic carbon contents (Table 3.1). Total organic carbon contents were measured determined by acid/dichromate titration method (Gaudette *et al.*, 1974). Approximately 0.3 g of sediment samples were dried at room temperature and placed into 500 ml Erlenmeyer flask. Exactly 10 ml of 1N $K_2Cr_2O_7$ solution was added by burette to the sediment and well mixed. 20 ml of concentrated H_2SO_4 were added by burette and were mixed by gentle rotation of the flask for about 1 minute. The mixture was allowed to stand for 30 min. A standardization blank without sediments was run with each new batch of samples. After 30 min, the solution was diluted to 200 ml volume with distilled water, and 10 ml of 85% H_3PO_4 , 0.2 g of NaF and 15 drops of diphenylamine indicator were added to the sample in flask. The solution was back titrated with 0.5N ferrous ammonium sulfate solutions. The color was progressed from an opaque green-brown, to green upon the addition of approximately 10 ml of ferrous solution ($Fe(NH_4)_2SO_4 \cdot 6H_2O$). The color continued to shift upon titration to a bluish-black-grey. At this point the addition of 10-20 drops of ferrous solution shifted the color to a brilliant green giving a one-drop end point. The results of the analysis were calculated by the following equation:

$$\% \text{ Organic Carbon} = 10 (1-T/S) [1.0N (0.003) (100/W)]$$

Where T= sample titration, ml ferrous solution, S= standardization blank titration, ml ferrous solution. (The T/S factor will cancel out the effect of the ferrous solution normality) 0.003 = meq. Wt of carbon, 1.0 N= normality of $K_2Cr_2O_7$, 10= volume of $K_2Cr_2O_7$ in ml, and W= weight of sediment sample in grams the organic carbon is converted to organic matter by multiplying the organic carbon values by the factor of 1.8 (Gaudette *et al.*, 1974).

For foraminiferal analyses, selected 26 sediment samples were used. Sediment samples of core M70b-St#822 were dried and 10 g of the samples were weighed. The weighed samples were washed with tap water over a 63- μ m sieve and dried at 60°C (Schilman *et al.*, 2001). The residual samples >63 μ m were split by using a Micro-Splitter. Total assemblages were determined in fractions of split samples including at least 300 specimens (Javaux and Scott, 2003). Foraminiferal species identification was following to Loeblich and Tappan (1964) (Fig. 3.7 and 3.8; Table 3.2). Stable carbon and oxygen isotopes of planktic foraminifera was performed. 40 specimens of *Globigerinoides ruber*, a surface-dwelling species (0–50 m), were picked up from the size fraction >250 μ m (Fontugne and

Calvert, 1992). Stable isotope measurements were performed by using IRMS Micromass Optima coupled to a Multiprep mass spectrometer at Environnements et Paléo-environnements Océaniques et Continentaux in Bordeaux, France. Isotope ratios are given in δ notations versus PDB after calibration against international NBS 18 and 19 (Coplen, 1988; Hut, 1987).

3.3. Results

3.3.1. TOC analysis

TOC contents were generally low less than 1 wt% at core M70b-St#822 (Fig. 3-2). Relatively high TOC contents were found at 20- 30 cm, 290-340 cm, 400 cm, and 430-440 cm. These timing were simultaneous with sapropel depositions.

3.3.2. Foraminiferal assemblage and stable isotopes

A total of 21 species of planktic and benthic species were identified in M70b-St#822 core sediment (Fig. 3.7 and 3.8; Table 3.2). Relative and absolute abundances of planktic and benthic foraminifera were summarized in Tables 3.3. and 3.4, respectively. Absolute abundances of planktic foraminifera showed three peaks in core M70b-St#822 at 150 cm, 280-300 cm (sapropel S3) and 420 cm (sapropel S4) (Fig. 3.4; Table 3.3). Absolute abundances of benthic foraminifera were relatively abundant in sapropel S1 and S3 but almost barren in sapropel S4 (Fig. 3.6; Table 3.4). The abundant planktic foraminiferal species were *Globigerinoides ruber* and *Globigerina bulloides*. Pronounced peaks of %*G. ruber* and % *G. bulloides* were found during sapropel S4 and S3, respectively (Fig. 3.3; Table 3.3). *Orbulina universa* was absent except for sapropel layers S3 and S4. Shannon diversity (H) of planktic foraminifera ranged from 1.2 to 1.6 except for sapropel layers where significantly low peaks were found (Fig. 3.2). Shannon diversity (H) of benthic foraminifera showed similar pattern with that of planktic foraminifera and the values were ~ 3 except for the sapropel layers (Fig. 3.2). Among sapropel layers, lowest Shannon diversity was observed in sapropel S4.

Down core profiles of stable oxygen and carbon isotopes of planktic foraminiferal species *G. ruber* at core M70b-St#822 were shown in Figure 3.2. Negative excursions of both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ were found in sapropel S3 and S4 layers.

3.4. Discussion

3.4.1. Sedimentary characteristics of sapropels

Hydrological change in North Africa and EMS is closely linked to the changes in African monsoon intensity which is mainly controlled by solar radiation received at low latitudes modulated by the precession cycle (Fontugne and Calvert, 1992; Rohling, 1994; Rossignol-Strick, 1985). During

periods with precession minima, northward migrated ITCZ causes the greening of Sahara (Brovkin *et al.*, 1998; Gasse, 2000) and the reduction of Saharan aeolian dust into EMS (Larrasoana *et al.*, 2003). Enhanced freshwater discharge plays a critical role in formation of sapropel layers by establishing halocline and providing terrigenous nutrients (Rohling *et al.*, 2015). While during periods with precession maxima, ITCZ migrates to southward and converts the Saharan region to barren desert and causes the increase in aeolian dust into EMS (Claussen *et al.*, 1998; Brovkin *et al.*, 1998).

Freshwater, particularly derived from heavy rain has light $\delta^{18}\text{O}$ comparing to the seawater. Hence, mixing of freshwater floods to seawater causes low $\delta^{18}\text{O}$ anomalies in planktic foraminifera (see Rohling *et al.*, 2015, review and references therein). Kallel *et al.*, (1997, 2000) showed low $\delta^{18}\text{O}$ anomalies due to increased precipitation over the EMS and its borderlands. Negative $\delta^{18}\text{O}$ excursions of planktic foraminifera at core M70b-St#822 in Fig. 5 indicates enhanced freshwater discharge via Nile River caused by increased precipitation in watershed area of Nile River during the sapropel S3 and S4 depositions. This leads to salinity reduction and halocline development, enhancing stratification in EMS (Rossignol-Strick *et al.*, 1982; Rossignol-Strick, 1985; Van Harten, 1987; Nolet and Corliss, 1990; Negri *et al.*, 2003). Our data corresponds to low $\delta^{18}\text{O}$ values of *G. ruber* (Kroon *et al.*, 2004) and significantly low Ti/Al ratios and hematite contents (Larrasoana *et al.*, 2003) at Site 967 that support the scenario of enhanced Nile River input and elevated soil moisture in North Africa during the sapropel layers formation.

