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Holocene Climate Evolution of Continental Western Eurasia Constrained By Stable-Isotope and Cation Geochemistry of U-Th-Dated Speleothems and Meteogenic Travertine

Jonathan Lloyd Baker
ageofrocks@gmail.com

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HOLOCENE CLIMATE EVOLUTION OF CONTINENTAL WESTERN EURASIA
CONSTRAINED BY STABLE-ISOTOPE AND CATION GEOCHEMISTRY OF
U-TH-DATED SPELEOTHEMS AND METEOGENIC TRAVERTINE

By

Jonathan L. Baker

Bachelor of Science – Geoscience
Weber State University
2008

Master of Science – Geoscience
University of Nevada, Las Vegas
2010

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Jonathan L. Baker

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Doctor of Philosophy – Geoscience
Department of Geoscience

Matthew Lachniet, Ph.D.
Examination Committee Co-Chair

Ganqing Jiang, Ph.D.
Examination Committee Co-Chair

David Kreamer, Ph.D.
Examination Committee Member

Elisabeth Hausrath, Ph.D.
Examination Committee Member

Paul Werth, Ph.D.
Graduate College Faculty Representative

Kathryn Hausbeck Korgan, Ph.D.
Graduate College Interim Dean
ABSTRACT

HOLOCENE CLIMATE EVOLUTION OF CONTINENTAL WESTERN EURASIA
CONSTRAINED BY STABLE-ISOTOPE AND CATION GEOCHEMISTRY OF
U-TH-DATED SPELEOTHEMS AND METEOGENIC TRAVERTINE

By

Jonathan Lloyd Baker

Dr. Matthew Lachniet, Examination Committee Chair
Professor of Geology
University of Nevada, Las Vegas

Reliable reconstructions of global and regional climate during the Holocene (11,700 years ago to present) are vital to constraining the natural range of climate variability and testing state-of-the-art models, which seek to forecast the near- and long-term impact of anthropogenic greenhouse forcing. Much of continental Eurasia is still underrepresented, however, in geological proxy reconstructions of Holocene climate variability, and the vast majority of paleoclimate data only reflect conditions during peak summer months (JJA) or the growing season. The paucity of winter proxy data has therefore been cited as a possible explanation for the current mismatch between geological proxy-based and climate-model reconstructions of Holocene temperature, but testing the hypothesis first requires additional datasets. In this series of studies, I seek to strengthen our knowledge of Holocene climate evolution in continental western Eurasia and mitigate the seasonal bias in paleoclimate proxy datasets by investigating two sites of freshwater carbonate deposition in western Russia: 1) Kinderlinskaya Cave, located in the southern Ural Mountains, and 2) the Izhora Plateau, south of the Gulf of Finland. Two speleothems collected
from Kinderlinskaya Cave, which grew over the entire Holocene epoch, were analyzed for stable isotopes of oxygen and carbon. Carbon-isotope data constrain the timing of permafrost degradation and afforestation for the southern Ural Mountains, and the stable-isotope composition of oxygen in speleothem calcite is shown to reflect Holocene temperature evolution during the winter season. Centennial-scale trends in oxygen-isotope data are further utilized to establish a climate dynamic relationship between winter air temperature over western Russia and perturbations to the North Atlantic Current system over the last 11,700 years, providing a foundation from which to evaluate the regional climate response to feedbacks associated with anthropogenic warming. Early–Middle Holocene deposits of meteogenic (cool-water) travertine were also analyzed for stable isotopes of oxygen and carbon, as well as their major-cation concentrations (Mg and Sr). The oxygen-isotope composition of travertine deposits is shown to reflect winter climate variability in the Peribaltic region, for which our dataset constitutes the first winter paleoclimate archive, whereas the remaining geochemical proxies document changes to the surface hydrology and environment of the Izhora Plateau from approximately 9,500 to 6,800 years ago. From the results of these studies, we conclude that the winter and summer climate evolution of western continental Eurasia followed opposing trajectories for much of the Holocene. We further corroborate the hypothesis that geological proxy reconstructions of Holocene surface temperature are likely biased toward conditions during the summer half year by presenting data that strongly support the veracity of existing climate model reconstructions.
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DEDICATION

To my wife, Natasha, who eagerly became my partner in developing this international research project, joined me in the icy depths of the mountainside, taught me a love for the Russian language and culture, and nudged me over the finish line. You endured years of my being present in body, yet absent in spirit. For this, I will ever be grateful.

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CHAPTER 1

OVERVIEW OF DISSERTATION

1.1 INTRODUCTION

Holocene climate variability is known from a wide range of geological proxies, including ice cores, coral, pollen, ocean and lake sediments, boreholes, and speleothems (Mayewski et al., 2004). Nonetheless, it has proven difficult to constrain the evolution of global surface temperature over the past 11,700 years, due to geographic and seasonal biases in these datasets (Liu et al., 2014). For example, the most comprehensive proxy-based reconstruction of global and hemispheric surface temperature to date, produced by Marcott et al. (2013), shows relatively rapid warming from the end of the Younger Dryas (11.7 ka) until the Holocene Climatic Optimum (HCO; ~9–5 ka), followed by gradual cooling of approximately 1°C until the beginning of the Industrial Revolution (1850 C.E.). This reconstruction contradicts the results of climate models, which show continual Holocene warming and lack of a prominent HCO (Liu et al., 2014; Alder and Hostetler, 2015). However, nearly all of the 73 proxy sites are located along coastal margins, leaving most of the non-glaciated continental interior (including all of Russia) unrepresented. Additionally, the most utilized proxy data types (pollen, foraminiferal Mg/Ca, and marine-sediment alkenones) are sensitive specifically to peak-summer (JJA) or growing-season temperature. In their assessment, Marcott et al. (2013) demonstrated that surface temperature at the 73 proxy sites could be used successfully to reconstruct global trends over the instrumental period (1850 C.E.–Present), but for this calibration interval, the dominant forcing of global climate change (greenhouse-gas concentrations) equally affects all seasons, whereas the major Holocene forcing (insolation) follows seasonally disparate trajectories.
It remains uncertain, therefore, whether the pattern of global Holocene surface temperature in the proxy stack is representative of mean annual conditions or whether it is biased toward regional trends driven by climate dynamics unique to the summer season (e.g. orbitally forced summer insolation). This uncertainty derives not from shortcomings in the methodology behind the proxy stack, but a paucity of continental and/or winter paleoclimate data. In a sensitivity test, Liu et al. (2014) highlight the fact that the pattern of HCO warming and subsequent cooling disappears with the removal of only 10–20 datasets, which most strongly reflect orbitally forced boreal-summer cooling from 10 ka to present. If it were shown that climate evolution of the continental interior was out of phase with the dominant boreal-summer trends, then the so-called “Holocene temperature conundrum” could be resolved in favor of climate model reconstructions. Alternatively, corroboration of the Marcott et al. (2013) proxy stack by winter-sensitive paleoclimate data from continental sites would indicate significant shortcomings in existing climate models, which are used to forecast the near- and long-term effects of anthropogenic greenhouse forcing.

In Chapter 2, I present a speleothem-based record of Holocene winter climate evolution from the continental interior of western Eurasia, which is the largest area still unrepresented in the global proxy stack. The Kinderlinskaya Cave record spans the Holocene (11.7 ka to present) and is comprised of 940 stable-isotope analyses (δ¹⁸O and δ¹³C) from two stalagmites, whose age and growth rate were constrained by 29 U-Th disequilibrium dates. Ours is the first speleothem paleoclimate dataset from Russia and one of the highest resolution and most precisely dated for all of Eurasia, given its decadal-scale average sampling resolution (12.5 years) and low age-model uncertainty (average ±36 years). By monitoring the cave climate over a period of 3 years and analyzing the stable-isotope composition of surface and drip water, we show that the
oxygen-isotope composition ($\delta^{18}O$) of speleothem calcite reflects that of winter half-year precipitation, which itself correlates to mean surface temperature and air circulation over western Eurasia. We interpret the upward trend in Holocene $\delta^{18}O$ as a record of continual warming (exceeding 6.8°C) during the winter half year at our study site from 11.7 ka to present, which is attributed to three dominant forcings: retreat of northern hemispheric ice sheets until ~6.8 ka, an increase in greenhouse-gas concentrations from 8 ka to present, and an increase in winter insolation. This warming trend contradicts the global proxy stack, but strongly corroborates climate model outputs (Alder and Hostetler, 2015; Jin et al., 2011; Liu et al., 2014; Timm and Timmerman, 2007).

