

A precise search for drastic temperature shifts of the past 40,000 years in southeastern Europe

Guillemette Ménot¹ and Edouard Bard¹

Received 26 January 2012; revised 12 April 2012; accepted 13 April 2012; published 7 June 2012.

[1] Climatic models simulate abrupt oscillations that are associated, in the North Atlantic, with Dansgaard-Oeschger and Heinrich events. However, the geographic extension of temperature anomalies is largely uncontrolled due to the scarcity of quantitative records of sufficient time resolution on the European continent. Here, we propose, based on a recently developed temperature proxy (TEX₈₆), a reconstruction of millennial-scale temperature variations in a Black Sea sediment archive for the last 40,000 years. Prior to any paleoclimatological interpretations the effects of potential bias, such as seasonality and depth of maximum export production on temperature reconstructions, are considered for the Black Sea. Based on previous work, a tentative method for temperature corrections, taking into account varying terrigenous inputs, is further proposed. Reconstructed temperatures for Black Sea core MD042790 were remarkably stable during the last glacial. However, significant shifts toward lower temperatures of 2°C occurred during Heinrich events 2 and 3. The deglaciation displayed a temperature increase of 10°C consistent with neighboring European reconstructions. A Younger Dryas cooling of approximately 5–6°C was clearly expressed in the reconstruction. In notable contrast to observations from nearby archives, Heinrich events imprinted our glacial temperature record consistent with a strong reorganization of oceanic circulation and a large spreading of the temperature anomaly from the North Atlantic toward the southeast. Furthermore, in contrast to high-latitude records, our Black Sea record lacks the signatures of Dansgaard-Oeschger interstadials, suggesting a decreasing temperature gradient away from the North Atlantic.

Citation: Ménot, G., and E. Bard (2012), A precise search for drastic temperature shifts of the past 40,000 years in southeastern Europe, *Paleoceanography*, 27, PA2210, doi:10.1029/2012PA002291.

1. Introduction

[2] Only a few data sets provide temperature reconstructions on continents at a sufficient time resolution for documenting Heinrich and Dansgaard-Oeschger variability [Fletcher *et al.*, 2010; Hemming, 2004; Voelker *et al.*, 2002], in contrast with marine records of temperature changes in the North Atlantic region [Kucera *et al.*, 2005]. Among continental records, the oxygen isotopic composition of speleothems provides a reconstruction of high-resolution variability over the last glacial on the Eurasian continent [Fleitmann *et al.*, 2009; Genty *et al.*, 2006; Wang *et al.*, 2001]. Since the interpretation of such a signal is not straightforward, the isotopic signal is a composite of temperature

and precipitation amount and origin [LeGrande *et al.*, 2006]. Pollen sequences within lakes or continental margins allow quantitative reconstructions of temperature through transfer functions or inverse modeling. Differentiation between temperature and precipitation signals, however, is not straightforward either [Grimm *et al.*, 1993, 2006]. Reviews of temperature changes have been performed for key periods such as the Younger Dryas or for the Last Glacial Maximum (among others [Kageyama *et al.*, 2006; Kuhlemann *et al.*, 2008; Peyron *et al.*, 1998; Wu *et al.*, 2007]). However, similar syntheses are not available for abrupt events of the last glacial. Quantitative reconstructions on continents, during this time period, are scarce, especially in central and eastern Europe [Ampel *et al.*, 2010; Fletcher *et al.*, 2010; Voelker *et al.*, 2002].

[3] Sea surface temperatures are often reconstructed, using multiple proxies, for various marine settings [Kucera *et al.*, 2005]. In the Mediterranean Sea, due to extreme salinity contrasts, their use is hampered by a lack of well-established biomarkers [Essallami *et al.*, 2007; Ferguson *et al.*, 2008; Kucera *et al.*, 2005; Sikes *et al.*, 1991; Ternois *et al.*, 1997]. The Black Sea has been deeply influenced by salinity or hydrological changes. Therefore, thus far, a quantitative

¹CEREGE, Aix-Marseille University, Collège de France, CNRS, IRD, Aix en Provence, France.

Corresponding author: G. Ménot, CEREGE, Aix-Marseille University, Collège de France, CNRS, IRD, 13545 Aix en Provence Cedex 4 F-13545, France. (menot@cerege.fr)

Copyright 2012 by the American Geophysical Union.
0883-8305/12/2012PA002291

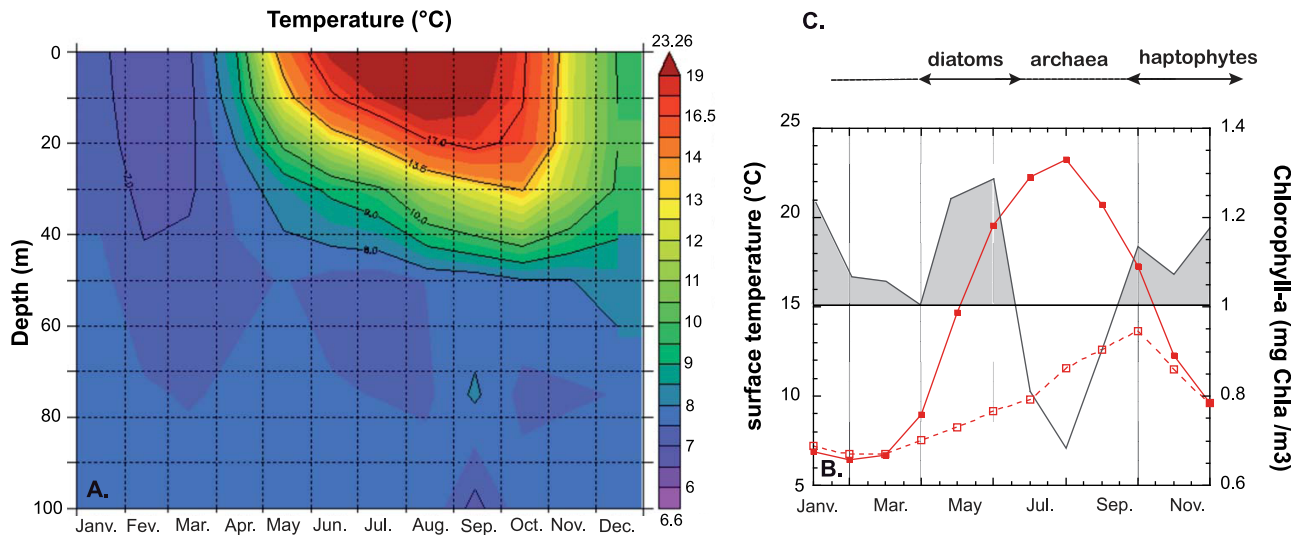


Figure 1. Black Sea present-day hydrology. (a) The annual cycle of water temperature variability in the upper 100 m from climatic monthly means in the Black Sea at the core location. (b) Monthly surface temperature variations at the surface (solid red line) and at 30 m (dashed red line), as well as the monthly chlorophyll *a* concentration (solid black line). (c) The succession of the planktonic community within the year (constructed after *Leider et al.* [2010], *Menzel et al.* [2006], and *Sur et al.* [1996]). Climatic data sets were obtained from *Boyer et al.* [2006].

temperature reconstruction for this basin has been unavailable [*Bahr et al.*, 2008]. To avoid the limitations of conventional temperature proxies, a recently developed index that is based on the abundance of water column produced tetraethers, the TEX₈₆ index [*Schouten et al.*, 2002], was used for this study. The use of the TEX₈₆ index in lacustrine and marine environments is supported by mesocosm experiments that underlie the lack of influence of salinity on this proxy [*Kim et al.*, 2010, 2008; *Powers et al.*, 2004, 2010; *Wuchter et al.*, 2005].

[4] For this work, we took advantage of the unique setting of the Black Sea as an enclosed basin in southeastern Europe in order to document temperatures since the last glacial period using the reconstruction of water column surface temperatures based on a newly developed tetraether paleothermometer. Interpretation of the TEX₈₆ record in terms of summer sea surface temperature, based on studies on modern ecology and hydrology of the Black Sea, is discussed. Finally, the clear signatures for Heinrich events 2 and 3 and the lack of imprints for Dansgaard-Oeschger events are put into a perspective of climatological reorganization on the European continent during abrupt events throughout the last glacial.

2. Material and Methods

2.1. Study Area and Core Location

[5] The Black Sea is the world's largest anoxic basin. It is linked to the Mediterranean Sea through two sills and switches between an endoreic basin and/or a sea connected to the global ocean, depending on sea level. Due to its unique setting, modern hydrology and planktonic abundance and production within the Black Sea have been intensively studied. Water column hydrology within the Black Sea is characterized by strong vertical stratification, with vertical

mixing limited by freshwater at the surface, creating strong anoxia beginning at a water depth of 100 m. Chemical stratification accompanies thermal stratification, resulting in a homogeneous deep reservoir with a constant temperature of 8°C (Figure 1a). The annual repartition of surface temperature shows a strong seasonality closely linked to incoming solar radiation (Figure 1).

[6] The northwestern shelf of the Black Sea is heavily influenced by the riverine input of nutrients, mainly from the Danube River but also from the Dnieper and the Dniester Rivers. Inflowing nutrients are redistributed along the western coast by a rim [*Humborg et al.*, 1997; *Morgan et al.*, 2006; *Özsoy and Ünlüata*, 1997]. Therefore, productivity is linked to nutrient loads in the photic zone that are controlled by fluvial inputs with peak floods during spring and/or by intense mixing by convection in the first 100 m of the water column during cold months [*Sur et al.*, 1996]. In early summer thermal stratification prevents photosynthetic blooms once nutrients are consumed (Figure 1b). The observed seasonal pattern of chlorophyll distribution in the open Black Sea, indicating phytoplanktonic productivity, fits a bimodal curve for the seasonal dynamics typical for temperate waters with high values during spring and winter [*Yunev et al.*, 2002] that are also observed in the Adriatic Sea [*Leider et al.*, 2010] or the eastern Mediterranean Sea [*Menzel et al.*, 2006].

[7] Different photosynthetic populations are associated with productivity maxima. Diatoms are associated with the spring peak, whereas the autumn peak is mainly composed of haptophytes [*Cokacar et al.*, 2001; *Sur et al.*, 1996] (Figure 1c). Between spring and autumn a mixed assemblage develops above the seasonal thermocline and is associated with a deep chlorophyll maximum [*Morgan et al.*, 2006; *Oguz and Merico*, 2006]. In the 1990s, Archaeal plankton has been revealed as being ubiquitous and abundant prokaryotes in the ocean [*Karner et al.*, 2001] in coastal

waters [DeLong, 1992] and in freshwater environments [Keough et al., 2003; Powers et al., 2004]. Specifically, in the nearshore waters of the northwestern Black Sea, Crenarchaeota and Euryarchaeota were recently found to constitute an important component of the coastal prokaryotic planktonic community [Stoica and Herndl, 2007]. In the Black Sea and elsewhere Archaea are particularly abundant in environments less favorable for phytoplankton both spatially (i.e., in settings characterized by high particule loads or deeper in the water column) and temporally (i.e., after blooms of other species, when nutrients are less abundant) [Huguet et al., 2007; Karner et al., 2001; Lopes dos Santos et al., 2010; Menzel et al., 2006; Stoica and Herndl, 2007].