Planktic foraminiferal carbon isotopes tell a carbon cycle in upper water column. Commonly, planktic foraminifera living in surface water forms calcite tests enriched in ^{13}C because ^{12}C is preferentially sequestered by marine algae during photosynthesis in euphotic layer and subsequently transfers to ocean interior by sinking particles (Rohling *et al.*, 2004). However, in areas where enhanced river input occur, surface waters have low $\delta^{13}\text{C}$ values due to light carbon content of freshwater ranging from -5‰ to -10‰ of inorganic carbon and as light as -27‰ of suspended organic carbon (Fontugne and Calvert, 1992). In semi-enclosed marginal sea with significant river inputs, effect of biological pumping is masked by light carbon dilution. Significantly negative $\delta^{13}\text{C}$ excursions at core M70b-St#822 during sapropel S3 and S4 are due to both elevated primary productivity fueled by nutrient supply from riverine inputs and direct influence of riverine carbon inputs.

3.4.2. Response of foraminiferal assemblages to sapropel depositions

Diversity of planktic foraminifera at core M70b-St#822 decreased during sapropel S3 and S4 depositions. Distribution of planktic foraminifera is controlled by number of environmental factors such as surface water hydrography (Zhang, 1985), water mass properties (Vincnet and Berger, 1981) and upwelling (Curry *et al.*, 1992). Rutherford *et al.*, (1999) suggests that diversity of planktic

foraminifera is controlled by structure of upper water column rather than SST because planktic foraminiferal diversity decreases in shallow thermocline. On the other hand, Rosenzweig and Abramsky (1993) suggest diversity of planktic foraminifera is controlled by productivity because the diversity decreased during an excess of productivity.

Significant decrease of planktic foraminiferal diversity during sapropel S3 and S4 at core M70b-St#822 can be explained by both intensified halocline and an excess of productivity. Pronounced negative $\delta^{18}\text{O}$ excursions of *G. ruber* indicate great influence of freshwater discharge during sapropel S3 and S4 depositions (Fig. 3.2). TOC contents showed pronounced peaks during both S3 and S4 layers, suggesting elevated productivity (Fig. 3.2). Sapropel S1 has clearly different feature of sedimentary properties without pronounced change of $\delta^{18}\text{O}$ compared to sapropels S3 and S4. Planktic foraminiferal assemblages showed difference between sapropel S3 and S4. Most abundant planktic foraminiferal species was *G. bulloides* during sapropel S3 whereas *G. ruber* during sapropel S4. *Globigerina bulloides* inhabits both mixed layer (< 400 m water depth) and known as upwelling indicator (Bé et al., 1985; Reynolds and Thunell, 1986). In the Mediterranean Sea, this species is abundant in winter (Reynolds and Thunell, 1986). *Globigerinoides ruber* is an omnivorous feeders bearing dinoflagellate symbiont (Bé and Hamlin, 1967; Hemleben *et al.*, 1989; Leeuwen, 1989) with wide ecological niche of temperatures and salinities that usually thrive in the warm, nutrient-poor waters of the summer mixed layer above the thermocline (Hemleben *et al.*, 1989). Therefore, abundant *G. bulloides* during sapropel S3 support an excess of productivity scenario. On the contrary, intensified halocline scenario is more likely for sapropel S4 inferred from abundant *G. ruber*. In addition, both absolute and relative abundances of *Globorotalia truncatulinoides*, living intermediate depth 200-500 m (Hemleben *et al.*, 1989), decreased during sapropel S1, S3 and S4. This is perhaps due to weaken vertical mixing by halocline because the distribution of this species is related to winter convection and vertical mixing (Pujol and Grazzini, 1995). Similar the patterns of *Globigerinita glutinata* support the weaken vertical mixing during sapropel layers because this species is a proxy for the presence deep mixed layer *Globigerinita glutinata* increases (Bé and Hamlin, 1967; Hemleben *et al.*, 1989; Leeuwen, 1989).

Similar to the planktic foraminifera, species diversity of benthic foraminifera significantly decreased during sapropel S3 and S4 depositions at core M70b-St#822 (Fig. 3.4). Benthic foraminiferal diversity depends on a sea-floor ecosystem. An ecosystem in stable environment is able to support a highly diverse fauna, whereas in severe environment diversity is generally low (Gooday et al., 1998). Jorissen *et al.*, (1995) have indicated that highest diversities occur in mesotrophic and well-ventilated environments. In contrast, diversities are generally low in oligotrophic as well as eutrophic and oxygen-depleted benthic ecosystems. Numbers of studies have suggested that export

flux of organic carbon plays a major role in density and diversity of benthic foraminifera (Alve and Bernhard, 1995; de Stigter *et al.*, 1998; Jorissen *et al.*, 1998; Loubere, 1998; Altenbach *et al.*, 1999; Bernhard and Sen Gupta, 1999; Schmiedl *et al.*, 2000; De Rijk *et al.*, 2000; Kitazato *et al.*, 2000; Morigi *et al.*, 2001, 2005, Fontanier *et al.*, 2002, 2003). A benthic foraminiferal assemblage with high absolute abundance suggests high organic carbon flux to the sea floor. With the bottom water oxygen consumption by organic carbon degradation, infaunal benthic foraminiferal species replace the less tolerant species of low oxygen condition (Jorissen *et al.*, 1995; Jorissen, 1999). During sapropel S4, benthic foraminifera at Core M70b-St#822 was barren suggesting anoxic condition on the seafloor. Several studies recorded the absence of benthic foraminifera in Mediterranean Sea during sapropel layers formation (Abu-Zied *et al.*, 2008; Casford *et al.*, 2003; Jorissen, 1999; Kuhnt *et al.*, 2007; Mercone *et al.*, 2001; Nijenhuis *et al.*, 1996; Nolet and Corliss, 1990; Rohling *et al.*, 1993; Schmiedl *et al.*, 2010, 2003; Verhallen, 1991). During sapropel S3, considerable occurrences of benthic foraminifera at Core M70b-St#822 indicate that bottom water was not anoxic. Melki *et al.*, (2010) also documented occurrences of benthic foraminifera during the deposition of sapropel S4, S6, S8 and S10 at core MD84-641.

Onset of sapropel S3 and S1 was characterized by replacement of epifaunal species (*Bolivina advena* and *Bolivina acuminata*) by infaunal species (*Bulimina costata*, *Cassidulina crassa*, *Cassidulina laevigata*, *Eponides frigidus*, *Gyroidina orbicularis*) suggesting dysoxic conditions. *Bolivina acuminata* was the most abundant benthic foraminiferal species during sapropel S3. Abu-Zied *et al.* (2008) mentioned that most of species in genus *Bolivina* is considered as opportunist sensitively responding to an organic matter input. The increased occurrence of *Bolivina acuminata* during sapropel S3 is consistent with an excess of productivity scenario based on abundant *G. bulloides*. Occurrences of *Bulimina costata*, *Cassidulina crassa*, *Cassidulina laevigata*, and *Uvigerina mediterranea* are shallow infauna less tolerant to low oxygen condition associated with oligotrophic to mesotrophic, well ventilated oceanic conditions (De Rijk *et al.*, 2000; Kuhnt *et al.*, 2007). They showed relatively high abundances during period between sapropel S1 and S3. This interval is corresponding to the last glacial period. During the last glacial period, African summer monsoon was weak and ITCZ shifted southward. Hooghiemstra *et al.*, (1992) documented that the glacial Sahara Desert extended hundreds of kilometers further south than at present based on ancient sand dune distributions. As a result, aeolian dust input into EMS was increased (Larrasoana *et al.*, 2003). Reduced freshwater discharge during glacial period was also evidenced by planktic foraminiferal assemblage at core M70b-St#822. Increased diversity of the planktic foraminifera suggests ventilated water mass by less freshwater discharge and SST cooling. This is supported by increase of deep dwelling species *Globorotalia truncatulinoides* and cold-water species *Globigerinita glutinata*. Benthic foraminiferal

diversity also increased during glacial period perhaps because of oxygenation in bottom water by ventilation.