In Chapter 3, I detrend the $\delta^{18}O$ record from Kinderlinskaya Cave to isolate Holocene winter climate variability not attributable to glacial retreat, greenhouse forcing, and winter insolation. The detrended record exhibits quasi-periodic oscillations that decrease in magnitude from Early to Late Holocene, but are characteristic of centennial- to millennial-scale variability observed in other proxy datasets (Bond et al., 1997; Debret et al., 2009; Wanner et al., 2011). We find a broad coherence between suborbital climate variability of the continental interior with that of the North Atlantic realm by comparison to representative proxy archives. In particular, we show that Holocene winter climate in the southern Ural Mountains was closely coupled to spatial gradients in sea-surface temperature (SST) between the Irminger Sea (south of Greenland; Berner et al., 2008) and the Vøring Plateau and Barents Sea (northeastern North Atlantic; Hald et al., 2007). These spatial SST gradients are influenced by the relative strength of the western and eastern branches of the North Atlantic Current (Miettinen et al., 2012; Peng et al., 2002), which delivers heat to high latitudes from the subtropical ocean. Furthermore, the spatial SST pattern modifies the baroclinic structure of the overlying atmosphere (Miettinen et al., 2010), which
affects the strength and zonality of winter air circulation over northern Eurasia. We therefore
demonstrate that oceanic and continental Holocene climates were coupled through a coherent
synoptic-scale mechanism. Finally, because Early–Middle Holocene perturbations to the current
system coincide with periods of enhanced glacial melt from the Scandinavian and Laurentide ice
sheets, our results provide a paleo-analogue for the regional climatic response over western
Russia to enhanced melting of the Greenland Ice Sheet under anthropogenic global warming.

In Chapter 4, I present the results of a collaborative investigation of Holocene freshwater
carbonate deposition in riverine and lacustrine settings on the Izhora Plateau in northwestern
Russia. Using geochemical data from this site, we were able to test the hypothesis that winter
warming over western continental Eurasia (Chapter 2) was coherent across a wide geographic
region. Through stable-isotope analysis of modern calcite formation and surface/spring waters,
we show that freshwater carbonate deposits—classified herein as meteogenic travertine—likely
recorded temporal variations in the oxygen-isotope composition of winter precipitation, which
itself is an indicator of winter climate change (Jouzel et al., 2000). Active deposition of
meteogenic travertine was constrained to the interval 9.5–6.8 ka through dating of material by
the radiocarbon and U-Th disequilibrium methods. The δ¹⁸O of lacustrine sediments steadily
increased over this interval along a trend similar to that in Kinderlinskaya Cave speleothems, as
well as proxy temperature reconstructions from the Fennoscandian region (Heikkilä et al., 2010;
Heikkilä and Seppä, 2010; Sejrup et al., 2016; Seppä and Poska, 2004). However, the δ¹⁸O of
modern meteogenic travertine, relative to Holocene deposits, suggests that the Early–Middle
Holocene continued to the present day, rather than reversing from a Middle Holocene climatic
optimum (Marcott et al., 2013; Sejrup et al., 2016). In addition to providing the first Holocene
winter paleoclimate archive for Peribaltic region, therefore, we present evidence that HCO
warming in the regional proxy temperature reconstruction (Sejrup et al., 2016) may be overestimated due to a seasonal bias in proxy data. These results are consistent with our findings in Chapter 2 and further support the contention by Liu et al. (2014) that the “Holocene temperature conundrum” may be resolved in favor of climate model reconstructions of surface temperature from 11.7 ka to present.
1.2 REFERENCES

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CHAPTER 2

HOLOCENE WARMING IN WESTERN CONTINENTAL EURASIA DRIVEN BY GLACIAL RETREAT AND GREENHOUSE FORCING*

2.1 INTRODUCTION

The global temperature evolution during the Holocene is poorly known. Whereas proxy data suggest that warm conditions prevailed in the Early to Mid-Holocene with subsequent cooling, model reconstructions show long-term warming associated with ice-sheet retreat and rising greenhouse-gas concentrations. One reason for this contradiction could be the underrepresentation of indicators for winter climate in current global proxy reconstructions. Here we present records of carbon and oxygen isotopes from two U-Th-dated stalagmites from Kinderlinskaya Cave in the southern Ural Mountains that document warming during the winter season from 11,700 years ago to the present. Our data are in line with the global Holocene temperature evolution reconstructed from transient model simulations. We interpret Eurasian winter warming during the Holocene as a response to the retreat of northern hemisphere ice sheets until about 7,000 years ago, and to rising atmospheric greenhouse gas concentrations and winter insolation thereafter. We attribute negative δ¹⁸O anomalies 11,000 and 8,200 years ago to enhanced meltwater forcing of North Atlantic Ocean circulation, and a rapid decline of δ¹³C during the early Holocene with stabilization after about 10,000 years ago to afforestation at our study site. We conclude that winter climate dynamics dominated Holocene temperature evolution in the continental interior of Eurasia, in contrast to regions more proximal to the ocean.

2.2 Main Article Text

Paleoclimate model outputs (Alder and Hostetler, 2015; Liu et al., 2014; Timm and Timmermann, 2007) showing continual Holocene warming contradict proxy data of an Early-Middle Holocene climatic optimum inferred from global surface temperature reconstructions (Marcott et al., 2013). This Holocene temperature paradox may result from a seasonal bias in proxy data or inaccurate model sensitivities to insolation, ice-sheet, and greenhouse-gas (GHG) forcings. Resolution of the paradox is required to make robust projections of future climate associated with anthropogenic warming. For example, the proxy reconstruction by Marcott et al. (2013) describes a broad Holocene Climatic Optimum (HCO) from ~10–5 ka, during which global surface temperature was comparable to that of recent decades, owing to enhanced Northern Hemisphere Summer Insolation (NHSI). This pattern is observed almost ubiquitously in high-latitude proxy data (Mayewski et al., 2004), especially in maritime proximal regions such as western Europe, Fennoscandia (Sejrup et al., 2016), the Mediterranean (Samartin et al., 2017), and the Siberian Arctic (Jiang et al., 2012; Klemm et al., 2013). However, gridded pollen-based temperature reconstructions of continental Eurasia—notably absent from the global proxy stack—show no significant temperature deviations from modern during the HCO (Bartlein et al., 2010; Davis and Brewer, 2009). Further complicating this global temperature reconstruction is the fact that much of continental Eurasia, including all of Russia, is entirely unrepresented and that few proxy archives capture winter temperature variability.

In contrast to the putative cooling trend from the HCO to the Pre-Industrial (PI) period, transient paleoclimate models suggest increasing global and Eurasian surface temperature in response to continental ice-sheet retreat prior to 6.8 ka and rising GHG concentrations from ~8 ka to present. These forcings drove substantial winter warming over most of Eurasia, which
exceeded the NHSI-forced summer cooling for a net annual surface warming of 1-3°C (Alder and Hostetler, 2015; Liu et al., 2014). Because the HCO is documented almost exclusively by summer-sensitive biological proxies, it is plausible that because of the large surface area of continental Eurasia that is under-sampled in the global proxy stack, recovery of additional winter temperature records could reconcile global temperature evolution with model reconstructions. For example, winter warming of ~2°C from 7 ka–PI was recently documented by low-resolution δ¹⁸O data from an ice wedge in the Siberian Arctic (Meyer et al., 2015). If this observation were substantiated in broader geographic areas, it would imply that the global temperature stack may not be representative of continental-scale climate evolution, due to the annual temperature signal being dominated by winter climate dynamics that exceeded the role of decreasing NHSI since ca. 10 ka.