[8] Hydrological and climatological histories of the Black Sea have gained considerable interest when the hypothesis of its catastrophic flooding by Mediterranean waters and its associated abrupt level rise at the early Holocene was proposed [Ryan et al., 1997]. Most studies, however, on the past behavior of the Black Sea have focused on its marine history (i.e., the last 9,000 years) [Soulet et al., 2011a]. Only recently have studies considered hydrological properties on a longer time scale [Bahr et al., 2006; Kwiecien et al., 2009; Major et al., 2002; Soulet et al., 2011b]. Since the catchment of this basin drains a large part of southeastern Europe through the Dnieper and Danube Rivers, its sedimentary archives are expected to integrate a regional climatic signal. In 2004, the ASSEMBLAGE cruise of the R/V *Marion Dufresne* retrieved large cores in the basin providing high-resolution climatic sequences. Core MD042790 (44°13'N, 30°60'E, 358 m water depth) was collected on the direct axis of the Danube River at 130 km of the actual coastline.

[9] Since reservoir ages in the basin vary significantly due to complex hydrology, establishing the chronology of sedimentary sequences in cores obtained from the Black Sea is a major challenge. A separate paper is dedicated to chronology and to establishment of core MD042790 age model by tuning of high-resolution data sets to the Hulu Cave speleothem record [Soulet et al., 2011b].

2.2. Extraction and Purification of Organic Compounds

[10] For lipid analysis, 1 to 5 g of sediment was extracted with the accelerated solvent extraction method (ASE 200 system, Dionex, California, USA) at 120°C and 100 bars, using dichloromethane/methanol (90:10 v/v). The total lipid extract was subsequently separated into polar and nonpolar fractions using columns packed with Al₂O₃ and hexane/dichloromethane (9:1, v/v) or dichloromethane/methanol (1:1, v/v) as eluents, respectively. Prior to injection, the polar fraction was filtered through a 0.45 μm, 4 mm diameter PTFE filter.

2.3. GDGT Measurements: The TEX₈₆ and BIT Indexes

[11] For the quantification of intact GDGTs, samples were analyzed at CEREGE by high-performance liquid chromatography/atmospheric pressure chemical ionization mass spectrometry (HPLC/APCI-MS) using positive ions on a HP LCMS1100 Series (Hewlett Packard, USA). Analytical conditions were similar to those of Hopmans et al. [2000]: a Prevail Cyano column (150 mm × 2.1 mm, 3 μm) was used with 99:1 hexane:propanol (vol:vol) as the eluent. After the first

5 min, over the next 24.5 min at a flow rate of 0.2 ml/min, the eluent increased by a linear gradient up to 1.4% isopropanol.

[12] Scanning was performed in single ion monitoring (SIM) mode. SIM was set to scan the five [M + H]⁺ ions of the GDGTs and the three [M + H]⁺ ions of the branched tetraethers. Similar to the approach proposed by Huguet et al. [2006], concentrations of individual GDGT were determined by relating chromatogram peak areas to the concentration of the internal standard C46 GDGT.

[13] The TEX₈₆ ratio was calculated according to Schouten et al. [2002]. Then, the Branched and Isoprenoid Tetraether (BIT) index, a proxy for soil versus marine organic matter input to sediments, was calculated per Hopmans et al. [2004]. Our analytical methodology was tested in the framework of an international laboratory comparison, and our results were found to compare favorably with results from other laboratories (with a standard deviation of 1.8% and 3.3% for BIT values greater and lower than 0.4 and 0.02, respectively; and a standard deviation of 1.9% and 0.3% for TEX₈₆ values close to 0.4 and 0.7, respectively [Schouten et al., 2009]). To ensure similar relative ionization efficiencies for the isoprenoid GDGT crenarchaeol and branched GDGTs throughout sample analyses, standard samples with known BIT and TEX indexes were analyzed at regular intervals. All samples (305) were measured at least twice. The mean standard deviation was 0.004 for TEX₈₆ and 0.006 BIT units of duplicate runs respectively, which corresponded to 0.2 to 0.3°C, depending on the chosen calibration data set for TEX₈₆. The values are consistent with the expected analytical error [Schouten et al., 2009].

3. Results and Discussion

3.1. The Black Sea Temperature Tetraether-Based Record

[14] The reconstructed temperatures derived from TEX₈₆ in core MD042790 vary between 15 and 4°C. The last glacial (i.e., between 15 and 40 kyr) was remarkably stable as compared to the deglaciation with an attenuated variability surrounding a low mean temperature (6.5 ± 1.2°C versus 12.2 ± 3.5°C for the two periods, respectively). Despite this low variability, significant shifts toward lower temperatures of 2°C in amplitude appeared during Heinrich events 2 and 3 (Figure 2). A plateau of high temperatures between 9 to 15 kyr was marked by a shift of 6°C toward lower values during the Younger Dryas (Figure 2b).

3.2. Potential Biases for the Tetraether Temperature Record

[15] *The influence of terrestrial input.* Given its location close to the mouth of both the Danube and the Dnieper Rivers, the sedimentary record of core MD042790 is prone to heavy influence by soil organic terrestrial inputs. Down-core fluctuations of organic matter composition were recorded by means of the BIT index, which displayed variations between 0.01 and 0.6, with a decreasing trend from 40 kyr toward the top of the record. Based on the distribution of GDGTs for the equatorial Atlantic Ocean region, Weijers et al. [2006] estimated no significant influence of organic matter input on temperature reconstructions within the error bars for BIT between 0.2 and 0.3 and an influence larger than 2°C for BIT values greater than 0.4. Following their approach, we

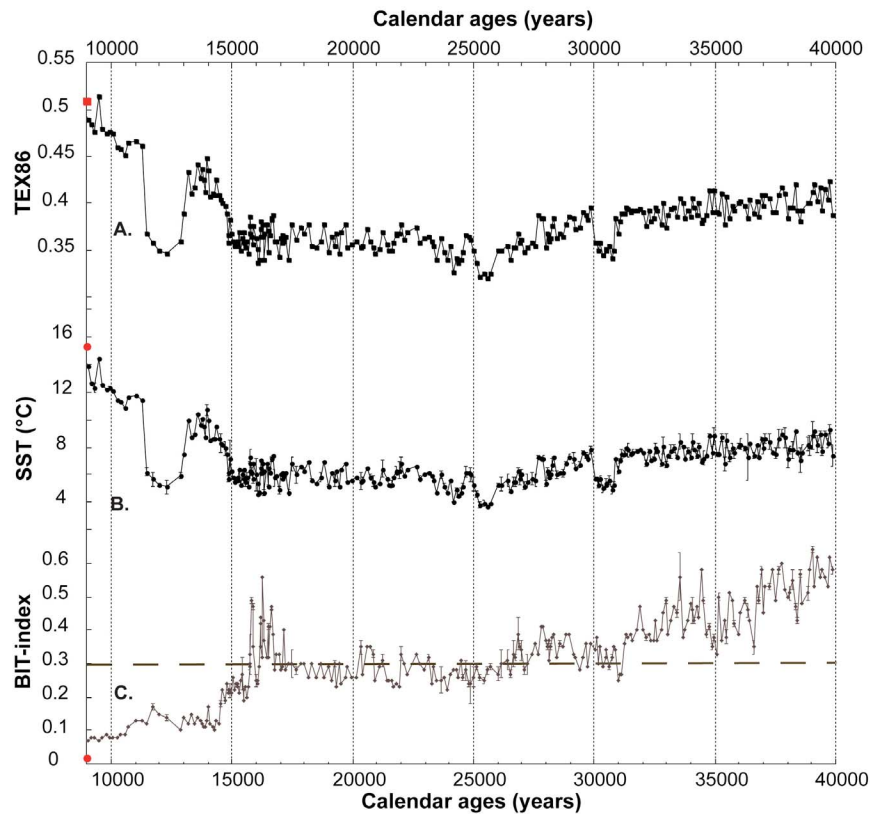


Figure 2. GDGT temperatures and terrestrial proxies. (a) TEX_{86} index variations through time. (b) Reconstructed SSTs based on the calibration data set from Powers *et al.* [2010] for the lacustrine portion based on Schouten *et al.* [2002] for marine core top sediments. Error bars on the indexes correspond to two standard deviations for replicated measurements. Errors were propagated on temperature values reconstructed using each equation. (c) BIT index variations versus time.

calculated a temperature deviation associated with the input of terrestrial material in marine sediments using a binary mixing model between two end-members in GDGT distributions: a marine end-member based on core top sediment samples for core MD042790, and a soil end-member corresponding to midlatitude to high-latitude soils selected from the database of Weijers *et al.* [2006] (Figures 3). Going one step further, we propose a correction for the “artificial warming” associated with the BIT record of MD042790, taking into account the equation derived from the previous mixing model. The derived correction is $\sim -4^{\circ}\text{C}$, associated with pulses of the BIT index between 17 and 20 kyr as well as a progressive cooling of $\sim -2.5^{\circ}\text{C}$ from 27 to 40 kyr (Figure 4c). As illustrated by the comparison of the light gray and black curves in Figure 4c, the correction does not affect the overall pattern of the reconstructed temperature record.

[16] *Changes in Archaeal composition.* Shifts in the dominant population of Archaea between Euryarchaeota and Crenarchaeota could induce a bias in temperature reconstructions [DeLong, 1992; Turich *et al.*, 2007]. However, GDGT-0/Crenarchaeol values are lower than 0.8 along the entire record, and, therefore, typical for Group I Crenarchaeota [Blaga *et al.*, 2009; Liu *et al.*, 2009b; Schouten *et al.*, 2002; Turich *et al.*, 2007]. The GDGT distribution within

the lacustrine part of the Black Sea record shows no evidence of changes in Archaeal composition.

[17] *Archaeal production away from the photic zone.* The production of tetraethers deep within the water column [Karner *et al.*, 2001; Wuchter *et al.*, 2005] and/or within the first centimeter of sediment [Lipp and Hinrichs, 2009] could be a limitation when using the TEX_{86} index for paleothermometry. A potential impact of Archaeal production away from the photic zone needs to be tested, since the Black Sea is characterized by important bacterial communities in these two habitats [Morgan *et al.*, 2006; Stoica and Herndl, 2007]. In different environments sedimentary tetraethers were shown to reflect production in the upper part of the water column and at midlatitudes/low latitudes [Ho *et al.*, 2011; Richey *et al.*, 2011; Shintani *et al.*, 2011] and high latitudes [Shevenell *et al.*, 2011], and more precisely in the Mediterranean area [Castañeda *et al.*, 2010; Leider *et al.*, 2010]. A specific case for use in the Black Sea is validated by studies of the structure of epipelagic communities either through direct counting [Morgan *et al.*, 2006], comprehensive biomarker studies [Wakeham *et al.*, 2003], or DNA/RNA-based studies [Coolen *et al.*, 2007; Lin *et al.*, 2006]. Particular attention has been given to Archaea and their repartition in the water column [Coolen *et al.*, 2007; Wakeham *et al.*, 2004, 2003]. Both direct organism counting and biomarker studies have revealed a