3.5. Conclusion

Sapropels S1, S3 and S4 were found in sediment of M70b-St#822 gravity core. Enhanced freshwater discharge via Nile River is suggested by negative excursions of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of *G. ruber* during sapropels S3 and S4. Simultaneously, planktic foraminiferal diversity decreased due to developed halocline. Benthic foraminiferal assemblage indicated the difference of bottom water environments between sapropel S3 and S4. Sapropel S3 was dysoxic condition whereas sapropel S4 was anoxic conditions. Notable species turnover of benthic foraminifera from epifauna to infauna was observed at the onset of sapropel S3 cause by reduced bottom water oxygen concentration.

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Table 3. 1. Core depth, calendar age, total organic carbon content, and carbon and oxygen isotope ratio of Core M70b-St#822.

Depth (cm)	Age (cal. kyr. BP)	TOC (wt%)	$\delta^{13}\text{C}$ of <i>G. ruber</i> (‰ VPDB)	$\delta^{18}\text{O}$ of <i>G. ruber</i> (‰ VPDB)	Depth (cm)	Age (cal. kyr. BP)	TOC (wt%)	$\delta^{13}\text{C}$ of <i>G. ruber</i> (‰ VPDB)	$\delta^{18}\text{O}$ of <i>G. ruber</i> (‰ VPDB)
0	0	0.52			270	79.1	0.57		
5	1.3		0.86		275	79.4		1.39	3.04
10	2.6	0.89		2.28	280	79.7	0.21		
20	5.1	1.63			295	80.6		1.13	2.28
30	6.1	1.55			300	80.9	1.46		
40	7.1	0.89			305	81.2		0.37	-0.30
45	7.7		1.04	1.52	310	81.5	0.88		
50	8.2	0.52			315	81.8		1.39	-0.47
60	9.2	0.63			320	82.1	1.5		
70	10.2	1.05			325	82.4		1.08	-0.45
80	14.1	0.31			330	82.7	1.72		
90	18.1	0.37			335	83		0.80	1.30
95	20.1		1.07	1.86	340	83.3	0.68		
100	22	0.10			345	83.6		0.72	1.55
110	26	0.52			350	83.9	0.16		
120	29.9	0.52			355	85.9		0.82	0.74
130	33.9	0.42			360	87.8	0.16		
140	37.8	0.57			365	89.8		0.89	1.17
145	39.8		1.08	2.58	370	91.8	0.62		
150	41.8	0.57			375	93.7		1.51	2.45
160	45.7	0.10			380	95.7	0.16		
170	49.7	0.17			390	99.6	0.10		
180	53.6	0.63			395	100		1.99	-0.16
190	57.6	0.73			400	100.3	2.45		
195	59.5		1.17	2.66	405	100.7		1.13	-0.69
200	61.5	0.05			410	101.1	0.73		
210	65.5	0.21			415	101.4		1.06	-0.77
215	67.4		0.96	2.86	420	101.8	0.68		
220	69.4	0.26			425	102.2		1.09	-0.69
230	73.4	0.31			430	102.5	3.28		
235	75.3		1.02	2.89	435	102.9		1.05	-1.17
240	77.3	0.10			440	103.3	2.71		
250	77.9	0.47			445	103.6		1.33	-1.40
255	78.2		1.16	2.72	450	104	0.68		
260	78.5	0.37							

Table 3.2. List of foraminiferal species in Core M70b-St#822

Planktonic foraminifera	Benthic foraminifera
<i>Globigerina bulloides</i>	<i>Bolivina acuminata</i>
<i>Globigerina calida</i>	<i>Bolivina advena</i>
<i>Globigerinita glutinata</i>	<i>Bulimina marginata</i>
<i>Globigerinoides immaturus</i>	<i>Cassidulina crassa</i>
<i>Globigerinoides obliquus</i>	<i>Cassidulina laevigata</i>
<i>Globigerinoides ruber</i>	<i>Cibicides tabaensis</i>
<i>Globorotalia truncatulinoides</i>	<i>Eponoides repandus</i>
<i>Orbulina universa</i>	<i>Gyroidina soldanii</i>
<i>Turborotalia clarkei</i>	<i>Hoeglundina elegans</i>
	<i>Pyrego</i> sp.
	<i>Quenqueloculina</i> sp.
	<i>Uvigerina mediterranea</i>

Table 3.4. Count, relative abundance (%) and absolute abundance (No. g⁻¹ sediment) data of benthic foraminifera at Core M70b-St#822.