2.2.1 Kinderlinskaya Cave δ¹⁸O as a winter temperature proxy

We have identified an ideal cave location in the southern Ural Mountains of Russia that hosts actively growing and geochemically ideal stalagmites with which to test orbital, ice-sheet, and GHG forcings on continental Eurasian paleoclimate (Fig. A1). Two stalagmites were collected in growth position from Kinderlinskaya Cave (KC; 54.2°N 56.9°E). The age and growth rate of KC-1 (11.72–1.8 ka; 34.5 cm) and KC-3 (11.75–0 ka; 13 cm) were constrained by 29 U-Th dates (Fig. 2.1a), for which the average 2-σ uncertainty is ± 36 years, making our dataset one of the most precisely dated Holocene records in Eurasia. All ages are reported as ka B2K (kilo-annum before C.E. 2000). A total of 940 paired δ¹³C and δ¹⁸O analyses from KC-1 and KC-3 yield an average sampling resolution of 12.5 years (Fig. 2.1b-c).
Microclimatic monitoring of the dead-end collection room over a 2.5-year period confirmed that relative humidity remained at 100%, while room-air temperature varied within a narrow range (6.1–8.0°C) in proportion to outside air temperature during the previous winter, due to buffered seasonal ventilation (Fig. A1). Both parameters indicate ideal conditions for stalagmite $\delta^{18}O$ to capture climate processes. Because drip rates during collection were too low to recover a sufficient volume of water for $\delta^{18}O$ analysis, we used the $\delta^{18}O$ value of local spring waters (-14.5±0.6‰ VSMOW; sec. A.2.2) as a proxy for cave dripwater to show that calcite precipitation likely occurred in isotopic equilibrium. Given the cave-room temperature of 6.2°C measured at the time of KC-3 collection (July 2013; Fig. A2) and a $\delta^{18}O$ of -10.9±0.1‰ VPDB for the youngest calcite, the calculated dripwater $\delta^{18}O_w$ assuming equilibrium (Coplen, 2007) is -14.0±0.1‰ VSMOW. Comparison to $\delta^{18}O_p$ of winter (Oct–Mar; -15.4 ± 1.9‰) and summer (Apr–Sep; -9.2 ± 1.4‰) half years suggests that the epikarst is recharged mainly by Fall, Winter, and Spring precipitation (Fig. A3). These lines of evidence support the interpretation of KC stalagmite $\delta^{18}O$ as a regional proxy for Holocene winter half-year precipitation.

Spatial analysis of GNIP data from continental Eurasia indicates that $\delta^{18}O_p$ in the study area is strongly linked to the continental effect as air masses are advected inland from the Atlantic, Mediterranean, and Arctic seas (Kurita, 2004). Distillation of heavy isotopes along transport results in a positive spatial correlation between mean air temperature and $\delta^{18}O_p$ for northern Eurasia ($r^2 = 0.95$ for 15 sites). Analysis of data (1980–2000) from the nearest GNIP station at Kirov, 660 km northwest of the cave, shows that mean air temperature explains 44–51% of the interannual variance in $\delta^{18}O_p$ during winter, spring, and fall months ($p<0.001$; slope = 0.4‰/°C) and 21% during summer ($p<0.02$). The weaker summer relationship is due to a competing signal from moisture recycling that is opposite in sign. These observations are in line
with the regional analysis by Meyer et al. (2015), who further argued from isotope-enabled atmospheric model (ECHAM5-wiso) outputs that a $\delta^{18}O$–T relationship of 0.48‰/°C is robust over the last glacial-interglacial transition.

In addition to the temperature effect, moisture source is also a significant control on $\delta^{18}O_p$ at our study area because it determines temperature at the site of oceanic evaporation and effective continentality along storm tracks of variable lengths. The moisture source control on $\delta^{18}O_p$ is strongest during the cold season, when mid-latitude westerlies are strengthened by enhanced meridional temperature and pressure gradients. We found that above-average winter $\delta^{18}O_p$ near the cave site is associated with enhanced westerly flow over the North Atlantic region at the 500-hPa level, whereas atmospheric blocking in the North Atlantic and Scandinavian regions resulted in more northerly moisture source and below-average $\delta^{18}O_p$ (Fig. A4). Therefore, we attribute stalagmite $\delta^{18}O$ variability primarily to long-term changes in winter half-year surface temperature near the cave site, which are strongly associated with changing moisture sources driven by atmospheric pressure anomalies. Holocene variability in the seasonality of precipitation, evapotranspiration, and $\delta^{18}O_w$ of the oceanic moisture sources (e.g. related to ice volume and meltwater input) likely contributed to a lesser extent to the KC $\delta^{18}O$ signal and are likely superimposed upon the predominant temperature effect according to our interpretation.

2.2.2 The Holocene warming trend in western continental Eurasia

Continual Holocene warming is the major feature of our regional paleoclimate record. The initiation of stalagmite growth after the Younger Dryas (YD) suggests that periglacial conditions prevented speleothem formation—a contention supported by very high $\delta^{13}C$ values
indicative of low soil productivity in the earliest part of our record, and the ground-temperature history reconstructed from pollen records and borehole temperature profiles (Demezhko and Shchapov, 2001; Golovanova et al., 2012; Velichko et al., 2002). The rapid decline in δ\textsuperscript{13}C from near the measured bedrock value (+1.8‰) at 11.7 ka to Holocene background values (-7 to -9‰) likely signifies the transition from steppe vegetation and poorly developed soils to the modern forested terrain by ca. 10 ka (Danukalova et al., 2011) (Fig 2.1c).

Following the YD, the KC δ\textsuperscript{18}O record exhibits a long-term 3‰ step-wise increase that reaches near-modern values at 4.8 ka (Fig. 2.1b), with the rate of δ\textsuperscript{18}O increase slowing to the present. We interpret this trend to reflect long-term atmospheric warming over the continental interior, concomitant with an equatorward shift in moisture source. Because speleothem growth was inhibited by apparent periglacial conditions (subzero cave and ground temperatures) during the YD and modern cave temperature is above 6°C, the Holocene δ\textsuperscript{18}O increase was associated with at least 6°C of warming. The maximum slope of this relationship (0.5‰/°C) is higher than the temporal δ\textsuperscript{18}O–T observed in modern GNIP data or isotope-enabled model outputs (0.3–0.48‰/°C; Guan et al., 2016; Meyer et al., 2015), especially after accounting for the T dependence of calcite precipitation (~0.23‰/°C). While it is plausible that winter half-year warming exceeded 6°C, we suggest that large-scale changes in atmospheric circulation amplified the winter temperature signal of the Holocene δ\textsuperscript{18}O increase (see discussion below).

The Early to Middle Holocene exhibits enhanced centennial- to millennial-scale variability than after 4.2 ka. This observation suggests that relative instability of Early to Middle Holocene climate is possibly related to increased NH ice-sheet extent as discussed below. Multicentennial-scale δ\textsuperscript{18}O anomalies up to 0.5‰ indicate several intervals of slow cooling superimposed on the longer Holocene warming trend at 11.6 to 11.0 ka, 9.8 to 8.2 ka, 7.8 to 6.6
ka, 5.6 to 5.1 ka, and 4.8 to 4.3 ka. These cooling phases tend to follow rapid warming. Notably, local $\delta^{18}O$ minima coincide with cold climate anomalies (Mayewski et al., 2004; Wanner et al., 2011) expressed in other NH records.