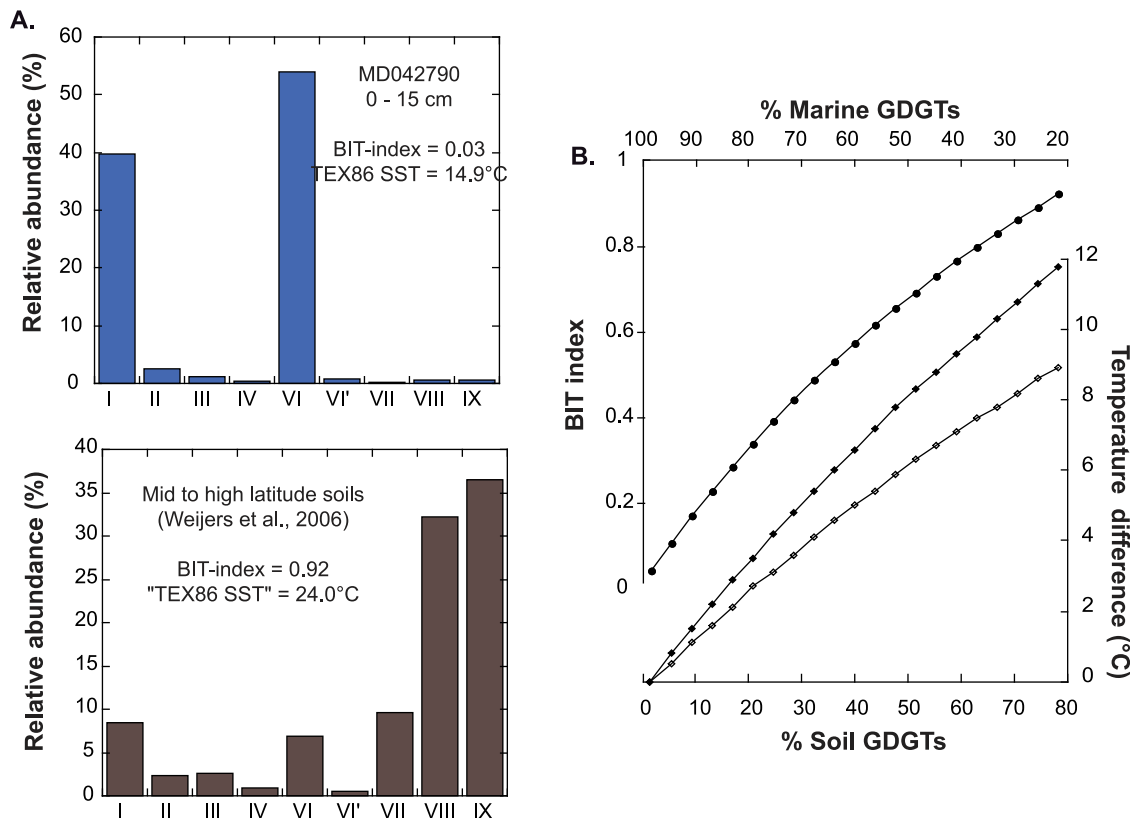


Figure 3. The influence of terrigenous material on temperature reconstructions based on a hypothetical binary mixing model (first proposed by *Weijers et al.* [2006]) for the midlatitude northern region composed of (a) an end-member representing the GDGT distribution in a marine sediment sample from the core top of MD042790 and an end-member representing an average GDGT distribution in midlatitudes to high latitudes. (b) The positive temperature difference from the original end-member value according to the TEX_{86} proxy using lacustrine (black diamonds, *Powers et al.* [2010]) and marine (empty diamonds, *Schouten et al.* [2002]) calibrations (with different mixing ratios).

strong concentration of Archaea in the first 100 m of the water column. A second maximum was observed for the methane oxidation zone at greater depths [*Wakeham et al.*, 2003]. An intense comparison of biomarker concentrations in sediment traps and at the surface of sediments indicated that this “deep GDGT signal” was not exported to the sediment. The lack of packaging prevents the exportation of small archaeal cells to the sedimentary surface [*Wakeham et al.*, 2003]. Therefore, the Black Sea sedimentary TEX_{86} record should reflect paleosurface or subsurface water conditions.

[18] *The seasonality of maximum export.* Shifts in the seasonality of production or maximum export could bias the temperature record. Core top temperature reconstruction is consistent with modern surface hydrology and archaeal growth in the first 30 m of the water column during summer in the Black Sea (Figure 1 and the red symbols in Figure 2), supporting results regarding the seasonality of GDGT maximum export production for midlatitude regions which are based on recent regional calibrations for the Adriatic Sea [*Leider et al.*, 2010] and additional work. However, little is known regarding the seasonality of production during the late Glacial. Inferred from differences in alkenones and tetraether-based paleothermometers, spring or autumn production for Archaea has been previously suggested for the eastern Mediterranean [*Castañeda et al.*, 2010]. However, as

a lake during the last glacial, the Black Sea is expected to exhibit midlatitude production patterns, with complete mixing of the water column twice a year in spring and winter [*Powers et al.*, 2010]. Therefore, similarly to present day, maximum Archaea export is expected during summer and no evidence supports a shift in the seasonality of maximum production during the last 40,000 years.

3.3. Millennial-Scale Temperature Variability During MIS3 on a Regional Scale

[19] *Last Glacial Maximum, Younger Dryas, and Heinrich stadials.* The Black Sea record shows a contrast of $\sim 10^\circ\text{C}$ between Holocene and glacial temperatures, in agreement with recent temperature reconstructions from the eastern portion of the Mediterranean basin [*Castañeda et al.*, 2010] and from the Marmara Sea [*Ménot and Bard*, 2010]. The amplitude is consistent with the temperature change encountered in the western Mediterranean and the North Atlantic basins (Figure 4) [*Bard et al.*, 2000; *Melki et al.*, 2009; *Pailler and Bard*, 2002; *Rouis-Zargouni et al.*, 2010].

[20] The Younger Dryas is characterized by a distinct minimum in temperature ($\Delta T \sim 6^\circ\text{C}$, Figure 4), similar to that observed in the western Mediterranean basin and in the Atlantic Ocean [*Bard et al.*, 2000; *Broecker et al.*, 2010]. The first temperature estimation for this interval, determined from

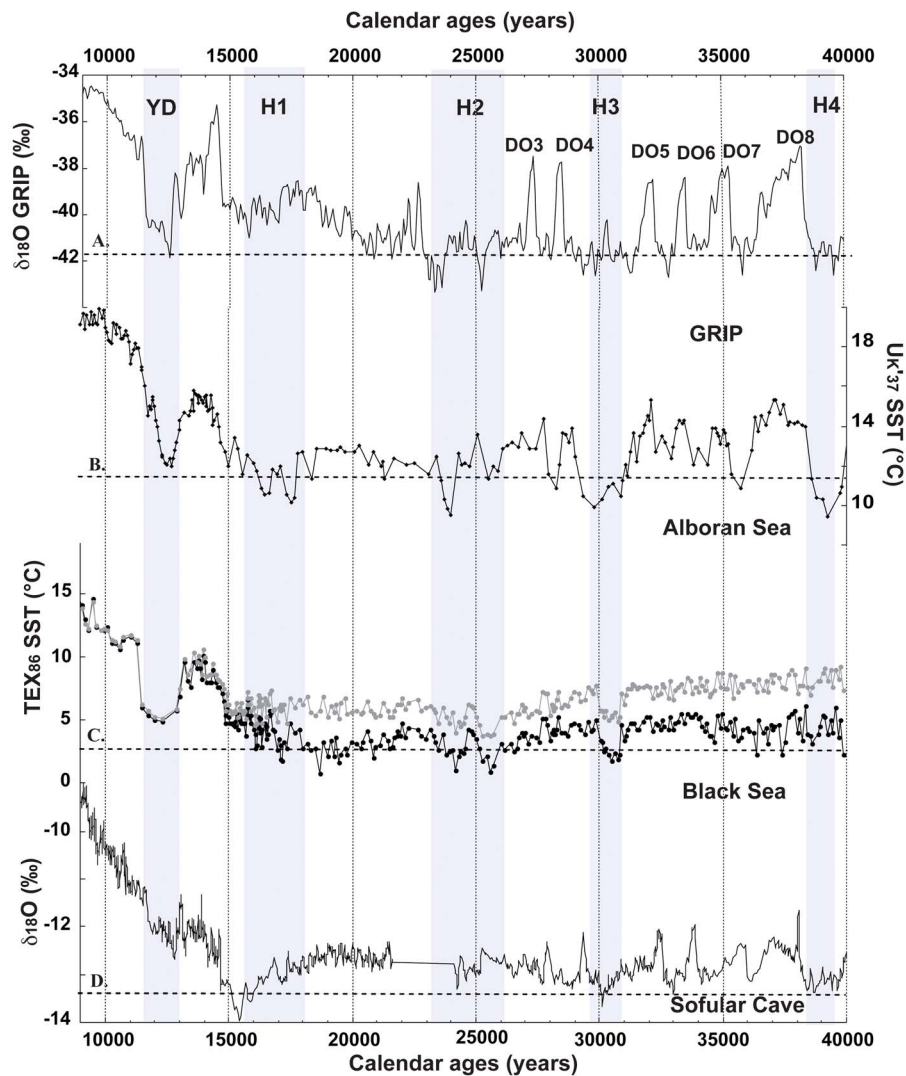


Figure 4. Millennial-scale variability during MIS3 on a regional scale. (a) The $\delta^{18}\text{O}$ GRIP record reflecting Greenland air temperatures [Johnsen *et al.*, 2001]. (b) Sea surface temperatures based on the alkenone record of core MD952043 in the Alboran Sea [Cacho *et al.*, 1999]. (c) Sea surface temperatures based on the GDGTs record of core MD042790. The BIT-corrected temperatures are shown by the black curve and symbols (this study). (d) The $\delta^{18}\text{O}$ record of Sofular cave, Turkey [Fleitmann *et al.*, 2009]. Gray areas indicate Heinrich events 1 to 4 in these records; numbers refer to Greenland interstadials or Dansgaard-Oeschger events (1 to 8).

thermally fractionated gases in polar ice, was recently revisited. Temperatures $\sim 10 \pm 4^\circ\text{C}$ lower during the YD than directly before or after were published for GISP2 [Grachev and Severinghaus, 2005; Severinghaus *et al.*, 1998]. In the Mediterranean Sea, the transitions to and from the Younger Dryas signature shows also a clear cooling, similar to that observed for the Atlantic Ocean and the western Mediterranean basin [Cacho *et al.*, 2001; Martrat *et al.*, 2004]. Thus far, the Younger Dryas is poorly marked or absent in the Marmara and Aegean Seas [Gogou *et al.*, 2007; Ménot and Bard, 2010]. Furthermore, reconstructed temperature Holocene-YD differences are either larger or similar between the western and eastern basins, depending on the selected proxy [Emeis *et al.*, 2000; Essallami *et al.*, 2007].

[21] The comparison of Younger Dryas temperature-sensitive proxies on continents leads to a complicated

picture due to uncertainties on the precise nature and sensitivity of the different records (among others [Lotter *et al.*, 2012]). The quantitative reconstructions of summer temperature for the interval have been mainly based on pollen, chironomids, beetle fossils, or glacier fluctuations [Atkinson *et al.*, 1987; Birks and Ammann, 2000; Isarin and Renssen, 1999; Lotter *et al.*, 2012; Renssen *et al.*, 2000]. Oxygen isotopic records from speleothems or in lacustrine deposits have been compared. However, their interpretation is not straightforward since they are influenced by temperatures, seasonality of precipitation, vapor sources, and ice volume [LeGrande and Schmidt, 2009; McDermott, 2004]. A clear shift toward more depleted values has been seen in Germany [von Grafenstein *et al.*, 1999] and in France [Genty *et al.*, 2006]. However, only a slight, or no, signal has been seen in Turkey [Fleitmann *et al.*, 2009], Israel [Bar-Matthews *et*

al., 2003], or Lebanon [Develle *et al.*, 2010]. In a similar manner, continental sequences of pollen assemblages or lake levels show a contrasting pattern [Allen *et al.*, 1999; Harrison *et al.*, 1996; Tarasov *et al.*, 2009].