Core depth (cm)	10	20	40	50	100	150	200	220	240	260	280	300	310	320	330	340	350	360	370	380	400	410	420	430	440	450
Age (cal. kyr. BP)	2.6	5.1	7.1	8.2	22.0	41.8	61.5	69.4	77.3	78.5	79.7	80.9	81.5	82.1	82.7	83.3	83.9	87.8	91.8	95.7	100.3	101.1	101.8	102.5	103.3	104.0
Number of sample splits	0	0	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	0	0	2	0	0	0	0	0	0
Fraction of splitted sample	1	1	0.25	0.25	0.25	0.25	0.25	0.25	0.25	1	0.25	0.25	0.25	0.25	0.25	0.25	0.25	1	1	0	1	1	1	1	1	1
Count																										
<i>Bolivina acuminata</i>	147	85	175	129	33	47	156	65	104	64	96	112	320	184	184	104	144	160	136	96	0	0	0	0	0	0
<i>Bolivina advena</i>	90	41	17	33	40	25	20	49	96	112	40	64	32	24	32	24	8	16	28	20	0	0	0	0	0	0
<i>Bulimina marginata</i>	83	47	63	64	49	32	56	31	80	0	24	32	56	24	72	56	88	0	16	36	0	0	0	0	0	0
<i>Cassidulina crassa</i>	40	35	27	24	49	73	28	17	48	0	0	40	0	8	16	16	56	32	40	44	0	0	0	0	0	0
<i>Cassidulina laevigata</i>	17	40	37	17	15	120	29	23	24	16	16	72	8	24	16	16	56	0	0	4	0	0	0	0	0	0
<i>Cibicides tabaensis</i>	41	62	51	113	137	73	19	57	24	32	40	40	0	8	104	88	56	16	8	24	0	0	0	0	0	0
<i>Eponoides repandus</i>	0	0	0	0	0	0	0	0	0	16	16	8	0	16	8	0	0	0	24	16	0	0	0	0	0	0
<i>Gyroidina soldanii</i>	0	9	0	0	0	0	8	7	0	0	0	8	0	16	32	24	0	40	48	20	0	0	0	0	0	0
<i>Hoeglundina elegans</i>	15	110	0	7	17	0	17	25	0	32	32	0	0	32	32	80	48	16	4	0	0	0	0	0	0	0
<i>Pyrgo</i> sp.	7	7	4	9	7	0	0	9	8	0	8	8	0	0	0	0	0	8	16	12	0	0	0	0	0	0
<i>Quenqueloculina</i> sp.	2	1	0	6	1	0	0	7	8	16	0	0	8	0	0	0	8	0	8	4	0	0	0	0	0	0
<i>Uvigerina mediterranea</i>	43	33	98	65	71	64	21	87	56	96	32	32	0	0	16	0	0	24	20	16	0	0	0	0	0	0
Total benthic foraminifera	485	470	472	467	419	434	354	377	448	384	304	416	424	336	512	408	464	312	348	292	0	0	0	0	0	0
%																										
<i>Bolivina acuminata</i>	30.3	18.1	37.1	27.6	7.9	10.8	44.1	17.2	23.2	16.7	31.6	26.9	75.5	54.8	35.9	25.5	31.0	51.3	39.1	32.9	0	0	0	0	0	0
<i>Bolivina advena</i>	18.6	8.7	3.6	7.1	9.5	5.8	5.6	13.0	21.4	29.2	13.2	15.4	7.5	7.1	6.3	5.9	1.7	5.1	8.0	6.8	0	0	0	0	0	0
<i>Bulimina marginata</i>	17.1	10.0	13.3	13.7	11.7	7.4	15.8	8.2	17.9	0.0	7.9	7.7	13.2	7.1	14.1	13.7	19.0	0.0	4.6	12.3	0	0	0	0	0	0
<i>Cassidulina crassa</i>	8.2	7.4	5.7	5.1	11.7	16.8	7.9	4.5	10.7	0.0	0.0	9.6	0.0	2.4	3.1	3.9	12.1	10.3	11.5	15.1	0	0	0	0	0	0
<i>Cassidulina laevigata</i>	3.5	8.5	7.8	3.6	3.6	27.6	8.2	6.1	5.4	4.2	5.3	17.3	1.9	7.1	3.1	3.9	12.1	0.0	0.0	1.4	0	0	0	0	0	0
<i>Cibicides tabaensis</i>	8.5	13.2	10.8	24.2	32.7	16.8	5.4	15.1	5.4	8.3	13.2	9.6	0.0	2.4	20.3	21.6	12.1	5.1	2.3	8.2	0	0	0	0	0	0
<i>Eponoides repandus</i>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.2	5.3	1.9	0.0	4.8	1.6	0.0	0.0	0.0	6.9	5.5	0	0	0	0	0	0
<i>Gyroidina soldanii</i>	0.0	1.9	0.0	0.0	0.0	0.0	2.3	1.9	0.0	0.0	0.0	1.9	0.0	4.8	6.3	5.9	0.0	12.8	13.8	6.8	0	0	0	0	0	0
<i>Hoeglundina elegans</i>	3.1	23.4	0.0	1.5	4.1	0.0	4.8	6.6	0.0	8.3	10.5	0.0	0.0	9.5	6.3	19.6	10.3	5.1	1.1	0.0	0	0	0	0	0	0
<i>Pyrgo</i> sp.	1.4	1.5	0.8	1.9	1.7	0.0	0.0	2.4	1.8	0.0	2.6	1.9	0.0	0.0	0.0	0.0	0.0	2.6	4.6	4.1	0	0	0	0	0	0
<i>Quenqueloculina</i> sp.	0.4	0.2	0.0	1.3	0.2	0.0	0.0	1.9	1.8	4.2	0.0	0.0	1.9	0.0	0.0	0.0	1.7	0.0	2.3	1.4	0	0	0	0	0	0
<i>Uvigerina mediterranea</i>	8.9	7.0	20.8	13.9	16.9	14.7	5.9	23.1	12.5	25.0	10.5	7.7	0.0	0.0	3.1	0.0	0.0	7.7	5.7	5.5	0	0	0	0	0	0
No. g ⁻¹ sediment																										
<i>Bolivina acuminata</i>	15	9	70	52	13	19	62	26	42	6	38	45	128	74	74	42	58	16	14	38	0	0	0	0	0	0
<i>Bolivina advena</i>	9	4	7	13	16	10	8	20	38	11	16	26	13	10	13	10	3	2	3	8	0	0	0	0	0	0
<i>Bulimina marginata</i>	8	5	25	26	20	13	22	12	32	0	10	13	22	10	29	22	35	0	2	14	0	0	0	0	0	0
<i>Cassidulina crassa</i>	4	4	11	10	20	29	11	7	19	0	0	16	0	3	6	6	22	3	4	18	0	0	0	0	0	0
<i>Cassidulina laevigata</i>	2	4	15	7	6	48	12	9	10	2	6	29	3	10	6	6	22	0	0	2	0	0	0	0	0	0
<i>Cibicides tabaensis</i>	4	6	20	45	55	29	8	23	10	3	16	16	0	3	42	35	22	2	1	10	0	0	0	0	0	0
<i>Eponoides repandus</i>	0	0	0	0	0	0	0	0	0	2	6	3	0	6	3	0	0	0	2	6	0	0	0	0	0	0
<i>Gyroidina soldanii</i>	0	1	0	0	0	0	3	3	0	0	0	3	0	6	13	10	0	4	5	8	0	0	0	0	0	0
<i>Hoeglundina elegans</i>	2	11	0	3	7	0	7	10	0	3	13	0	0	13	13	32	19	2	0	0	0	0	0	0	0	0
<i>Pyrgo</i> sp.	1	1	2	4	3	0	4	3	0	3	3	3	0	0	0	0	0	1	2	5	0	0	0	0	0	0
<i>Quenqueloculina</i> sp.	0	0	0	2	0	0	0	3	3	2	0	0	3	0	0	0	3	0	1	2	0	0	0	0	0	0
<i>Uvigerina mediterranea</i>	4	3	39	26	28	26	8	35	22	10	13	13	0	0	6	0	0	2	2	6	0	0	0	0	0	0
Total BF (No. g ⁻¹)	49	47	189	187	168	174	142	151	179	38	122	166	170	134	205	163	186	31	35	117	0	0	0	0	0	0