The $\delta^{18}O$ time series suggests maximum winter half-year temperatures over easternmost Europe were attained during the last millennium, rather than the HCO that is prominent in the NH proxy stack (Marcott et al., 2013). The implication of this observation is that modern anthropogenic warming due to rising GHG concentration is superimposed on a natural warming trend. Further, because we do not observe an HCO warming, we argue that its use as a paleoclimate analog for future winter warming is inapt for continental Eurasia (Novenko et al., 2009). We note that KC $\delta^{18}O$ may not have recorded HCO warming if higher Middle Holocene temperatures were limited to summer, due to the winter-season bias of our proxy. Although our observation of a cool Early to Middle Holocene is supported by gridded pollen and lake data that indicate cooler summers and higher water balance in the continental interior at 6 ka (Bartlein et al., 2010; Wanner et al., 2008), these evidences are refuted by a recent study of chironomid-based reconstructions from the northern Mediterranean region, which clearly document a summertime HCO of 1–2°C that is consistent with modeled paleotemperature (Samartin et al., 2017).

2.2.3 Climate dynamics attribution of continental warming

Our reconstruction of pronounced Holocene warming in continental Eurasia contradicts inferences based on the hemispheric temperature stack and summer-sensitive proxy archives in maritime regions (Klemm et al., 2013; Sejrup et al., 2016), but is consistent with several other lines of evidence. For example, pollen-based annual temperature reconstructions from northern
Europe (Davis et al., 2003; Mauri et al., 2015) and Lake Baikal (Tarasov et al., 2007), shrub and pine pollen abundance in the Caspian Sea (Leroy et al., 2014), ice-wedge $\delta^{18}$O in the Siberian Arctic (Meyer et al., 2015), and inversion modeling of borehole temperature from the southern Ural Mountains (Demezhko and Shchapov, 2001; Golovanova et al., 2012) all indicate long-term annual or winter surface warming. Additionally, the Holocene $\delta^{18}$O trend from KC resembles those documented in Poleva and Ascunsa caves in Romania (Constantin et al., 2007; Drăgușin et al., 2014), as well as Sofular Cave in Turkey (Göktürk et al., 2011), which are supplied mainly by winter storms tracking over the Black Sea watershed to the west of our study area (Fig. 2.3). Because $\delta^{18}$O in the Romanian and Turkish stalagmites is not a direct temperature proxy and is strongly influenced by moisture source and the $\delta^{18}$O of the Black Sea itself, to infer a common warming signal with KC $\delta^{18}$O would require a substantially different interpretation of those records. Their similarity to KC, however, still suggests a common forcing of winter temperature at our study site, winter air circulation over south-central Europe, and the $\delta^{18}$O of inflow to the Black Sea reservoir. We therefore show for the first time that a substantial Holocene warming trend is regionally coherent over much of western continental Eurasia, so long as the proxy archives capture winter climate variability. Because this feature is not observed in the northern hemisphere proxy stack (Marcott et al., 2013; see final discussion), we support the contention (Liu et al., 2014) that the stack contains biases related to the paucity of winter-sensitive proxies and reliable continental records.

What, then, explains Eurasian Holocene temperature evolution? The warming trends in Figure 2.3 are opposite in direction to the cooling predicted by NHSI from 11 ka to present (Fig. 2.1d), suggesting that a direct radiative forcing via NHSI was not the dominant control. This discrepancy is explained by a winter bias in several records, including KCC, but otherwise
indicates that winter warming exceeded orbitally forced summer cooling. Ground-temperature reconstructions from the southern Urals (Demezhko and Shchapov, 2001; Golovanova et al., 2012) (Fig. 2.3h) and evidence for periglacial conditions at KC prior to 11.7 ka support this conclusion for our study site. Because KC $\delta^{18}O$ tracks the increase in winter half-year insolation (Oct-Mar, 55°N, Fig. 2.1d) from 11 ka to present, our record is consistent with orbital forcing of winter climate. However, the increase in Oct–Mar insolation (14.8 W/m²) is balanced by a reduction in Apr–Sep insolation (16.5 W/m2), which could not result in net annual warming. Therefore, any orbitally forced winter warming must have been amplified by additional forcings or feedbacks. Winter insolation is further unlikely to explain a 3‰ shift in $\delta^{18}O$, because meridional atmospheric heat transport contributes up to half of the wintertime thermal budget at high latitudes (Davis and Brewer, 2009), and SST of the oceanic moisture sources for our cave site was relatively stable or cooling during the Holocene (Rimbu et al., 2004). Finally, model outputs for our study site from the FAMOUS climate simulation do not show significant warming during the winter half year in response to Oct–Mar insolation (Fig. A5). For these reasons, we suggest that forcings other than NH insolation are required to explain the Holocene warming seen in the KC record. Two such possible forcings are the retreat of NH ice sheets and changes in GHG concentrations (primarily CO₂).

2.2.4 Atmospheric response to northern hemisphere glacial retreat

We observe a poor fit between KC $\delta^{18}O$ and GHG forcing (Luthi et al., 2008) prior to ca. 6–7 ka, indicating the importance of a strong forcing mechanism to produce substantially cooler winter temperatures during the Early Holocene. Because of the striking correspondence between LIS retreat the KC $\delta^{18}O$ rise in the Early to Middle Holocene (Fig. 2.2), we argue that NH ice-
sheet retreat paced continental temperature evolution in western Eurasia until 7-8 ka, when the modern ice configuration was attained (Dyke, 2004). This attribution is supported by paleoclimate simulations, which ubiquitously show that ice-sheet extent and topography depressed northern Eurasian surface temperatures, especially during winter (Alder and Hostetler, 2015; Brayshaw et al., 2010; Jin et al., 2011; Liu et al., 2014; Timm and Timmermann, 2007).

We suggest that downwind changes in atmospheric circulation associated with the disintegration of the NH ice sheets is the most plausible explanation for the post-YD warming in the Early to Middle Holocene. Supporting evidence for our conclusion is the presence of anticyclonic circulation over the Fennoscandian sector of the Scandinavian Ice Sheet (SIS) during expanded ice extent, which depressed surface temperatures over western Eurasia until the Early Holocene (Harrison et al., 1992; Siegert, 2004). However, our observations suggest this effect persisted beyond the collapse of the SIS at ca. 10 ka. The Laurentide Ice Sheet (LIS) remained sufficiently large into the Middle Holocene to interrupt atmospheric flow, especially during winter by development of a topographically induced stable anticyclone over and immediately east of the ice sheet, relocation of dipolar pressure centers downstream, and a southeastward deflection and strengthening of the Atlantic jet (Alder and Hostetler, 2015; Anderson et al., 1988; Brayshaw et al., 2010; Carlson et al., 2008; Jin et al., 2011). We argue, therefore, that the Early-Middle Holocene rise in δ¹⁸O is explained by relaxation and northward displacement of the polar jet stream and concomitant warming over western Eurasia in response to ice-sheet disintegration.

An ice-sheet induced perturbation of atmospheric circulation dynamics is supported by results from the GENMOM coupled atmosphere-ocean model, which produced positive (negative) 500-hPa geopotential height and sea-level pressure anomalies during winter at high
(mid) latitudes from 12–6 ka (Alder and Hostetler, 2015). This pattern, which roughly mimics the negative phase of the Arctic Oscillation and enhanced Scandinavian blocking, diminishes with ice-sheet retreat. We suggest that the Early–Middle Holocene was characterized by a higher frequency of northern air masses reaching continental Europe along the eastward flank of a high-pressure cell located over the northeastern Atlantic and Scandinavia.