[22] Glacial temperatures reconstructed from the Black Sea are stable but have three significant fluctuations toward low temperatures with values of approximately 3°C, simultaneous with Heinrich events 2 and 3. The structure of these events is surprisingly similar to that of Atlantic Ocean marine records with a paired event for Heinrich 2 and a single temperature depression for Heinrich 3 [Hemming, 2004] (Figure 4). The amplitude of the temperature changes is equivalent with that off of the Iberian Margin and in the western Mediterranean Sea [Martrat *et al.*, 2004; Pailler and Bard, 2002]. Despite the strong impact that these events have in marine records [Hemming, 2004], only a few studies have reported them with a sufficient time resolution for resolving abrupt events in continental archives, especially for Central to Eastern Europe [see Voelker *et al.*, 2002, Figure 1].

[23] *Dansgaard-Oeschger interstadials*. When comparing the glacial Black Sea temperature record to the reference climatic sequence of Greenland ice cores, a surprising feature in our record is the lack of warm events associated with Dansgaard-Oeschger interstadials (Figures 4a and 4d). Warming associated with Dansgaard-Oeschger interstadials in the north GRIP record are on the order of 10 to 15°C for DO 8 to 17 (i.e., beyond the time period covered by our lacustrine record), and no temperature reconstructions have been published, thus far, for the past 30 kyr [Huber *et al.*, 2006; Landais *et al.*, 2004]. In North Atlantic marine archives, warm events could be identified (not as well as cold events), although the amplitude of these events was small—2–4°C [Martrat *et al.*, 2007; Pailler and Bard, 2002].

[24] In continental archives, shifts associated with these events are recorded in speleothems [Fleitmann *et al.*, 2009; Wang *et al.*, 2001] and in a few pollen sequences [Fletcher *et al.*, 2010; Margari *et al.*, 2009; Müller *et al.*, 2011; Wohlfarth *et al.*, 2008]. For one of the few quantitative reconstructions for continents, an amplitude of 0.5 to 2°C was reported for the paleolacustrine sequence of Les Echets in western Europe [Ampel *et al.*, 2010]. A general characterization of the vegetation response to millennial-scale variability from pollen records on the European continent revealed, despite the influence of site specific factors related to altitude, topography, and microclimatic effects, a west-east contrast that could partly be attributed to the decreasing severity of the stadial condition away from the North Atlantic, as well as a north-south latitudinal gradient [Fletcher *et al.*, 2010].

3.4. The Pattern of Millennial-Scale Temperature Variability in Central Europe

[25] *Simulated millennial-scale temperature variability*. Millennial-scale climatic variability for the last glacial period, particularly the temperature anomalies associated with Dansgaard-Oeschger interstadials and Heinrich cold events are well reproduced using earth system models of intermediate complexity and fully coupled atmosphere-ocean general circulation models [Stouffer *et al.*, 2006]. Water hosing experiments using simplified ocean-atmosphere models show a nonlinear response for the North Atlantic

and for Greenland temperatures associated with different states of thermohaline circulation during the glacial period—a “warm” (i.e., interstadial interval), a “cold” (i.e., stadial interval), and an “off” (i.e., Heinrich event) state [Ganopolski and Rahmstorf, 2001; Rahmstorf, 2002; Rasmussen and Thomsen, 2004]. However, models provide generic ocean-atmosphere interactions thereby preventing direct comparison with temperature records. The histogram repartition of simulated temperatures for Greenland and for the North Atlantic illustrates multiple modes, and points out differences in the amplitude of the changes between the models. The differences are larger between Heinrich and glacial states and lower between Dansgaard-Oeschger interstadials and glacial states for North Atlantic sea surface temperatures than for Greenland temperatures (Figures 5a and 5b).

[26] Transitions to states of “cold” and “off” are driven by freshwater perturbations at high latitudes that induce some weakening of thermohaline circulation and a large cooling over the North Atlantic [Stouffer *et al.*, 2006]. Ice sheet dynamics and the release of heat stored in deep-sea reservoirs restore the “warm” oceanic circulation state. Sea ice has been found to play a major dynamic role due to its albedo effect (i.e., the atmosphere energy balance), and due to insulating the ocean from the atmosphere, thereby significantly reducing heat air-sea fluxes [Kaspi *et al.*, 2004]. Therefore, sea ice changes are a strong amplifier of small freshwater inputs and appear sufficient for reproducing warming associated with Dansgaard-Oeschger interstadials in Greenland without major changes to oceanic heat transport [Li *et al.*, 2005]. The hydrologic cycle at high and low latitudes is also enhanced by small temperature anomalies [Bigg *et al.*, 2011].

[27] The climate system is also influenced by stochastic noise, which is controlled by ice cap size that results in significant freshwater forcing in the North Atlantic. Larger ice sheets store more fresh water in ice caps or in subglacial lakes and are prone to rapidly shrink, thereby impacting North Atlantic circulation [Alley *et al.*, 2001]. Such an outcome leads to the temporal pattern seen throughout the last glacial period, which is well captured in paleorecords as the decreasing strength of signals associated with Dansgaard-Oeschger interstadials from the initiation of the last glacial period to its end [Fletcher *et al.*, 2010; Tzedakis *et al.*, 2004].

[28] The driving mechanisms behind DO and Heinrich (abrupt) climatic events under glacial conditions are reasonably well understood (see references above). However, the Younger Dryas and the Bølling-Allerød are different in their initiation since they represent cold and warm events, respectively, that occurred during deglaciation (i.e., forced by changes in insulation, atmospheric greenhouse gas concentrations, continental ice sheets and coastlines [Liu *et al.*, 2009a; Shakun *et al.*, 2012]). Questions remain as to how they compare in terms of amplitude and driving mechanisms with abrupt events during glacial conditions. The spatial distributions of the temperature anomalies associated with abrupt events show, in cases of both cooling and warming, a strong response centered at high latitudes in the North Atlantic and an attenuation while spreading southward and eastward (previous references as well as Liu *et al.* [2009a] and Stouffer *et al.* [2006]).

[29] Transient simulations have captured the succession of Heinrich event 1 and the Bølling-Allerød, and have identified

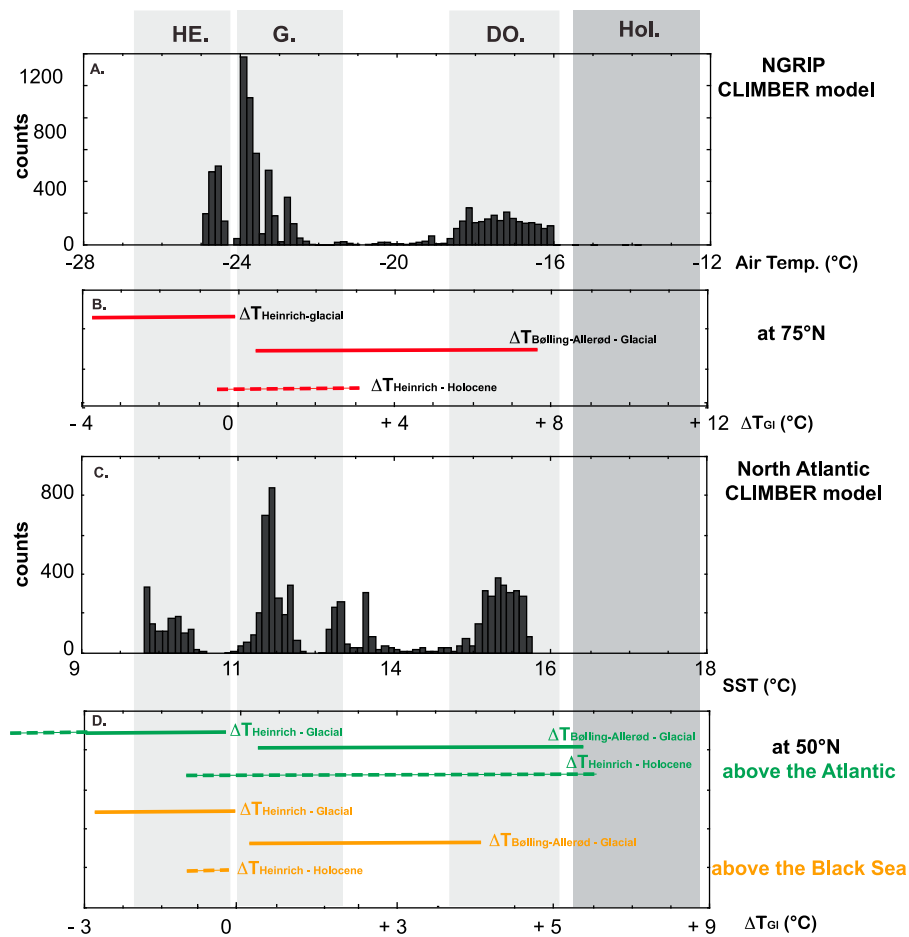


Figure 5. A comparison of modeled patterns of millennial-scale variability in Europe during MIS3 and the deglaciation. (a) Histograms of modeled NGRIP air temperature using the CLIMBER model [Bard, 2002; Ganopolski and Rahmstorf, 2001]. (b) Modeled temperature anomalies during abrupt events of the deglaciation at high latitudes (solid red lines, Liu *et al.* [2009a]; dashed red lines, Weaver *et al.* [2003]). (c) Histograms of modeled North Atlantic temperatures using the CLIMBER model [Bard, 2002; Ganopolski and Rahmstorf, 2001]. (d) Modeled temperature anomalies during abrupt events of deglaciation at midlatitudes are shown as green lines above the Atlantic Ocean and as orange lines above the Black Sea (solid lines, Liu *et al.* [2009a]; dashed lines, Weaver *et al.* [2003]). Each histogram has a fixed number of bins of 100. The letters H, G, HE, and DO represent the Holocene, the Glacial, a Heinrich event, and Dansgaard-Oeschger interstadial temperatures, respectively.

the mechanism driving the onset of the Bølling-Allerød as fresh water input at high latitudes in the Southern Hemisphere while Atlantic Ocean circulation is in an “off” mode [Liu *et al.*, 2009a; Weaver *et al.*, 2003]. The Younger Dryas temperature event is reproduced in response to an Atlantic Ocean meridional overturning circulation slowdown that is forced by fresh water discharge from the Fennoscandian and Laurentide Ice sheets [Lunt *et al.*, 2006; Tarasov and Peltier, 2005].

[30] The amplitude of temperature changes modeled for abrupt events during deglaciation greatly differ depending on models and assumptions regarding the source of fresh water discharge (Figures 5b and 5d) [Bigg *et al.*, 2011; Liu *et al.*, 2009a; Weaver *et al.*, 2003]. At high latitudes, the difference between Bølling-Allerød and Dansgaard-Oeschger temperatures is of the same amplitude as the shifts during the glacial period, while the amplitude of temperature change is larger for the transition to the Bølling-Allerød than for the transitions to the Dansgaard-Oeschger 50°N above the

Atlantic Ocean (Figures 5a–5c). However, the amplitude of the Bølling-Allerød transition is strongly attenuated at 50°N above the Black Sea (Figure 5d).