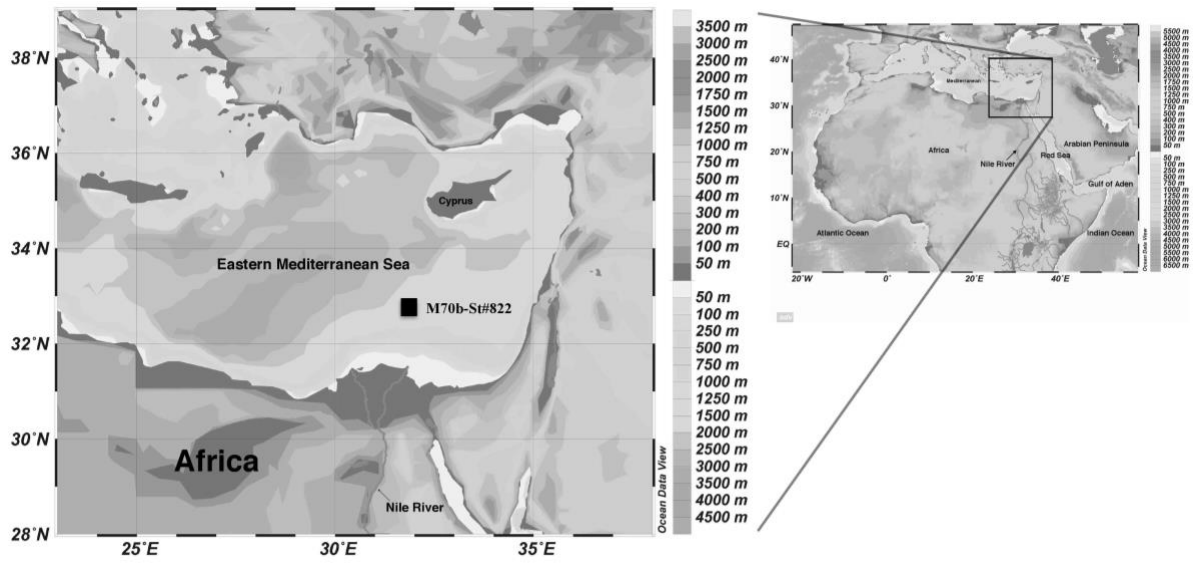


Figure 3. 1. Map of EMS and its surrounding area with bathymetric and topographic information. Black square indicates the study site of M70b-St#822. Map drawn by Ocean Data View (Schlitzer, R., Ocean Data View, <http://odv.awi.de>, 2015).

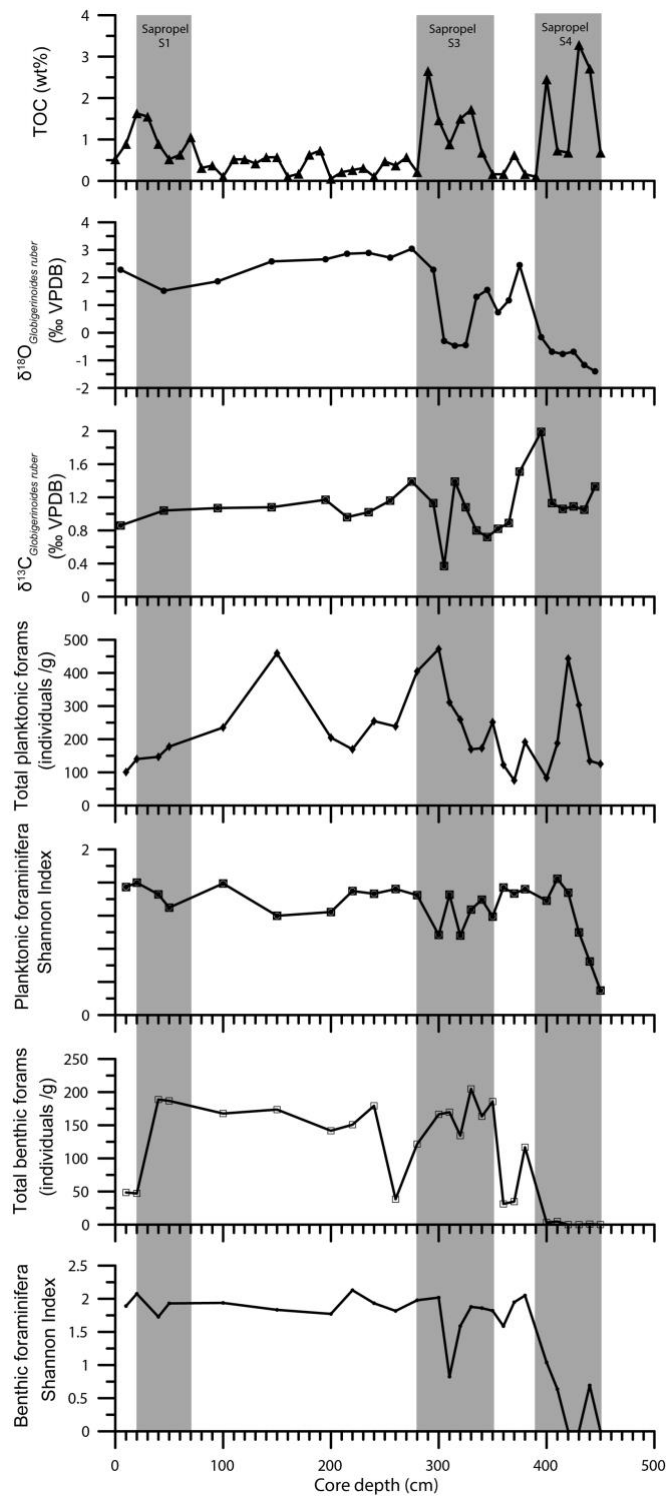


Figure 3. 2. Down core profiles of total organic carbon (TOC, wt%), planktic foraminiferal (*Globigerinoides ruber*) $\delta^{18}\text{O}$ (‰ VPDB) and $\delta^{13}\text{C}$ (‰ VPDB), total planktic and benthic foraminifera abundances (individual/g) and Shannon index of planktic and benthic foraminifera at core M70b-St#822. Sapropel layers (gray color) are indicated.

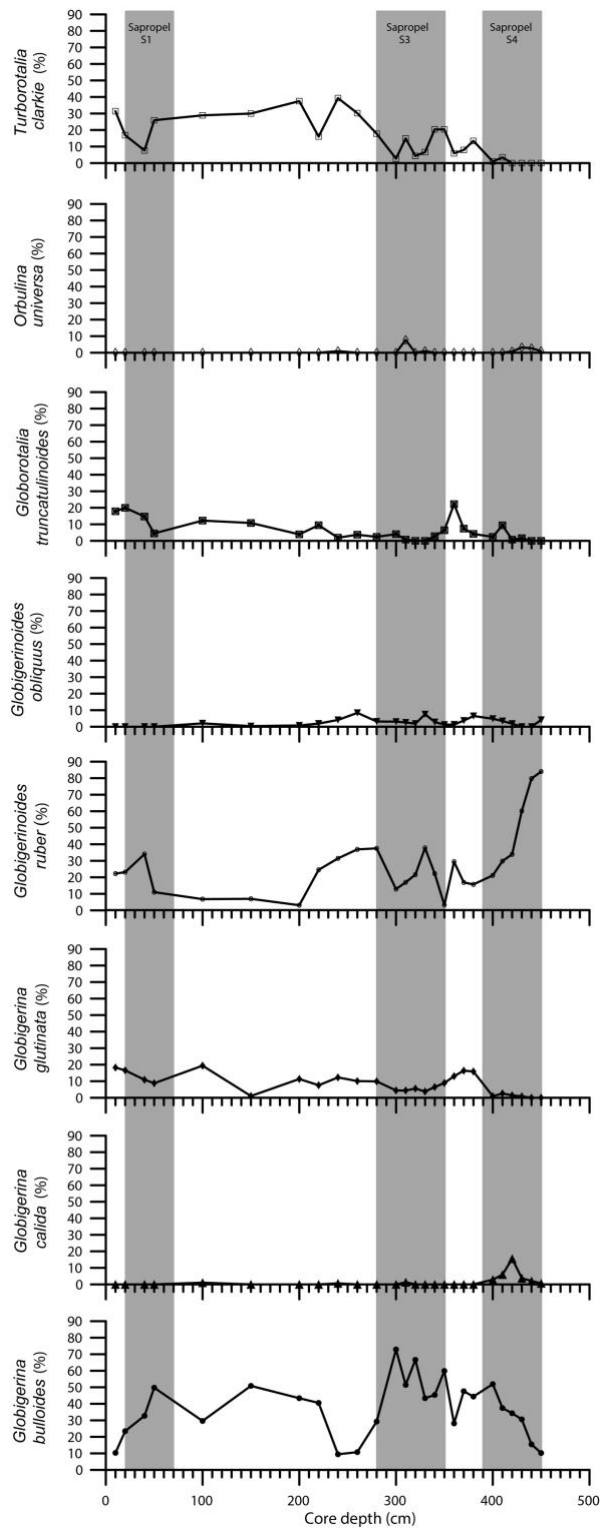


Figure 3. 3. Relative abundance of planktonic foraminiferal species at core M70b-St#822.