If this mechanism is correct, it should also be reflected in isotopic proxy records from other regions. We test this idea by calculation of the $\delta^{18}$O gradient between the DYE-3 and Renland ice cores (Vinther et al., 2008) as a first-order proxy of atmospheric blocking in the North Atlantic sector and Scandinavia, because this circulation type results in positive $\delta^{18}$O anomalies in eastern relative to southern Greenland (Ortega et al., 2014). The $\Delta \delta^{18}$O time series (Fig. 2.2b) correlates strongly to the KC record ($r^2 = 0.84$), and the larger $\delta^{18}$O gradient observed for the Early Holocene is best explained by the persistence of blocking near Scandinavia that formed in response to the ice-sheet forcing. Additional support for our hypothesis is the strong similarity between KC $\delta^{18}$O evolution and the second EOF of northern hemisphere geopotential height variability (Fig. 2.2c) in transient simulations by the ECBilt-CLIO model (Timm and Timmermann, 2007). This configuration resembles the loading pattern of the Arctic Oscillation and characterizes the zonality of mid-latitude atmospheric circulation over western Eurasia. Similarly, we calculated the $\delta^{18}$O gradient between the DYE-3 and Agassiz ice cores (Fig. 2.2d), because predominantly anticyclonic circulation over the LIS would have resulted in positive $\delta^{18}$O and surface temperature anomalies along its western and northern flanks, but negative anomalies to the east and south (Gajewski, 2015). This gradient similarly diminishes over the Holocene to reflect a trend toward enhanced westerly flow. It is highly correlated to the KC $\delta^{18}$O
record \((r^2 = 0.83)\), and several millennial-scale oscillations overlap within age-model uncertainties, lending strong support to the hemispheric link.

Finally, we note that a concave-down reduction in surface-temperature gradient between southeastern Greenland and the Canadian Arctic is observed in recently compiled multiproxy data (Briner et al.; Gajewski, 2015). Enhanced atmospheric blocking in the North Atlantic sector and reduced surface temperature in easternmost Europe were thus associated with a prominent atmospheric ridge over Central-Eastern Canada. These observations support a mechanistic control of LIS retreat on atmospheric teleconnections and winter temperature evolution in the study area. By analogy, we conclude that a strengthening of westerly flow in the North Atlantic region in response to ice-sheet retreat is a plausible mechanism to shift from low-\(\delta^{18}O\) high-latitude moisture to high-\(\delta^{18}O\) mid-latitude moisture being delivered to continental Eurasia, as recorded in the KC \(\delta^{18}O\) time series.

### 2.2.5 Greenhouse-gas forcing of mid to late Holocene climate

Following the disintegration of NH ice sheets, the KC record exhibits a continued \(\delta^{18}O\) rise that tracks atmospheric \(CO_2\) (Fig. 2e) from ca. 7 ka to present. Although the 20 ppm (100 ppb) increase in \(CO_2 (CH_4)\) corresponds to a relatively small direct radiative forcing (0.5 W/m\(^2\); Marcott et al., 2013), equilibration of the climate system to positive feedbacks including vegetation, sea ice, and water vapor feedbacks could have dynamically warmed global surface climate by 0.2–0.8°C from 7 ka to PI (Kutzbach et al., 2011). Due to high-latitude amplification of GHG forcing, mean annual surface temperature at our cave site has risen by an average of 1.3°C per century—or 1.8°C per century during the winter half year—since the late 19\(^{th}\) century, which is nearly twice the global rate. Thus we deem it plausible that Mid-Late Holocene GHG
forcing accounts for a significant portion of the ~1‰ increase in KC $\delta^{18}$O. Our attribution is supported by the FAMOUS simulation, which estimates 1°C warming at our study site from 7 ka to PI due to GHG forcing (Fig. A5). The finding that GHG concentrations paced winter half-year temperature over continental Eurasia in the absence of the LIS provides an important context for modern anthropogenic warming.

2.2.6 Millennial-scale cooling in response to glacial melt

In addition to the long-term warming trend in our data, the presence of millennial-scale cooling, for example at 9.8–8.2 ka, presents an opportunity to investigate other sources of climate forcing on continental Eurasian climate. Proxy constraints of deglaciation indicate that regional NH ice-sheet retreat was episodic and associated with a series of Meltwater Pulses (MWP) and accelerated sea-level rise (Carlson and Clark, 2012; Carlson et al., 2008). The climatic impact of enhanced meltwater input to the Atlantic and Arctic seas has been extensively explored, for example, in model-proxy comparisons for the ‘8.2 ka Event’ (Wiersma and Renssen, 2006). Freshwater forcing of North Atlantic circulation decreased poleward heat transport, which provoked cooling anomalies over western Eurasia (Nesje et al., 2004) and a compression of climate zones southward to the tropics. A coincidence between meltwater forcing and millennial-scale $\delta^{18}$O minima could be interpreted as a meltwater forcing of midlatitude climate in KC $\delta^{18}$O.

Indeed, the most prominent negative $\delta^{18}$O anomaly in our record at 11.5–10.3 ka coincides with a period of enhanced meltwater forcing during MWP-1B (Carlson and Clark, 2012), which originated from both the LIS and SIS (Fig. 2.2f). The reduction in poleward heat transport was significant along the Norwegian Shelf (Hald et al., 2007), supporting the
contention that freshwater forcing contributes to cold conditions deep within the continent. Following a period of rapid warming and/or enhanced westerly flow from 10.2–9.8 ka, gradual cooling in our record from 9.8–8.4 ka is again mirrored by increasing freshwater contributions from the LIS (Carlson et al., 2008) that culminates with an abrupt 0.6‰ decrease in $\delta^{18}O$ at 8.4–8.2 ka associated with catastrophic drainage of glacial lakes Ojibway and Agassiz (Lewis et al., 2012). Lastly, rapid warming from 8.2–7.8 ka is followed by cooling from 7.8–6.6 ka that mirrors freshwater contributions during the final disintegration of the LIS. We conclude that the reduction of poleward heat transport during North Atlantic meltwater forcing provoked cooling anomalies in the Urals that were superimposed upon the long-term warming trend. The observation of reduced $\delta^{18}O$ variance after 4.8 ka is consistent with the loss of ice sheets and associated freshwater forcing.

2.2.7 Eurasian warming captured by transient model simulations

We have shown that variations in stalagmite $\delta^{18}O$ at KC were principally forced by ice-sheet retreat, GHG concentrations, and winter half-year insolation over the Holocene, based on a mechanistic comparison to GCM model results and proxy data for continental Eurasia. Our finding contradicts the major feature of the northern hemisphere proxy temperature stack (Marcott et al., 2013; Fig. 2.4), and shows instead that the inferred winter temperature evolution over continental western Eurasia almost perfectly tracks the local surface temperature history produced by several transient model simulations (Alder and Hostetler, 2015; Liu et al., 2014) parameterized with assigned forcings of ice sheet extent and topography, GHG concentrations, insolation, and sea-ice extent. Our data validate transient model simulations showing progressive Holocene warming, dominated by the winter temperature signal (Fig. 2.4). Continued Eurasian
warming after disintegration of the SIS and LIS supports a GHG forcing of winter temperature evolution over the last 6–7 kyr. Because of the large area in continental Eurasia currently undersampled in global temperature compilations, paleotemperature proxy data from there may have a strong impact on estimated global climate evolution. Warming in instrumental records over the last century is thus superimposed upon a natural warming trend, resulting in an anthropogenically altered Eurasian climate that is unprecedented for at least the last 11.7 kyr.