[31] *Reconstructed millennial-scale temperature variability in Europe and in the North Atlantic.* The simulated amplitudes of temperature changes should be compared with those of paleosequences. Due to the scarcity of high-resolution continental temperature sequences, both the amplitude and the extent of temperature anomalies associated with abrupt climatic changes over the last glacial for central Europe are poorly constrained. We selected archives of temperature or temperature-sensitive proxies. In Figure 6, histogram repartitions are compared with the modeled temperature series. The Greenland ice core and the Sofular cave sequences display two modes of oxygen isotopic values, with a larger dispersion for the second (Figures 6a and 6b). Due to the growth hiatus linked with the scarcity of precipitation, there is a few isotopic values associated with Heinrich events in the Sofular cave

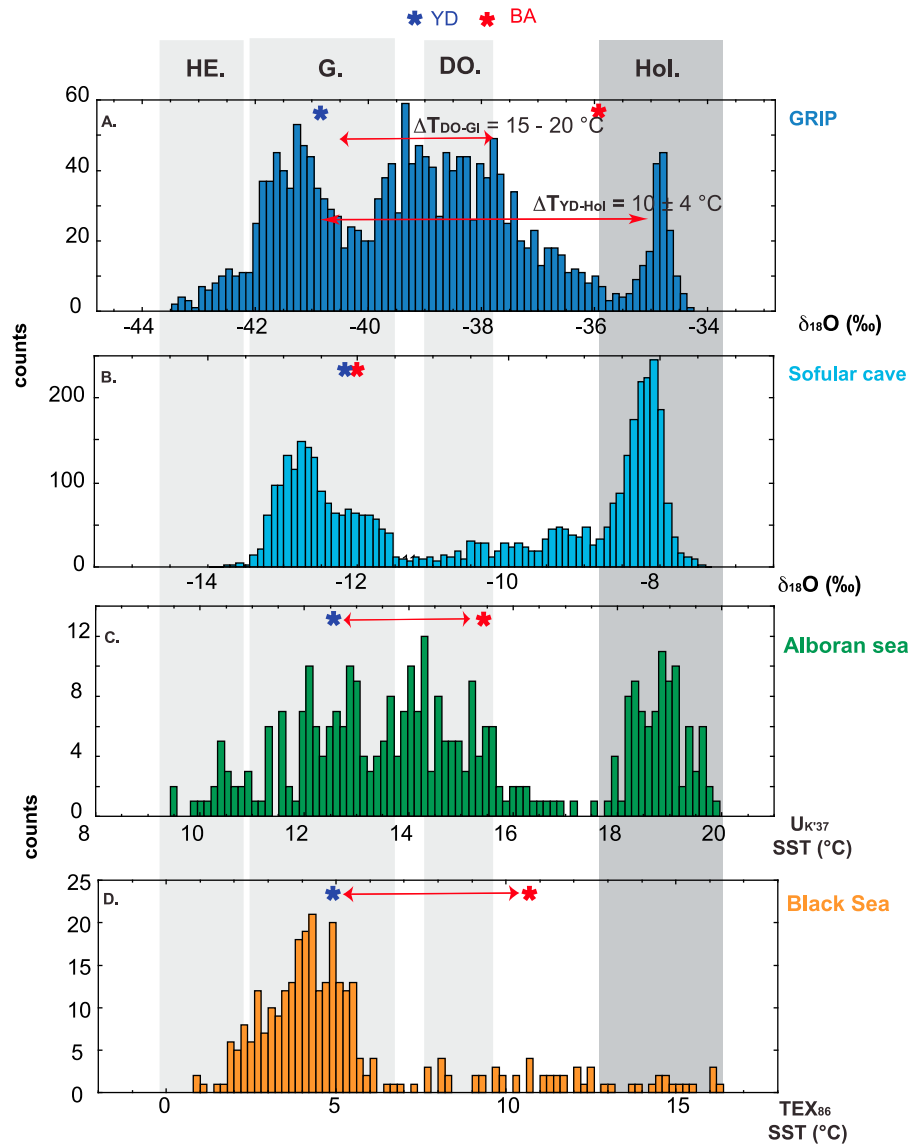


Figure 6. A comparison of the measured patterns of millennial-scale variability in Europe during MIS3—histograms of (a) the $\delta^{18}\text{O}$ GRIP record reflecting Greenland air temperatures [Johnsen *et al.*, 2001]; (b) the $\delta^{18}\text{O}$ record of Sofular cave, Turkey [Fleitmann *et al.*, 2009]; (c) sea surface temperatures based on the alkenone record of core MD952043 in the Alboran Sea [Cacho *et al.*, 1999]; and (d) sea surface temperatures based on the GDGT record of core MD042790. Each histogram has a fixed number of bins of 100. Note that the number of counts for each mode is dependant on the time resolution of the concerned record, which explains the high mode of Holocene values for the NGRIP ice core and for Sofular cave speleothems. The letters H, G, HE, and DO represent the Holocene, the Glacial, a Heinrich event, and Dansgaard-Oeschger interstadial temperatures, respectively. Red and blue stars represent the respective positions of the Bølling-Allerød and Younger Dryas values.

[Fleitmann *et al.*, 2009]. Furthermore, the contrast in $\delta^{18}\text{O}$ between Dansgaard-Oeschger and Holocene values is larger in ice cores than in speleothems (Figures 6a and 6b). The Black Sea displays a larger temperature amplitude than the modeled North Atlantic and the reconstructed Alboran Sea temperatures. Part of these differences in amplitude could depend on the proxy temperature calibration equations used for the TEX_{86} and U_{37}^{K} reconstructions (Figures 6c, 6d, and 5c). However, common features are, first, a distinct Heinrich mode in the temperature sequences, absent or weak in climate-dependant $\delta^{18}\text{O}$ sequences; and, then, an attenuation of the

Dansgaard-Oeschger mode between North Atlantic modeled temperatures and the Black Sea, where it is lacking.

[32] Since it shows distinct Heinrich and glacial modes (Figures 4c and 6d), the Black Sea temperature record for the last glacial is consistent with previously presented driving mechanisms. Heinrich events are characterized by thermohaline circulation changes [Keigwin and Lehman, 1994] and the associated temperature anomalies are transmitted through oceanic circulation. Strongly spread over the Atlantic Ocean, they also imprint Mediterranean region temperature records (Figures 6c and 6d). In contrast, the Dansgaard-Oeschger

interstadials that are clearly described in the Greenland record are partly attributed to sea ice forcing and have little impact on thermohaline circulation. The geographic spread of the temperature anomalies is, then, limited to the western border of the European continent [Ampel *et al.*, 2010] (Figures 6c and 6d). Signatures in paleoreconstructions based on speleothems and pollen sequences are likely linked with a reactivation of the hydrologic cycle, with small perturbations in oceanic circulation and temperature [Vellinga and Wood, 2002] (Figure 6b).

[33] *Abrupt events during the deglaciation in Europe and in the North Atlantic.* The temperature histogram repartition indicates that Bølling-Allerød values range close to Holocene values in the Black Sea in a similar manner to simulations (Figures 5d and 6d), whereas none of the other considered records exhibited such a large response. In parallel, in all of the records, the Younger Dryas temperature cluster within the glacial mode which is consistent with recent modeling. Therefore, the Bølling-Allerød/Younger Dryas temperature difference is large in the Black Sea record in contrast to other climatic sequences (Figure 6), but of the same order of magnitude in recent modeling experiments designed to reproduce Bølling-Allerød/Younger Dryas succession (Figure 5). The large offset is consistent with a major oceanographic reorganization and the wide geographical extension of the associated temperature anomaly [Liu *et al.*, 2009a].

4. Conclusions

[34] We present a continuous quantitative record of Black Sea surface temperatures on the basis of the TEX₈₆ proxy for the past 40,000 years.

[35] 1. Prior to deriving any paleoclimatic interpretations of the temperature record, the commonly cited bias, such as changes in the Archaeal composition, the production of GDGTs away from the photic zone, and the seasonality of maximum export were considered and discarded for the Black Sea. Furthermore, following the direction mentioned by Weijers *et al.* [2006], we have proposed a tentative method for temperature correction in order to take into account varying terrigenous inputs. The temperature reconstruction illustrates the reliability of the GDGT based organic biomarker proxy in reconstructing temperature variations of large and low amplitudes (i.e., from 10 to 2°C).

[36] 2. The last glacial period is characterized by low and stable temperatures close to 5°C. In contrast to other climate archives, Heinrich events imprint the glacial temperature background with shifts of 2–3°C toward lower values, synchronous with HE2 and HE3. By comparison, the signature of Dansgaard-Oeschger interstadials is absent in the Black Sea temperature record. Contrasting transmissions of warm and cold anomalies on the European continent are consistent with the various proposed mechanisms. Since Heinrich events are characterized by severe thermohaline circulation changes and, thus, the transmission of temperature anomalies throughout oceanic circulation, they are strongly spread over the Atlantic Ocean and also imprint on Mediterranean region temperature records. In contrast, the Dansgaard-Oeschger interstadials that are clearly described in the Greenland record are partly attributed to sea ice forcing and have little or no impact on thermohaline circulation. The geographic spread of temperature anomalies is then limited to the

western border of the European continent, and Dansgaard-Oeschger signatures are expressed in archives based on proxies that are influenced by precipitation and the hydrologic cycle [Fleitmann *et al.*, 2009; Müller *et al.*, 2011].

[37] 3. During deglaciation, the reconstructed temperature profile for the Black Sea displayed an abrupt warming of 10°C synchronous with the Bølling-Allerød and a return to glacial temperatures during the Younger Dryas. The amplitude of the warm/cold transition is large as compared to neighboring locations in continental or marine records, but on the same order of magnitude as temperature differences obtained by recent modeling experiments designed to reproduce the succession of the Bølling-Allerød/Younger Dryas [Liu *et al.*, 2009a]. Our Black Sea record provides a control point in southeastern Europe for testing the geographical extension of the temperature anomaly associated with simulations of coupled atmosphere-ocean general circulation models and it can validate the proposed mechanisms.

[38] **Acknowledgments.** We thank F. Rostek for sample extractions and G. Soulet for useful discussions regarding Black Sea hydrology. Core MD042790 was retrieved during a *Marion Dufresne* cruise in 2004 as part of the ASSEMBLAGE project conducted by G. Lericolais and funded by the European Commission (EVK3-CT-2002-00090). We would like to thank W. Flechter and two anonymous reviewers for their thoughtful reviews and constructive comments on this manuscript. Paleoclimate work at CEREGE is supported by the European Community (Project Past4Future) and the Collège de France.