Sapropel layers (gray color) are indicated.

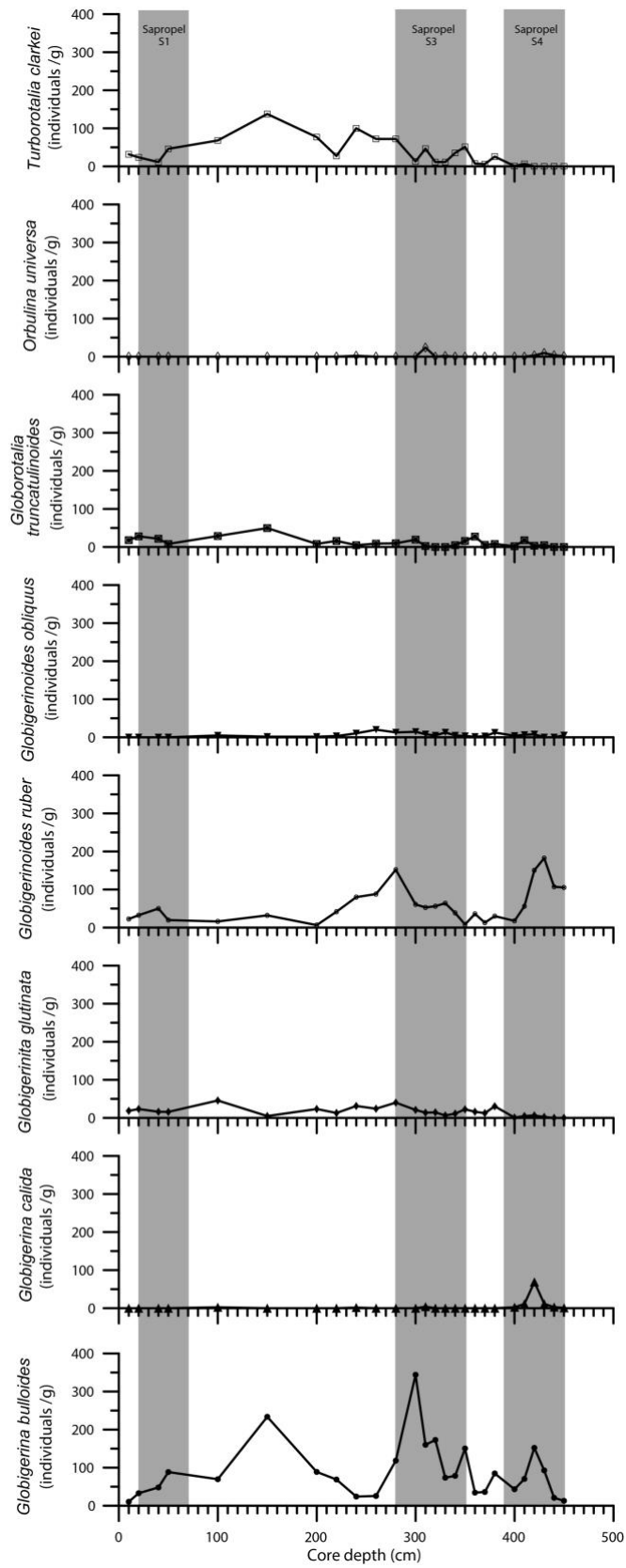


Figure 3. 4. Absolute abundance of planktonic foraminiferal species at core M70b-St#822.

Sapropel layers (gray color) are indicated.

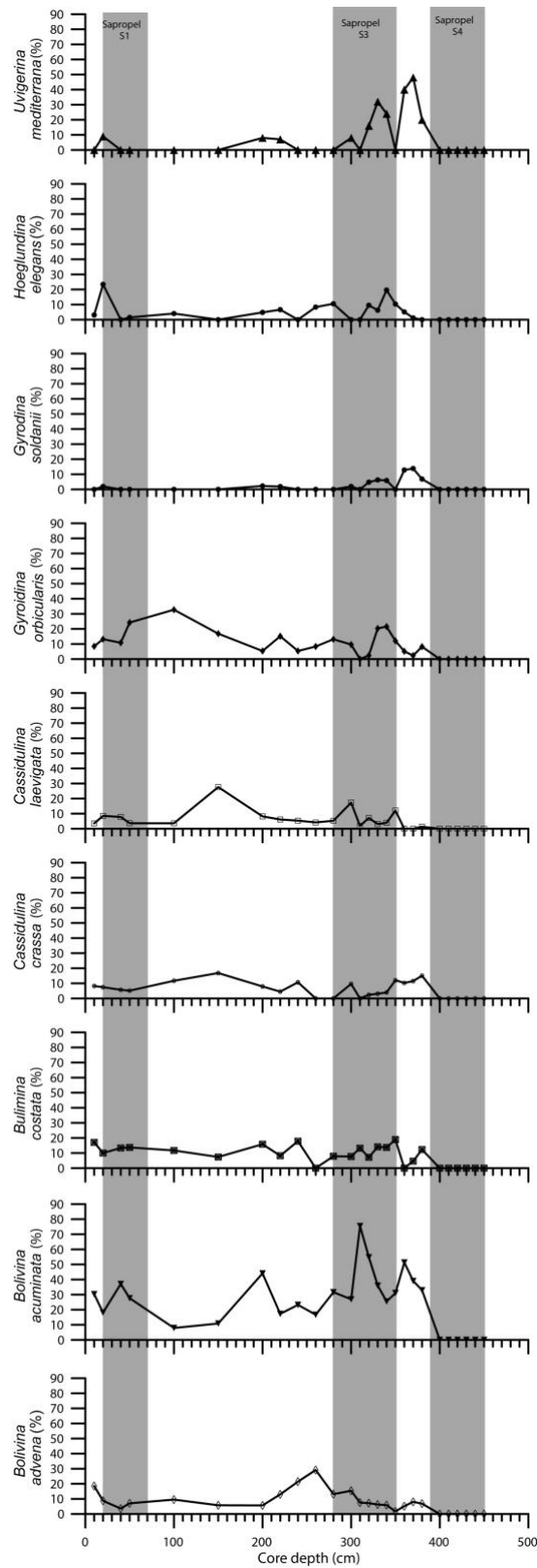


Figure 3. 5. Relative abundance of benthic foraminiferal species at core M70b-St#822.

Sapropel layers (gray color) are indicated.