2.3 METHODS

2.3.1 Stable-isotope analysis of stalagmites and water samples

Stalagmites KC-1 and KC-3 were collected from a climatically stable, dead-end room in Kinderlinskaya Cave (Fig. A1). KC-3 was collected beneath an active drip, whereas KC-1 does not contain modern calcite growth. Each specimen was cut along the growth axis and polished before sampling carbonate powders every 0.5 mm using a 0.4-mm bit on a drill stage. δ¹⁸O and δ¹³C were determined by phosphoric-acid reaction at 70°C in a Kiel IV automated carbonate preparation device coupled to a ThermoElectron Delta V Plus mass spectrometer at the Las Vegas Isotope Science (LVIS) lab, University of Nevada, Las Vegas. δ¹⁸O and δ¹³C were corrected with internal and external standards, and precision is better than 0.08‰ and 0.06‰, respectively. Values are reported as per mil (‰) deviations from the Vienna Pee Dee Belemnite (VPDB) standard (Tables A2 & A3).

Collections of locally sourced springs were made in July 2012 and 2013 (see discussion of Fig. A2). Water samples were analyzed for δ¹⁸O and δD on a ThermoElectron high-temperature conversion elemental analyzer (TC/EA) using a continuous flow pyrolysis technique. The TC/EA was fitted with a GC PAL auto-sampler equipped with a 10-μl syringe.
Water samples were reacted at 1450°C in a ceramic column lined with glassy carbon and packed with glassy carbon fragments to reduce H₂O injections to CO and H₂ gases. The gases were carried by high-purity helium through a gas chromatograph at 90°C, where they were separated prior to isotopic analysis by the Delta V mass spectrometer via a Conflo-III open split. All δ¹⁸O and δD values have been corrected by four internal standards that were calibrated to VSMOW, SLAP, and GISP standards. Final data are the mean of at least five repeat injections and analysis per sample to ensure a minimal memory effect. δ values are reported as per mil (‰) deviations from Vienna Standard Mean Ocean Water (VSMOW), with precisions better than ± 0.2‰ for δ¹⁸O and 2‰ for δD.

Global Network of Isotopes in Precipitation (GNIP) data referenced herein were accessed from the IAEA/WMO (2015) database at http://www.iaea.org/water.

2.3.2 U-Th dating and age model construction for composite time series

U-series ages (Table A1) were determined at the Radiogenic Isotope Laboratory, University of New Mexico, by dissolving subsample powders (50–200 mg) in 15 M nitric acid and adding a mixed ²²⁹Th-²³³U-²³⁶U spike. The U and Th separation chemistry used an anion resin. Isotopic measurements were made on a Thermo Neptune Plus multi-collector inductively coupled plasma mass spectrometer. U and Th aliquots were analyzed separately using a static routine where all isotopes are measured using Faraday cups, except for ²³⁰Th, which is measured using an in-house ²³⁰Th standard that was run as a standard-5-samples-standard routine. Analytical uncertainties are 2σ of the mean; age uncertainties include analytical errors and uncertainties in the initial ²³⁰Th/²³²Th ratios, the latter of which is an atomic ratio equal to 4.4 ppm
by assuming a bulk earth $^{232}\text{Th}/^{238}\text{U}$ atomic ratio of 3.8. All ages were adjusted to years before C.E. 2000 (B2K). Decay constants for $^{234}\text{U}$ and $^{230}\text{Th}$ are from Cheng et al. (2013).

Age models for KC-1 and KC-3 (Fig. A6) and the composite $\delta^{18}\text{O}$ time series (Fig. 2.1a) were constructed by linear interpolation using the intra-site correlation age modeling ($iscam$) software written for MatLab (Fohlmeister, 2012) after visual and geochemical identification of growth hiatuses. The KC-3 age model was further constrained by assumption of a modern tip age and four tie points between the two samples determined by visual tuning to the better dated $\delta^{18}\text{O}$ time series of KC-1 (see Appendix 2.5). Parameters used in $iscam$ were 1,000 AR1 simulations with 1,000 Monte Carlo simulations each to determine possible age models, which were screened for maximum correlation of detrended and normalized $\delta^{18}\text{O}$ time series after applying a 50-year $\delta^{18}\text{O}$ smoothing filter. Positive stable-isotope anomalies observed within 1 mm of each hiatus were removed before plotting and $iscam$ analysis, because they likely reflect evaporative effects as the drip was abandoned.

2.3.3 Adjustment of mean $\delta^{18}\text{O}$ in KC-3

Precipitation of calcite $\delta^{18}\text{O}$ in isotopic equilibrium with cave waters was estimated for the time of collection (Fig. A2), but KC-3 $\delta^{18}\text{O}$ exhibits a systematic offset relative to KC-1 that reaches +0.38‰ during the Early Holocene. We interpreted the offset to be related to disequilibrium fractionation associated with a slower drip and closer proximity to the cave ceiling that further resulted in the smaller growth rate and diameter measured in KC-3 (Deininger et al., 2012; Dreybrodt et al., 2016). Prior to $iscam$ analysis and for Figure 2.1b, we therefore adjusted the mean $\delta^{18}\text{O}$ of KC-3 in Early, Middle, and Late Holocene segments downward by 0.38‰, 0.24‰, and 0.07‰, respectively, to match that of KC-1 over the same intervals.
Figure 2.1: Results from stable-isotope and geochronological analysis. (A) $\delta^{18}$O values from KC-1 (blue line) and KC-3 (red line; adjusted, see Methods) plotted alongside the composite $\delta^{18}$O curve (bold blue line), which was smoothed with a 250-year LOESS filter. U-Th dates ($\pm 2-\sigma$) and tie points used in the age model are shown above the time series. (B) Linearly interpolated growth rates for KC-1 (blue) and KC-3 (red). (C) $\delta^{13}$C values from KC-1 (green) and KC-3 (orange). (D) Oct-Mar and JJA insolation at 55°N latitude relative to Holocene mean.
Figure 2.2: Overview of Holocene climate dynamics related to KC $\delta^{18}O$. (A) Areal extent of the LIS relative to the last glacial maximum (Dyke, 2004); (B) $\delta^{18}O$ gradient between DYE-3 and Renland ice cores (Vinther et al., 2008) reflecting atmospheric blocking over Scandinavia; (C) second EOF of northern hemispheric GPH (500 hPa) variability in the ECBilt-CLIO simulation (Timm and Timmerman, 2007); (D) $\delta^{18}O$ gradient between DYE-3 and Agassiz ice cores (Vinther et al., 2008) reflecting atmospheric blocking over the Canadian Arctic; (E) atmospheric CO$_2$ (Luthi et al., 2008); (F) KC $\delta^{18}O$ with a 250-year LOESS filter (bold line); (G) meltwater pulses from NH ice sheets (Nesje et al., 2004). Map inset shows path of $\delta^{18}O$ gradients for (B) and (D).
Figure 2.3: Continental proxy records of Holocene warming. Standardized time series of speleothem δ¹⁸O from (A) Kinderlinskaya Cave, Russia, (B) Ascunsă Cave, Romania (Drăgușin et al., 2014), (C) Poleva Cave, Romania (Constantin et al., 2007), and (D) Sofular Cave, Turkey (Göktürk et al., 2011); (E) pollen-reconstructed MAT, Europe (shaded area; Davis et al., 2003; Mauri et al., 2015); (F) PC1 of shrubs and Pinus in core GS18, central Caspian Sea (Leroy et al., 2014); (G) pollen-reconstructed MAT in core VER93-2 st.24GC, Lake Baikal (Tarasov et al., 2007); (H) ground-surface temperature, Ural superdeep borehole SG-4 (Demezhko et al., 2001); (I) ice-wedge δ¹⁸O from Lena River Delta (Meyer et al., 2015). Vertical axes are in standard-deviation units. Dashed lines are linear regressions of Holocene data and suggest regional warming or shifts in predominant circulation. Data were accessed from the NOAA online repository or digitized from original publications.
Figure 2.4: Comparison of KC $\delta^{18}O$ with model and proxy reconstructions of Holocene surface temperature. (A) Composite KC $\delta^{18}O$ (dark blue) parallels winter temperature evolution at our cave site in three transient simulations (Liu et al., 2014); CCSM3, FAMOUS, and LOVECLIM) and time-slice reconstructions by the GENMOM coupled ocean-atmosphere model at 3-kyr intervals (Alder and Hostetler, 2015). Northern-hemisphere temperature proxy stack (Marcott et al., 2013; red line, for which shading denotes 2-$\sigma$ uncertainty) is opposite the trend in KC and model simulations for most of the Holocene. (B) Modeled rise in annual surface temperature results mainly from warming during the winter half year, consistent with our interpretation of KC $\delta^{18}O$. 