References

- Allen, J. R. M., *et al.* (1999), Rapid environmental changes in southern Europe during the last glacial period, *Nature*, *400*, 740–743, doi:10.1038/23432.
- Alley, R. B., S. Anandakrishnan, and P. Jung (2001), Stochastic resonance in the North Atlantic, *Paleoceanography*, *16*(2), 190–198, doi:10.1029/2000PA000518.
- Ampel, L., C. Bigler, B. Wohlfarth, J. Risberg, A. F. Lotter, and D. Veres (2010), Modest summer temperature variability during DO cycles in western Europe, *Quat. Sci. Rev.*, *29*, 1322–1327, doi:10.1016/j.quascirev.2010.03.002.
- Atkinson, T. C., K. R. Briffa, and G. R. Coope (1987), Seasonal temperatures in Britain during the past 22,000 years, reconstructed using beetle remains, *Nature*, *325*(6105), 587–592, doi:10.1038/325587a0.
- Bahr, A., H. W. Arz, F. Lamy, and G. Wefer (2006), Late Glacial to Holocene paleoenvironmental evolution of the Black Sea, reconstructed with stable oxygen isotope records obtained on ostracod shells, *Earth Planet. Sci. Lett.*, *241*, 863–875, doi:10.1016/j.epsl.2005.10.036.
- Bahr, A., F. Lamy, H. W. Arz, C. O. Major, O. Kwiecien, and G. Wefer (2008), Abrupt changes of temperature and water chemistry in the late Pleistocene and early Holocene Black Sea, *Geochem. Geophys. Geosyst.*, *9*, Q01004, doi:10.1029/2007GC001683.
- Bard, E. (2002), Abrupt climate changes over millennial time scales: Climate shock, *Phys. Today*, *55*(12), 32–38, doi:10.1063/1.1537910.
- Bard, E., F. Rostek, J.-L. Turon, and S. Gendreau (2000), Hydrological impact of Heinrich events in the subtropical northeast Atlantic, *Science*, *289*, 1321–1324, doi:10.1126/science.289.5483.1321.
- Bar-Matthews, M., A. Ayalon, M. Gilmour, A. Matthews, and C. J. Hawkesworth (2003), Sea-land oxygen isotopic relationships from planktonic foraminifera and speleothems in the eastern Mediterranean region and their implication for paleorainfall during interglacial intervals, *Geochim. Cosmochim. Acta*, *67*, 3181–3199, doi:10.1016/S0016-7037(02)01031-1.
- Bigg, G. R., R. C. Levine, and C. L. Green (2011), Modelling abrupt glacial North Atlantic freshening: Rates of change and their implications for Heinrich events, *Global Planet. Change*, *79*(3–4), 176–192, doi:10.1016/j.gloplacha.2010.11.001.
- Birks, H. H., and B. Ammann (2000), Two terrestrial records of rapid climatic change during the glacial–Holocene transition (14,000–9,000 calendar years B.P.) from Europe, *Proc. Natl. Acad. Sci. U. S. A.*, *97*(4), 1390–1394, doi:10.1073/pnas.97.4.1390.
- Blaga, C., G.-J. Reichert, O. Heiri, and J. Sinninghe Damsté (2009), Tetraether membrane lipid distributions in water-column particulate matter

- and sediments: A study of 47 European lakes along a north-south transect, *J. Paleolimnol.*, 41(3), 523–540, doi:10.1007/s10933-008-9242-2.
- Boyer, T. P., J. I. Antonov, H. E. Garcia, D. R. Johnson, R. A. Locamini, A. V. Mishonov, M. T. Pitcher, O. K. Baranova, and I. V. Smolyar (2006), *World Ocean Database 2005*, vol. 60, *NOAA Atlas NESDIS*, edited by S. Levitus, 190 pp., U.S. Gov. Print. Off., Washington, D. C.
- Broecker, W. S., G. H. Denton, R. L. Edwards, H. Cheng, R. B. Alley, and A. E. Putnam (2010), Putting the Younger Dryas cold event into context, *Quat. Sci. Rev.*, 29, 1078–1081, doi:10.1016/j.quascirev.2010.02.019.
- Cacho, I., J. O. Grimalt, C. Pelejero, M. Canals, F. J. Sierro, J. A. Flores, and N. J. Shackleton (1999), Dansgaard-Oeschger and Heinrich event imprints in the Alboran Sea paleotemperatures, *Paleoceanography*, 14(6), 698–705, doi:10.1029/1999PA900044.
- Cacho, I., J. O. Grimalt, M. Canals, L. Sbaifi, N. J. Shackleton, J. Schonfeld, and R. Zahn (2001), Variability of the western Mediterranean Sea surface temperature during the last 25,000 years and its connection with the Northern Hemisphere climatic changes, *Paleoceanography*, 16(1), 40–52, doi:10.1029/2000PA000502.
- Castañeda, I. S., E. Schefuß, J. Pätzold, J. S. Sinninghe Damsté, S. Weldeab, and S. Schouten (2010), Millennial-scale sea surface temperature changes in the eastern Mediterranean (Nile River Delta region) over the last 27,000 years, *Paleoceanography*, 25, PA1208, doi:10.1029/2009PA001740.
- Cokacar, T., N. Kubilay, and T. Oguz (2001), Structure of *Emiliania huxleyi* blooms in the Black Sea surface waters as detected by SeaWiFS imagery, *Geophys. Res. Lett.*, 28(24), 4607–4610, doi:10.1029/2001GL013770.
- Coolen, M. J. L., B. Abbas, J. van Bleijswijk, E. C. Hopmans, M. M. M. Kuypers, S. G. Wakeham, and J. S. Sinninghe Damsté (2007), Putative ammonia-oxidizing Crenarchaeota in suboxic waters of the Black Sea: A basin-wide ecological study using 16S ribosomal and functional genes and membrane lipids, *Environ. Microbiol.*, 9(4), 1001–1016, doi:10.1111/j.1462-2920.2006.01227.x.
- DeLong, E. F. (1992), Archaea in coastal marine environments, *Proc. Natl. Acad. Sci. U. S. A.*, 89, 5685–5689, doi:10.1073/pnas.89.12.5685.
- Develle, A.-L., J. Herreros, L. Vidal, A. Surssock, and F. Gasse (2010), Controlling factors on a paleo-lake oxygen isotope record (Yammouneh, Lebanon) since the last glacial maximum, *Quat. Sci. Rev.*, 29, 865–886, doi:10.1016/j.quascirev.2009.12.005.
- Emeis, K.-C., U. Struck, H.-M. Schulz, R. Rosenberg, S. Bernasconi, H. Erlenkeuser, T. Sakamoto, and F. Martinez-Ruiz (2000), Temperature and salinity variations of Mediterranean Sea surface waters over the last 16,000 years from records of planktonic stable oxygen isotopes and alkenone unsaturation ratios, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 158(3–4), 259–280, doi:10.1016/S0031-0182(00)00053-5.
- Essalami, L., M. A. Sicre, N. Kallel, L. Labeyrie, and G. Siani (2007), Hydrological changes in the Mediterranean Sea over the last 30,000 years, *Geochim. Geophys. Geosyst.*, 8, Q07002, doi:10.1029/2007GC001587.
- Ferguson, J. E., G. M. Henderson, M. Kucera, and R. E. M. Rickaby (2008), Systematic change of foraminiferal Mg/Ca ratios across a strong salinity gradient, *Earth Planet. Sci. Lett.*, 265(1–2), 153–166, doi:10.1016/j.epsl.2007.10.011.
- Fleitmann, D., et al. (2009), Timing and climatic impact of Greenland interstadials recorded in stalagmites from northern Turkey, *Geophys. Res. Lett.*, 36, L19707, doi:10.1029/2009GL040050.
- Fletcher, W. J., et al. (2010), Millennial-scale variability during the last glacial in vegetation records from Europe, *Quat. Sci. Rev.*, 29(21–22), 2839–2864, doi:10.1016/j.quascirev.2009.11.015.
- Ganopolski, A., and S. Rahmstorf (2001), Rapid changes of glacial climate simulated in a coupled climate model, *Nature*, 409(6817), 153–158, doi:10.1038/35051500.
- Genty, D., et al. (2006), Timing and dynamics of the last deglaciation from European and North African $\delta^{13}\text{C}$ stalagmite profiles—Comparison with Chinese and South Hemisphere stalagmites, *Quat. Sci. Rev.*, 25, 2118–2142, doi:10.1016/j.quascirev.2006.01.030.
- Gogou, A., I. Bouloubassi, V. Lykousis, M. Arnaboldi, P. Gaitani, and P. A. Meyers (2007), Organic geochemical evidence of late Glacial-Holocene climate instability in the North Aegean Sea, *Paleogeogr. Palaeoclimatol. Palaeoecol.*, 256, 1–20, doi:10.1016/j.palaeo.2007.08.002.
- Grachev, A. M., and J. P. Severinghaus (2005), A revised $\pm 10 \pm 4^\circ\text{C}$ magnitude of the abrupt change in Greenland temperature at the Younger Dryas termination using published GISP2 gas isotope data and air thermal diffusion constants, *Quat. Sci. Rev.*, 24(5–6), 513–519, doi:10.1016/j.quascirev.2004.10.016.
- Grimm, E. C., G. L. Jacobson, W. A. Watts, B. C. S. Hansen, and K. A. Maasch (1993), A 50,000-year record of climate oscillations from Florida and its temporal correlation with the Heinrich events, *Science*, 261(5118), 198–200, doi:10.1126/science.261.5118.198.
- Grimm, E. C., W. A. Watts, G. L. Jacobson Jr., B. C. S. Hansen, H. R. Almqvist, and A. C. Dieffenbacher-Krall (2006), Evidence for warm wet Heinrich events in Florida, *Quat. Sci. Rev.*, 25(17–18), 2197–2211, doi:10.1016/j.quascirev.2006.04.008.
- Harrison, S. P., G. Yu, and P. E. Tarasov (1996), Late Quaternary lake-level record from northern Eurasia, *Quat. Res.*, 45, 138–159, doi:10.1006/qres.1996.0016.
- Hemming, S. R. (2004), Heinrich events: Massive late Pleistocene detritus layers of the North Atlantic and their global climate imprint, *Rev. Geophys.*, 42, RG1005, doi:10.1029/2003RG000128.
- Ho, S. L., M. Yamamoto, G. Mollenhauer, and M. Minagawa (2011), Core top TEX_{86} values in the south and equatorial Pacific, *Org. Geochem.*, 42, 94–99, doi:10.1016/j.orggeochem.2010.10.012.
- Hopmans, E. C., S. Schouten, R. Pancost, M. T. J. van der Meer, and J. S. Sinninghe Damsté (2000), Analysis of intact tetraether lipids in archaeal cell material and sediments by high performance liquid chromatography/atmospheric pressure chemical ionization mass spectrometry, *Rapid Commun. Mass Spectrom.*, 14, 585–589, doi:10.1002/(SICI)1097-0231(20000415)14:7<585::AID-RCM913>3.0.CO;2-N.
- Hopmans, E. C., J. W. H. Weijers, E. Schefuß, L. Herfort, J. S. Sinninghe Damsté, and S. Schouten (2004), A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids, *Earth Planet. Sci. Lett.*, 224(1–2), 107–116, doi:10.1016/j.epsl.2004.05.012.
- Huber, C., M. Leuenberger, R. Spahni, J. Flückiger, J. Schwander, T. F. Stocker, S. Johnsen, A. Landais, and J. Jouzel (2006), Isotope calibrated Greenland temperature record over Marine Isotope Stage 3 and its relation to CH_4 , *Earth Planet. Sci. Lett.*, 243(3–4), 504–519, doi:10.1016/j.epsl.2006.01.002.
- Huguet, C., E. C. Hopmans, W. Febo-Ayala, D. H. Thompson, J. S. Sinninghe Damsté, and S. Schouten (2006), An improved method to determine the absolute abundance of glycerol dibiphytanyl glycerol tetraether lipids, *Org. Geochem.*, 37, 1036–1041, doi:10.1016/j.orggeochem.2006.05.008.
- Huguet, C., A. Schimmelmarm, R. Thunell, L. J. Lourens, J. S. Sinninghe Damsté, and S. Schouten (2007), A study of the TEX_{86} paleothermometer in the water column and sediments of the Santa Barbara basin, California, *Paleoceanography*, 22, PA3203, doi:10.1029/2006PA001310.
- Humborg, C., V. Ittekkot, A. Cociasu, and B. v Bodungen (1997), Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure, *Nature*, 386, 385–388, doi:10.1038/386385a0.
- Isarin, R. F. B., and H. Renssen (1999), Reconstructing and modelling late Weichselian climates: The Younger Dryas in Europe as a case study, *Earth Sci. Rev.*, 48, 1–38, doi:10.1016/S0012-8252(99)00047-1.
- Johnsen, S. J., D. Dahl-Jensen, N. Gundestrup, J. P. Steffensen, H. B. Clausen, H. Miller, V. Masson-Delmotte, A. E. Sveinbjornsdottir, and J. White (2001), Oxygen isotope and paleotemperature records from six Greenland ice-core stations: Camp Century, Dye-3, GRIP, GISP2, Renland and NorthGRIP, *J. Quat. Sci.*, 16(4), 299–307, doi:10.1002/jqs.622.
- Kageyama, M., et al. (2006), Last glacial maximum temperatures over the North Atlantic, Europe and western Siberia: A comparison between PMP models, MARGO sea-surface temperatures and pollen-based reconstructions, *Quat. Sci. Rev.*, 25, 2082–2102, doi:10.1016/j.quascirev.2006.02.010.
- Karner, M. B., E. F. DeLong, and D. M. Karl (2001), Archaeal dominance in the mesopelagic zone of the Pacific Ocean, *Nature*, 409, 507–510, doi:10.1038/35054051.
- Kaspi, Y., R. Sayag, and E. Tziperman (2004), A “triple sea-ice state” mechanism for the abrupt warming and synchronous ice sheet collapses during Heinrich events, *Paleoceanography*, 19, PA3004, doi:10.1029/2004PA001009.
- Keigwin, L. D., and S. J. Lehman (1994), Deep circulation change linked to Heinrich event 1 and Younger Dryas in a middepth North Atlantic core, *Paleoceanography*, 9(2), 185–194, doi:10.1029/94PA00032.
- Keough, B. P., T. M. Schmidt, and R. E. Hicks (2003), Archaeal nucleic acids in picoplankton from great lakes on three continents, *Microb. Ecol.*, 46, 238–248, doi:10.1007/s00248-003-1003-1.
- Kim, J.-H., S. Schouten, E. C. Hopmans, B. Donner, and J. S. Sinninghe Damsté (2008), Global sediment core-top calibration of the TEX_{86} paleothermometer in the ocean, *Geochim. Cosmochim. Acta*, 72(4), 1154–1173, doi:10.1016/j.gca.2007.12.010.
- Kim, J.-H., J. van der Meer, S. Schouten, P. Helmke, V. Willmott, F. Sangiorgi, N. Koç, E. C. Hopmans, and J. S. Sinninghe Damsté (2010), New indices and calibrations derived from the distribution of crenarchaeal isoprenoid tetraether lipids: Implications for past sea surface temperature reconstructions, *Geochim. Cosmochim. Acta*, 74, 4639–4654, doi:10.1016/j.gca.2010.05.027.
- Kucera, M., A. Rosell-Melé, R. Schneider, C. Waelbroeck, and M. Weinelt (2005), Multiproxy approach for the reconstruction of the glacial ocean surface (MARGO), *Quat. Sci. Rev.*, 24, 813–819, doi:10.1016/j.quascirev.2004.07.017.