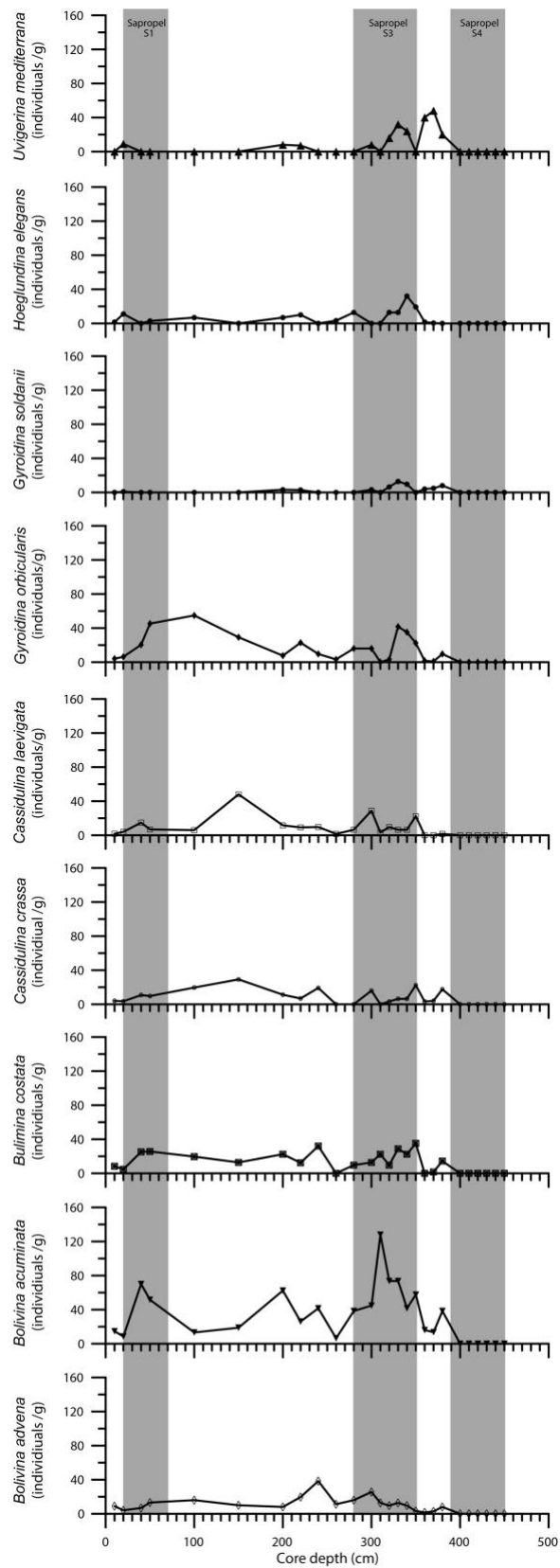


Figure 3. 6. Absolute abundance of benthic foraminiferal species at core M70b-St#822.

Sapropel layers (gray color) are indicated.

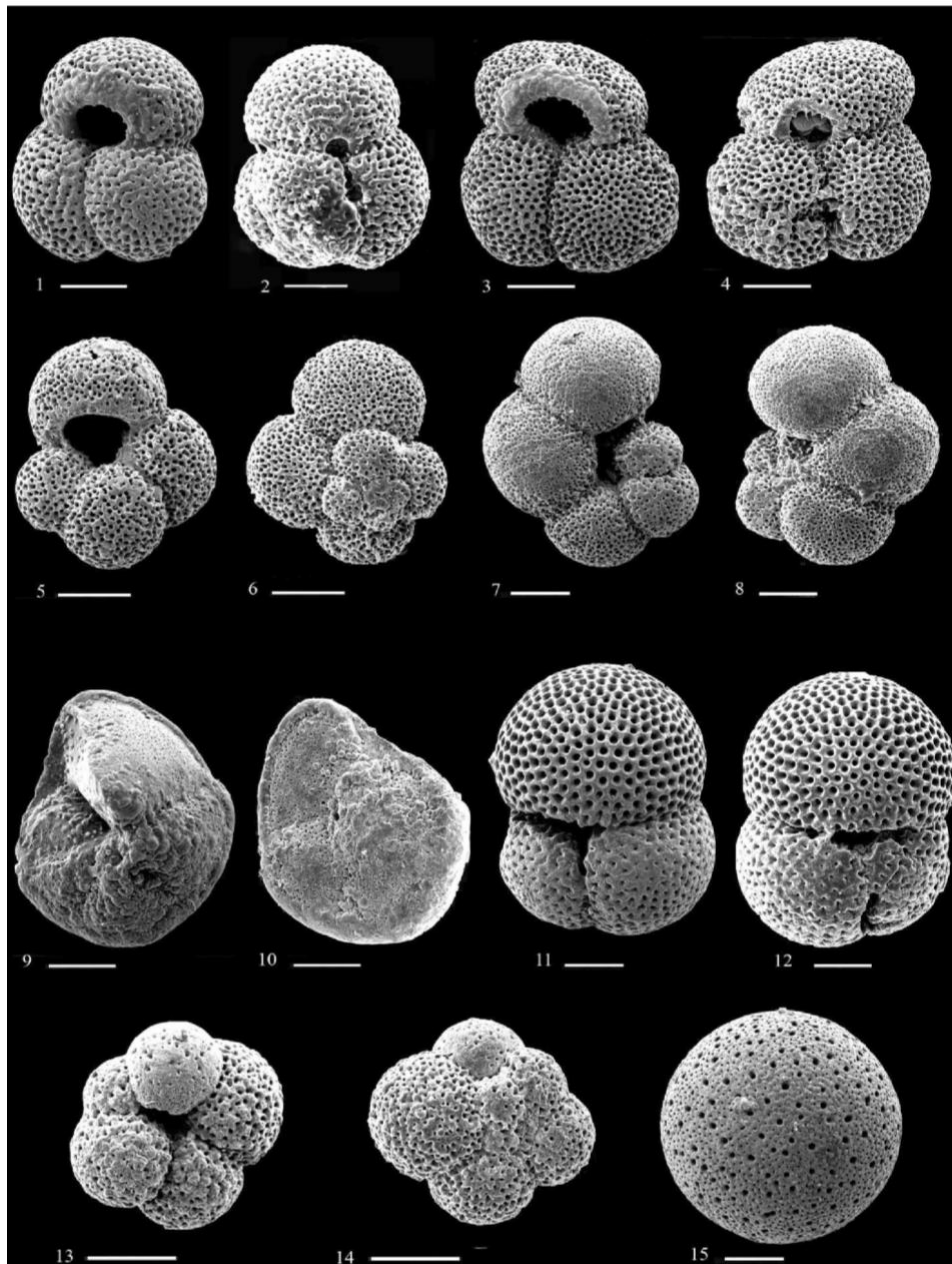


Figure 3. 7: SEM photomicrograph of some selected foraminifera. Species name is followed by depth in cm. Scale bar = 200 μ m for Figs. 1-10; 13-14, and = 150 μ m for Figs. 11-12, 15. 1-2 *Globigerinoides ruber* (D'Orbigny), 1839, 420 cm. 3-4 *Globigerinoides obliquus* Bolli 1957, 450 cm. 5-6 *Globigerina bulloides* D'orbigny, 1826, 450 cm. 7-8 *Globigerina calida* Parker 1962, 440 cm. 9-10 *Globorotalia truncatulinoides* (d'Orbigny), 1839, 410 cm. 11-12 *Globigerinoides immaturus* Le Roy 1939, 420 cm. 13-14 *Turborotalia clarkei* Rogl & Bolli 1973, 410 cm. 15 *Orbulina universa* D'orbigny, 1839, 430 cm.