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**Note:** The diagram and text are not properly aligned, and the description of the diagram is not consistent with the actual content. The text and diagram are not accurately represented.
2.5 REFERENCES

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CHAPTER 3

SUBORBITAL VARIABILITY IN THE STRENGTH OF WINTERTIME WESTERLIES
OVER CONTINENTAL WESTERN EURASIA COUPLED WITH POLEWARD HEAT
TRANSPORT TO THE NORTHEASTERN ATLANTIC OCEAN

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Baker, J.L., Lachniet, M.S., Chervyatsova, O., Asmerom, Y., and Polyak, V.J.

3.1 ABSTRACT

A Holocene record of stalagmite $\delta^{18}$O from Kinderlinskaya Cave, Russia was investigated to isolate suborbital climate variability from long-term warming (11.75 ka to present). The chronology of two stalagmites comprising the composite record was constrained by 29 U-Th dates obtained through MC-ICP-MS analysis. Stable-isotope analysis at 0.5-mm resolution along the growth axes resulted in an average sampling frequency of 12.5 years. Stalagmite $\delta^{18}$O primarily reflects multidecadal changes in $\delta^{18}$O$_p$ during the winter half-year, which is shown to be sensitive to the AO/NAO-analogue strength and position of mid-latitude westerlies over continental western Eurasia. Spectral density and wavelet analysis of the detrended record revealed significant periodicities near 2.3 ka, 1.4 ka, and 1.0 ka, which are common in northern hemispheric paleoclimate records and related to solar and oceanic forcing during the Holocene. Coherent hemispheric coupling of continental and oceanic paleoclimate at centennial to millennial timescales is demonstrated by comparison of our record with reconstructions of sea-surface temperature (SST) and poleward heat transport in the North Atlantic sector. Specifically, SST at cores MD-23258 and LO09-14 in the Barents Sea and Reykjanes Ridge, respectively, exhibit opposite phasing during the Holocene, due to alternating
strength between the eastern and western branches of the North Atlantic Current, a major surface component of AMOC. Estimating the SST gradient between these sites as a proxy for poleward heat transport to the northeastern Atlantic Ocean, we find a strong covariance with detrended stalagmite δ¹⁸O. This relationship suggests that persistent strengthening (weakening) of wintertime westerlies, analogous to positive (negative) phases of the AO/NAO, was forced by enhanced (reduced) poleward heat transport along the Norwegian Current—the eastern branch of the NAC. Our record complements existing reconstructions of Holocene AO/NAO variability and provides a paleoanalog for the oceanographic response to rapid melting of the Greenland Ice Sheet under modern anthropogenic warming.

3.2 INTRODUCTION

Suborbital Holocene climate variability is well documented in the North Atlantic sector, including western Europe and Fennoscandia (Mayewski et al., 2004; Schulz and Paul, 2002; Wanner et al., 2011). In contrast to the relatively stable Greenland ice-core records, centennial- to millennial-scale fluctuations in temperature (Hald et al., 2007; Risebrobakken et al., 2011; Sejrup et al., 2016), precipitation (Fletcher et al., 2012), ocean current strength (Bianchi and McCave, 1999; Giraudeau et al., 2010; Hoogakker et al., 2011; Thornalley et al., 2013), drift ice (Andrews, 2009), and salinity (Thornalley et al., 2009) characterize most proxy reconstructions. These features have been attributed primarily to three dynamic controls: Total Solar Irradiance (TSI), atmospheric circulation modes analogous to the Arctic Oscillation (AO) and North Atlantic Oscillation (NAO), and freshwater forcing of Atlantic Meridional Overturning Circulation (AMOC), which collectively modulated Holocene temperature evolution paced by
insolation, greenhouse-gas forcing, and continental ice-sheet retreat (Kaplan and Wolfe, 2006; Marcott et al., 2013).

Persistence of the Scandinavian Ice Sheet (SIS) and Laurentide Ice Sheet (LIS) into the Early Holocene delayed the orbitally forced thermal maximum in the North Atlantic, North America, and Europe until 9–5 ka (Kaplan and Wolfe, 2006; Marcott et al., 2013; Renssen et al., 2009) and produced anomalously cold and dry winters over continental Eurasia (Alder and Hostetler, 2015; Jin et al., 2011; Mauri et al., 2015). Surface temperature steadily increased as northern hemisphere ice sheets retreated (Baker et al., 2017), but higher freshwater input during Early–Middle Holocene deglaciation also enhanced the sensitivity of the North Atlantic current systems. For example, the ‘8.2 ka event’ associated with the catastrophic drainage of glacial lakes Agassiz and Ojibway (Wiersma and Renssen, 2006) initiated centennial-scale cooling and/or drought that is superimposed on Holocene warming trends for much of the northern hemisphere, including the tropics (Wang et al., 2005). Apart from this major perturbation, however, it has proven difficult to attribute suborbital climate variability in North Atlantic and Eurasian proxy data to common forcings, despite that TSI, AMOC, and the AO/NAO influence both realms.

The challenges intrinsic to compiling paleoclimate data from diverse proxy methods and sampling sites certainly contribute uncertainty to our understanding of Holocene climate variability (Wanner et al., 2011), as demonstrated by conflicting reconstructions of important variables—e.g. Ice-Rafted Debris (IRD), North Atlantic Deepwater (NADW) currents, and Sea-Surface Temperature (SST). More problematic, however, is that a lack of corroborating proxy data from the inner continent still impedes our ability to delineate between ‘noise’ in local archives and the hypothesized forcings that should have coupled oceanic and continental
climates at centennial to millennial timescales. Investigations of suborbital Holocene climate variability should therefore attempt to reconcile regionally disparate datasets if the variability is attributed to such forcings.

3.2.1 Cyclicity in Holocene climate records

 Documented quasi-periodic rhythms of 2.5 ka, 1.5 ka, and 1 ka in Holocene proxy data seem to indicate a common underlying forcing on both mid-latitude and tropical climates (Wanner et al., 2011), similar to the millennial-scale variability observed during glacial periods (Fleitmann et al., 2009) but on a dampened scale. Because of the overlap with known solar cycles near these frequencies, variation in TSI has been suggested as a primary driver (Dima and Lohmann, 2008). Although TSI is a relatively small radiative forcing, its influence on freshwater input to the North Atlantic Ocean, salinity changes along the Gulf Stream (via glacial melt and evaporation, respectively), and atmospheric circulation (Moffa-Sánchez et al., 2014; Woollings et al., 2010) are plausible feedback mechanisms by which minor TSI variability could result in widespread perturbations to the climate system. A well-known example is the proposed link between solar forcing and ice-rafted debris (IRD) in marine cores off the Icelandic coast by Bond et al. (1997; 2001). Their hypothesis was supported by a 1,500-year spectral peak that appears in both IRD and atmospheric Δ¹⁴C data—the latter of which tracks solar-modulated atmospheric ¹⁴C production.