- Kuhlemann, J., E. J. Rohling, I. Krumrei, P. Kubik, S. Ivy-Ochs, and M. Kucera (2008), Regional synthesis of Mediterranean atmospheric circulation during the last glacial maximum, *Science*, *321*, 1338–1340.
- Kwiecien, O., H. W. Arz, F. Lamy, B. Plessen, A. Bahr, and G. H. Haug (2009), North Atlantic control on precipitation pattern in the eastern Mediterranean/Black Sea region during the last glacial, *Quat. Res.*, *71*, 375–384, doi:10.1016/j.yqres.2008.12.004.
- Landais, A., J. M. Barnola, V. Masson-Delmotte, J. Jouzel, J. Chappellaz, N. Caillon, C. Huber, M. Leuenberger, and S. J. Johnsen (2004), A continuous record of temperature evolution over a sequence of Dansgaard-Oeschger events during Marine Isotopic Stage 4 (76 to 62 kyr B.P.), *Geophys. Res. Lett.*, *31*, L22211, doi:10.1029/2004GL021193.
- LeGrande, A. N., and G. A. Schmidt (2009), Sources of Holocene variability of oxygen isotopes in paleoclimate archives, *Clim. Past*, *5*, 441–455.
- LeGrande, A. N., G. A. Schmidt, D. T. Shindell, C. V. Field, R. L. Miller, D. M. Koch, G. Faluvegi, and G. Hoffman (2006), Consistent simulations of multiple proxy responses to an abrupt climate change event, *Proc. Natl. Acad. Sci. U. S. A.*, *103*(4), 837–842, doi:10.1073/pnas.0510095103.
- Leider, A., K.-U. Hinrichs, G. Mollenhauer, and G. J. M. Versteegh (2010), Core-top calibration of the lipid-based U^{K}_{37} and TEX_{86} temperature proxies on the southern Italian shelf (SW Adriatic Sea, Gulf of Taranto), *Earth Planet. Sci. Lett.*, *300*, 112–124, doi:10.1016/j.epsl.2010.09.042.
- Li, C., D. S. Battisti, D. P. Schrag, and E. Tziperman (2005), Abrupt climate shifts in Greenland due to displacements of the sea ice edge, *Geophys. Res. Lett.*, *32*, L19702, doi:10.1029/2005GL023492.
- Lin, X., S. G. Wakeham, I. F. Putnam, Y. M. Astor, M. I. Scranton, A. Y. Chistoserdov, and G. T. Taylor (2006), Comparison of vertical distributions of prokaryotic assemblages in the anoxic Cariaco basin and Black Sea by use of fluorescence in situ hybridization, *Appl. Environ. Microbiol.*, *72*(4), 2679–2690, doi:10.1128/AEM.72.4.2679-2690.2006.
- Lipp, J. S., and K.-U. Hinrichs (2009), Structural diversity and fate of intact polar lipids in marine sediments, *Geochim. Cosmochim. Acta*, *73*(22), 6816–6833, doi:10.1016/j.gca.2009.08.003.
- Liu, Z., et al. (2009a), Transient simulation of last deglaciation with a new mechanism for Bølling-Allerød warming, *Science*, *325*(5938), 310–314, doi:10.1126/science.1171041.
- Liu, Z., M. Pagani, D. Zimiker, R. DeConto, M. Huber, H. Brinkhuis, S. R. Shah, R. M. Leckie, and A. Pearson (2009b), Global cooling during the Eocene–Oligocene climate transition, *Science*, *323*, 1187–1190, doi:10.1126/science.1166368.
- Lopes dos Santos, R. A., M. Prange, I. S. Castañeda, E. Schefuß, S. Mulitza, M. Schulz, E. M. Niedermeyer, J. S. Sinninghe Damsté, and S. Schouten (2010), Glacial–interglacial variability in Atlantic meridional overturning circulation and thermocline adjustments in the tropical North Atlantic, *Earth Planet. Sci. Lett.*, *300*, 407–414.
- Lotter, A. F., O. Heiri, S. Brooks, J. F. N. van Leeuwen, U. Eicher, and B. Ammann (2012), Rapid summer temperature changes during Termination 1a: High-resolution multi-proxy climate reconstructions from Gerzensee (Switzerland), *Quat. Sci. Rev.*, *36*, 103–113, doi:10.1016/j.quascirev.2010.06.022.
- Lunt, D. J., M. S. Williamson, P. J. Valdes, T. M. Lenton, and R. Marsh (2006), Comparing transient, accelerated, and equilibrium simulations of the last 30,000 years with the GENIE-1 model, *Clim. Past*, *2*, 221–235, doi:10.5194/cp-2-221-2006.
- Major, C., W. F. Ryan, G. Lericolais, and I. Hajdas (2002), Constraints on Black Sea outflow to the Sea of Marmara during the last glacial–interglacial transition, *Mar. Geol.*, *315*, 1–16.
- Margari, V., P. L. Gibbard, C. L. Bryant, and P. C. Tzedakis (2009), Character of vegetational and environmental changes in southern Europe during the last glacial period; evidence from Lesvos Island, Greece, *Quat. Sci. Rev.*, *28*, 1317–1339, doi:10.1016/j.quascirev.2009.01.008.
- Martrat, B., J. O. Grimalt, C. Lopez-Martinez, I. Cacho, F. J. Sierro, J. A. Flores, R. Zahn, M. Canals, J. H. Curtis, and D. A. Hodell (2004), Abrupt temperature changes in the western Mediterranean over the past 250,000 years, *Science*, *306*, 1762–1765, doi:10.1126/science.1101706.
- Martrat, B., J. O. Grimalt, N. J. Shackleton, L. de Abreu, M. A. Hutterli, and T. F. Stocker (2007), Four climate cycles of recurring deep and surface water destabilizations on the Iberian margin, *Science*, *317*(5837), 502–507, doi:10.1126/science.1139994.
- McDermott, F. (2004), Palaeo-climate reconstruction from stable isotope variations in speleothems: A review, *Quat. Sci. Rev.*, *23*(7–8), 901–918, doi:10.1016/j.quascirev.2003.06.021.
- Melki, T., N. Kallel, F. J. Jorissen, F. Guichard, B. Dennielou, S. Berné, L. Labeyrie, and M. Fontugne (2009), Abrupt climate change, sea surface salinity and paleoproductivity in the western Mediterranean Sea (Gulf of Lion) during the last 28 kyr, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *279*(1–2), 96–113, doi:10.1016/j.palaeo.2009.05.005.
- Ménot, G., and E. Bard (2010), Geochemical evidence for a large methane release during the last deglaciation from Marmara Sea sediments, *Geochim. Cosmochim. Acta*, *74*(5), 1537–1550, doi:10.1016/j.gca.2009.11.022.
- Menzel, D., E. C. Hopmans, S. Schouten, and J. S. Sinninghe Damsté (2006), Membrane tetraether lipids of planktonic *Crenarchaeota* in Pliocene sapropels of the eastern Mediterranean Sea, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *239*(1–2), 1–15, doi:10.1016/j.palaeo.2006.01.002.
- Morgan, J. A., H. L. Quinby, and H. W. Ducklow (2006), Bacterial abundance and production in the western Black Sea, *Deep Sea Res., Part II*, *53*(17–19), 1945–1960, doi:10.1016/j.dsr2.2006.03.023.
- Müller, U. C., J. Pross, P. C. Tzedakis, C. Gamble, U. Kotthoff, G. Schmiedl, S. Wulf, and K. Christanis (2011), The role of climate in the spread of modern humans into Europe, *Quat. Sci. Rev.*, *30*(3–4), 273–279, doi:10.1016/j.quascirev.2010.11.016.
- Oguz, T., and A. Merico (2006), Factors controlling the summer *Emiliania huxleyi* bloom in the Black Sea: A modeling study, *J. Mar. Syst.*, *59*, 173–188, doi:10.1016/j.jmarsys.2005.08.002.
- Özsoy, E., and Ü. Ünlüata (1997), Oceanography of the Black Sea: A review of some recent results, *Earth Sci. Rev.*, *42*, 231–272, doi:10.1016/S0012-8252(97)81859-4.
- Pailler, D., and E. Bard (2002), High frequency paleoceanographic changes during the past 140,000 years recorded by the organic matter in sediments off the Iberian Margin, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *181*, 431–452, doi:10.1016/S0031-0182(01)00444-8.
- Peyron, O., J. Guiot, R. Cheddadi, P. E. Tarasov, M. Reille, J.-L. de Beaulieu, S. Bottema, and V. Andrieu-Ponel (1998), Climatic reconstruction in Europe for 18,000 yr B.P. from pollen data, *Quat. Res.*, *49*, 183–196, doi:10.1006/qres.1997.1961.
- Powers, L. A., J. P. Werne, T. C. Johnson, E. C. Hopmans, J. S. Damsté, and S. Schouten (2004), Crenarchaeotal membrane lipids in lake sediments: A new paleotemperature proxy for continental paleoclimate reconstruction?, *Geology*, *32*(7), 613–616, doi:10.1130/G20434.1.
- Powers, L., J. P. Werne, A. J. Vanderwoude, J. S. Sinninghe Damsté, E. C. Hopmans, and S. Schouten (2010), Applicability and calibration of the TEX_{86} paleothermometer in lakes, *Org. Geochem.*, *41*, 404–413, doi:10.1016/j.orggeochem.2009.11.009.
- Rahmstorf, S. (2002), Ocean circulation and climate during the past 120,000 years, *Nature*, *419*, 207–214, doi:10.1038/nature01090.
- Rasmussen, T. L., and E. Thomsen (2004), The role of the North Atlantic Drift in the millennial timescale glacial climate fluctuations, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *210*(1), 101–116, doi:10.1016/j.palaeo.2004.04.005.
- Renssen, H., R. F. B. Isarin, J. Vandenberghe, M. Lautenschlager, and U. Schlese (2000), Permafrost as a critical factor in paleoclimate modeling: The Younger Dryas case in Europe, *Earth Planet. Sci. Lett.*, *176*, 1–5, doi:10.1016/S0012-821X(99)00322-2.
- Richey, J. N., D. J. Hollander, B. P. Flower, and T. I. Eglinton (2011), Merging late Holocene molecular organic and foraminiferal-based geochemical records of sea surface temperature in the Gulf of Mexico, *Paleoceanography*, *26*, PA1209, doi:10.1029/2010PA002000.
- Rouis-Zargouni, I., J.-L. Turoň, L. Londeix, L. Essallami, N. Kallel, and M.-A. Sicre (2010), Environmental and climatic changes in the central Mediterranean Sea (Siculo–Tunisian Strait) during the last 30 ka based on dinoflagellate cyst and planktonic foraminifera assemblages, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *285*(1–2), 17–29, doi:10.1016/j.palaeo.2009.10.015.
- Ryan, W., W. C. Pitman, C. O. Major, K. Shimkus, V. Moskalenko, G. A. Jones, P. Dimitrov, N. Görür, M. Sakıncı, and H. Yüce (1997), An abrupt drowning of the Black Sea shelf, *Mar. Geol.*, *138*, 119–126, doi:10.1016/S0025-3227(97)00007-8.
- Schouten, S., E. C. Hopmans, E. Schefuss, and J. S. Sinninghe Damsté (2002), Distributional variations in marine crenarchaeotal membrane lipids: A new tool for reconstructing ancient sea water temperatures?, *Earth Planet. Sci. Lett.*, *204*, 265–274, doi:10.1016/S0012-821X(02)00979-2.
- Schouten, S., et al. (2009), An interlaboratory study of TEX_{86} and BIT analysis using high performance liquid chromatography/mass spectrometry, *Geochim. Geophys. Geosyst.*, *10*, Q03012, doi:10.1029/2008GC002221.
- Severinghaus, J. P., T. Sowers, E. J. Brook, R. B. Alley, and M. L. Bender (1998), Timing of abrupt climate change at the end of the Younger Dryas interval from thermally fractionated gases in polar ice, *Nature*, *391*, 141–146, doi:10.1038/34346.
- Shakun, J. D., P. U. Clark, F. He, S. A. Marcott, A. C. Mix, Z. Liu, B. Otto-Bliesner, A. Schmittner, and E. Bard (2012), Global warming preceded by increasing carbon dioxide concentrations during the last deglaciation, *Nature*, *484*(7392), 49–54, doi:10.1038/nature10915.