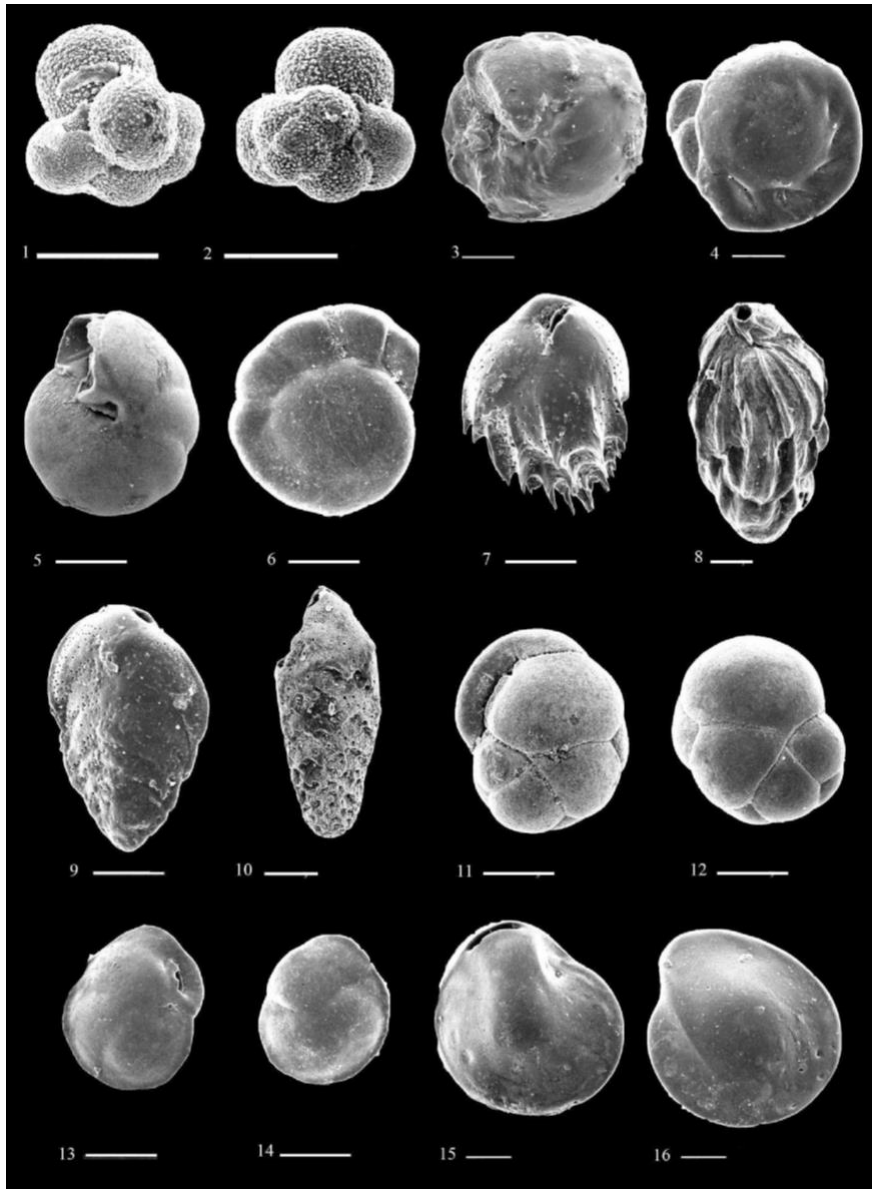


Figure 3. 8: SEM photomicrograph of some selected foraminifera. Species name is followed by depth in cm. Scale bar = 200 μm for Figs. 1-7, 9-14, and = 150 μm for Figs. 15-16, and = 100 μm for Fig. 8. 1-2 *Globigerinita glutinata* (Egger), 1895, 410 cm. 3-4 *Gyroidina soldanii* d'Orbigny, 1826, 410 cm. 5-6 *Gyroidina orbicularis* d'Orbigny, 1826, 410 cm. 7 *Bulimina costata* d'Orbigny, 1852, 340 cm. 8 *Uvigerina mediterranea* Hofker, 1932, 370 cm. 9 *Bolivina acuminata* (Natland), 1946, 380 cm. 10 *Bolivina advena* Cushman var. *striatella* Cushman, 1925, 380 cm. 11-12 *Cassidulina crassa* d'Orbigny, 1839, 380 cm. 13-14 *Cassidulina laevigata* d'Orbigny, 1826, 200 cm. 15-16 *Hoeglundina elegans* d'Orbigny, 1826, 380 cm.

Chapter 4. Conclusions

Within this thesis, compound-specific isotope signature (Carbon and hydrogen) of long-chain n-alkanes from marine sediment core ODP site 967B and foraminiferal assemblages from marine sediment core M70b-St#822 were scrutinized in order to understand the hydrological cycle system effect of the North African monsoon since the Last Glacial Maximum (LGM) on terrestrial ecosystems of North Africa and effect of humid periods on marine ecosystems of Eastern Mediterranean Sea. In particular the focus is placed on the drastic regime shift from arid conditions of LGM to the humid and vegetated conditions of the mid-Holocene in North Africa. $\delta D_{n\text{-alkanes}}$ and $\delta^{13}C_{n\text{-alkanes}}$ measurements agree well with previous results which, $\delta D_{n\text{-alkanes}}$ co-varied with insolation change response to orbital forcing. Depleted $\delta D_{n\text{-alkanes}}$ were found from deglaciation to middle Holocene, suggesting increased precipitation during the African Humid Period (AHP) caused by northward migration of the Intertropical Convergence Zone (ITCZ). $\delta^{13}C_{n\text{-alkanes}}$ at Site 967 did not show a trend in harmony with $\delta D_{n\text{-alkanes}}$ but exhibiting millennial-scale variations ranging from -25.9‰ to -33.2‰ . These $\delta^{13}C_{n\text{-alkanes}}$ values are consistently C4 grass dominated environment in the watershed area of River Nile since LGM even during AHP. The greening of Sahara Desert was dominated by C4 plants during AHP coupled with formation of Sapropel layers in Eastern Mediterranean Sea fueled by African monsoon changes in North Africa. The discharge of freshwater into Mediterranean Sea via Nile River and Wadi connective system in Sahara Desert could alter marine ecosystems in EMS. The focus is placed on the drastic changes of foraminiferal assemblages during Sapropels (AHPs) and non-sapropelic layers (dry periods). These isotopic excursions of *Globigerinoides ruber* are interpreted as a result of enhanced freshwater discharge caused by increased precipitation and terrigenous input in watershed area of Nile River. Increased %*Globigerina bulloides*, a high productivity indicator, suggest nutrient rich condition. Benthic foraminiferal assemblages were employed to reconstruct oxygen conditions in pore water. Notable species turnover to deep infauna species, dysoxic indicator, were observed in sapropel layers. Low species diversities of both planktic and benthic foraminifera are likely due to thermocline shallowing by enhanced freshwater discharge and dysoxic bottom water caused by high productivity during sapropel layer formations.