- Shevenell, A. E., A. E. Ingalls, E. W. Domack, and C. Kelly (2011), Holocene Southern Ocean surface temperature variability west of the Antarctic Peninsula, *Nature*, *470*, 250–254, doi:10.1038/nature09751.
- Shintani, T., M. Yamamoto, and M.-T. Chen (2011), Paleoenvironmental changes in the northern South China Sea over the past 28,000 years: A study of TEX₈₆-derived sea surface temperatures and terrestrial biomarkers, *J. Asian Earth Sci.*, *40*, 1221–1229, doi:10.1016/j.jseas.2010.09.013.
- Sikes, E. L., J. W. Farrington, and L. D. Keigwin (1991), Use of the alkenone unsaturation ratio U₃₇^k to determine past sea surface temperatures: Core-top SST calibrations and methodology considerations, *Earth Planet. Sci. Lett.*, *104*(1), 36–47, doi:10.1016/0012-821X(91)90235-A.
- Soulet, G., G. Ménot, G. Lericolais, and E. Bard (2011a), A revised calendar age for the last reconnection of the Black Sea to the global ocean, *Quat. Sci. Rev.*, *30*(9–10), 1019–1026, doi:10.1016/j.quascirev.2011.03.001.
- Soulet, G., G. Ménot, V. Garreta, F. Rostek, S. Zaragosi, G. Lericolais, and E. Bard (2011b), Black Sea “lake” reservoir age evolution since the last glacial—Hydrologic and climatic implications, *Earth Planet. Sci. Lett.*, *308*(1–2), 245–258, doi:10.1016/j.epsl.2011.06.002.
- Stoica, E., and G. J. Herndl (2007), Contribution of *Crenarchaeota* and *Euryarchaeota* to the prokaryotic plankton in the coastal northwestern Black Sea, *J. Plankton Res.*, *29*(8), 699–706, doi:10.1093/plankt/fbm051.
- Stouffer, R. J., et al. (2006), Investigating the causes of the response of the thermohaline circulation to past and future climate changes, *J. Clim.*, *19*(8), 1365–1387, doi:10.1175/JCLI3689.1.
- Sur, H. İ., E. Ozsoy, Y. P. Ilyin, and U. Unluata (1996), Coastal/deep ocean interactions in the Black Sea and their ecological/environmental impacts, *J. Mar. Syst.*, *7*(2–4), 293–320, doi:10.1016/0924-7963(95)00030-5.
- Tarasov, L., and W. R. Peltier (2005), Arctic freshwater forcing of the Younger Dryas cold reversal, *Nature*, *435*(7042), 662–665, doi:10.1038/nature03617.
- Tarasov, P. E., E. V. Bezrukova, and S. K. Krivonogov (2009), Late Glacial and Holocene changes in vegetation cover and climate in southern Siberia derived from a 15 kyr long pollen record from Lake Kotokel, *Clim. Past.*, *5*, 285–295, doi:10.5194/cp-5-285-2009.
- Ternois, Y., M. A. Sicre, A. Boireau, M. H. Conte, and G. Eglinton (1997), Evaluation of long-chain alkenones as paleo-temperature indicators in the Mediterranean Sea, *Deep Sea Res., Part I*, *44*(2), 271–286, doi:10.1016/S0967-0637(97)89915-3.
- Turich, C., K. H. Freeman, M. A. Bruns, M. Conte, A. D. Jones, and S. G. Wakeham (2007), Lipids of marine *Archaea*: Patterns and provenance in the water-column and sediments, *Geochim. Cosmochim. Acta*, *71*(13), 3272–3291, doi:10.1016/j.gca.2007.04.013.
- Tzedakis, P. C., M. R. Frogley, I. T. Lawson, R. C. Preece, I. Cacho, and L. de Abreu (2004), Ecological thresholds and patterns of millennial-scale climate variability: The response of vegetation in Greece during the last glacial period, *Geology*, *32*(2), 109–112, doi:10.1130/G20118.1.
- Vellinga, M., and R. A. Wood (2002), Global climatic impacts of a collapse of the Atlantic thermohaline circulation, *Clim. Change*, *54*(3), 251–267, doi:10.1023/A:1016168827653.
- Voelker, A. H. L., et al. (2002), Global distribution of centennial-scale records for Marine Isotope Stage (MIS) 3: A database, *Quat. Sci. Rev.*, *21*, 1185–1212, doi:10.1016/S0277-3791(01)00139-1.
- von Grafenstein, U., H. Erlenkeuser, A. Brauer, J. Jouzel, and S. J. Johnsen (1999), A mid-European decadal isotope-climate record from 15,500 to 5000 years B.P., *Science*, *284*, 1654–1657, doi:10.1126/science.284.5420.1654.
- Wakeham, S. G., C. M. Lewis, E. C. Hopmans, S. Schouten, and J. S. Sinninghe Damsté (2003), *Archaea* mediate anaerobic oxidation of methane in deep euxinic waters of the Black Sea, *Geochim. Cosmochim. Acta*, *67*(7), 1359–1374, doi:10.1016/S0016-7037(02)01220-6.
- Wakeham, S. G., E. C. Hopmans, S. Schouten, and J. S. Sinninghe Damsté (2004), Archaeal lipids and anaerobic oxidation of methane in euxinic water columns: A comparative study of the Black Sea and Cariaco basin, *Chem. Geol.*, *205*(3–4), 427–442, doi:10.1016/j.chemgeo.2003.12.024.
- Wang, Y. J., H. Cheng, R. L. Edwards, Z. S. An, J. Y. Wu, C.-C. Shen, and J. A. Dorale (2001), A high-resolution absolute-dated late Pleistocene monsoon record from Hulu cave, China, *Science*, *294*, 2345–2348, doi:10.1126/science.1064618.
- Weaver, A. J., O. A. Saenko, P. U. Clark, and J. X. Mitrovica (2003), Melt-water pulse 1A from Antarctica as a trigger of the Bølling-Allerød warm interval, *Science*, *299*(5613), 1709–1713, doi:10.1126/science.1081002.
- Weijers, J. W. H., S. Schouten, O. C. Spaargaren, and J. S. Sinninghe Damsté (2006), Occurrence and distribution of tetraether membrane lipids in soils: Implications for the use of the TEX₈₆ proxy and the BIT index, *Org. Geochem.*, *37*(12), 1680–1693, doi:10.1016/j.orggeochem.2006.07.018.
- Wohlfarth, B., et al. (2008), Rapid ecosystem response to abrupt climate changes during the last glacial period in western Europe, 40–16 ka, *Geology*, *36*(5), 407–410, doi:10.1130/G24600A.1.
- Wu, H., J. Guiot, S. Brewer, and Z. Guo (2007), Climatic changes in Eurasia and Africa at the last glacial maximum and mid-Holocene: Reconstruction from pollen data using inverse vegetation modelling, *Clim. Dyn.*, *29*, 211–229, doi:10.1007/s00382-007-0231-3.
- Wuchter, C., S. Schouten, S. G. Wakeham, and J. S. Sinninghe Damsté (2005), Temporal and spatial variation in tetraether membrane lipids of marine *Crenarchaeota* in particulate organic matter: Implications for TEX₈₆ paleothermometry, *Paleoceanography*, *20*, PA3013, doi:10.1029/2004PA001110.
- Yunev, O. A., V. I. Vedernikov, O. Basturk, A. Yilmaz, A. E. Kideys, S. Moncheva, and S. K. Kononov (2002), Long-term variations of surface chlorophyll *a* and primary production in the open Black Sea, *Mar. Ecol. Prog. Ser.*, *230*, 11–28, doi:10.3354/meps230011.