 In subsequent investigations of Holocene paleoclimate, the Bond IRD stack has become a litmus test for the covariance of proxy data with North Atlantic cold events. But while the inference of cold events in the IRD stack has been corroborated by some terrestrial records (Mangini et al., 2005), it has not been replicated in additional IRD reconstructions (Andrews,
Moreover, the 1,500-year cycle—commonly used to establish a link to North Atlantic dynamics—is not statistically robust in wavelet analysis of the Bond IRD stack and likely results from the superimposition of 2.5-ka and 1.0-ka cycles (Debret et al., 2009). The results of this reanalysis are still consistent with documented solar cycles in TSI, but since atmospheric Δ¹⁴C is also modified by oceanic uptake of CO₂, it may not simply reflect solar output. Therefore, the 2.5-ka and 1.0-ka cycles in Holocene proxy data may be attributable to TSI variability, especially if the relationship is proven to be in phase. Conversely, the 1.5-ka cycle also common in proxy datasets has only vaguely been explained by oceanic inertia (Dima and Lohmann, 2008). Though it is evident that solar forcing influenced the climatic rhythm of the North Atlantic and Eurasia, the precise mechanism by which TSI variability coupled oceanic and continental climates remains uncertain.

3.2.2 Ocean-atmosphere teleconnections and continental climate

Eurasian climate is linked to the North Atlantic system principally via mid-latitude westerly winds, which advect heat and moisture inland (Hurrell, 1995; Kurita, 2004). The position and strength of mid-latitude westerlies are determined by several dipolar atmospheric teleconnections—most notably the NAO (Hurrell et al., 2003), AO, and Scandinavian Pattern (SCA; Bueh and Nakamura, 2007)—that reflect the gradient in Sea-Level Pressure (SLP) or Geopotential Height (GPH) between the subpolar low (60–70°N) and subtropical high (30–40°N) belts. A steeper latitudinal pressure gradient during winter, concomitant with high-latitude cooling, strengthens westerly winds over the Atlantic Ocean and northern Europe, thereby increasing their influence on continental climate and oceanic currents (Blindheim et al., 2000). For example, the NAO and SCA indices explain ~60% of the variance in DJF Land-Surface
Temperatures (LST) over northern Eurasian from 1950–2005 (Popova and Shmakin, 2010). The multidecadal shift from predominantly NAO- to NAO+ conditions contributed significantly to late 20th-century warming in northern Europe (Visbeck et al., 2001), whereas anomalously cold Eurasian winters during the first decade of the 21st century have been attributed to weakening of midlatitude storm tracks (Cohen et al., 2014; Walsh, 2014) associated with the NAO- mode.

The NAO is influenced by SST anomalies in the North Atlantic Ocean at seasonal to multidecadal timescales (Buchan et al., 2014; Gastineau et al., 2012; Gastineau and Frankignoul, 2015; Miettinen et al., 2010; Peng et al., 2002). Up to 15% of the variance in the winter NAO index is explained by a tripole SST pattern that precedes NAO events by up to 6 months (Czaja and Frankignoul, 2002). Positive winter NAO events and enhanced westerlies are typically associated with cold summer SST anomalies in the subpolar and eastern subtropical North Atlantic and a warm anomaly in the Gulf Stream region near Cape Hatteras (Cassou et al., 2004; Visbeck et al., 1998). Similarly, SST anomalies in the marginal ice zone between Greenland and the Barents Sea (1982–2006) were found to substantially modify the baroclinic structure of the overlying troposphere through ocean-air heat exchange, forcing atmospheric circulation downstream (Schlichtholz, 2014). Given its observed modern impact on the strength and position of midlatitude westerlies, the Holocene evolution of SST patterns in the North Atlantic sector is one plausible, synoptic-scale mechanism by which to explain suborbital climate variability over continental Eurasia.

Because atmospheric indices were found to project back onto subsequent SST anomalies, these studies describe the ocean-atmosphere system in terms of a positive feedback loop and explain how externally forced SST and atmospheric pressure anomalies could persist beyond seasonal timescales. For example, Gámiz-Fortis et al. (2011) found that the principal mode of
variability in North Atlantic SST from 1872–2004 explained ~12% of the annual variance in northwestern European LST, with quasiperiodic oscillations at 40-60 years that corresponded to the Atlantic Multidecadal Oscillation (AMO). Theoretically, therefore, long-term perturbations to major North Atlantic currents could alter SST patterns with sufficient persistence that one mode of atmospheric circulation dominated, thereby driving centennial-scale variability in continental Eurasian climate. In recent decades, multiple proxy reconstructions have explained suborbital Holocene climate variability through changes in the strength of wintertime westerlies (Bakke et al., 2008; Fletcher et al., 2012; Lauterbach et al., 2014; Nesje et al., 2001). However, the hypothesis that persistent (multicentennial) intervals of atmospheric circulation modes analogous to the NAO/SCAN were driven by externally forced SST anomalies and reinforced by a positive feedback between SST and GPH has not been fully developed.

3.2.3 The North Atlantic Current system

Surface climate of the subpolar North Atlantic is governed primarily by two major current systems (Fig. 3.1). The warmer North Atlantic Current (NAC) is the northeastward extension of the Gulf Stream and a major component of AMOC, which accounts for nearly half of the high-latitude thermal budget during winter (Davis and Brewer, 2009). Conversely, the East Greenland Current (EGC) returns cold Arctic waters to the North Atlantic along the Greenland coast and into the subpolar gyre. Relative current strength in these two systems governs the west-east thermal gradient in the subpolar North Atlantic, which in turn constitutes a positive feedback to cyclonic air circulation, due to ocean-air heat flux and associated pressure anomalies. The zonal thermal gradient is also strongly correlated to sea-ice extent in the Barents Sea and sea-ice export through the Fram and Denmark straits.
The NAC branches into multiple subcurrents in the Icelandic and Nordic seas. Warm Atlantic water is advected along the Nordic coastline via the Norwegian Atlantic Slope Current (NwASC), where it splits into the North Cape (NCaC) and West Spitsbergen (WSC) currents. Enhanced meridional transport along this eastern branch of the NAC significantly increases SST and reduces sea-ice extent in the Barents, Kara, and eastern Arctic seas (Risebrobakken et al., 2011). Additionally, it constitutes the surface expression of AMOC, which returns cold, saline water through North Atlantic Deepwater (NADW) currents, including the Iceland-Scotland Overflow Water (ISOW). The western branch of the NAC curls back into the Irminger Sea and along the western coast of Iceland, due to rotation of the subpolar gyre. Therefore, it is closely linked with surface salinity and temperature anomalies in the Irminger and Labrador seas.

3.2.4 Study region and Holocene climate reconstruction of western continental Eurasia

Were North Atlantic and continental Eurasian paleoclimate coupled at suborbital scales during the Holocene? We attempt to answer this question through analysis of a composite, decadal-scale $\delta^{18}O$ time series (11.75 ka to present) of two U-Th-dated stalagmites from Kinderlinskaya Cave (KC) in the southern Ural Mountains (Fig. 3.3). Ours is the easternmost stable-isotope proxy dataset in Europe and is analyzed herein to reconstruct the suborbital Holocene climate variability of the inner continent. Due to the high temporal resolution of stable-isotope data and precision of the age model, our record may be utilized to anchor regional paleoclimatic variations. The $\delta^{18}O$ value of KC stalagmites exhibits a concave-down, Holocene increase (Fig. 3.3b), which was previously interpreted to reflect warming during the winter half-year over western continental Eurasia (Baker et al., 2017). This warming trend is attributed to forcing principally by continental ice-sheet retreat (Fig. 3.3a), greenhouse gases (Fig. 3.3c), and
winter insolation. In this paper, we seek to isolate centennial- to millennial-scale climate variability in KC $\delta^{18}O$ from that explained by these three Holocene-long forcings. Therefore, we detrended the time series according to a best-fit, 2nd-order polynomial (Fig. 3.3b, red dashed line) that well captures a Holocene trend explained by the inferred long-term forcings. Assuming a roughly linear relationship between the forcings and $\delta^{18}O$, the resulting time series (Fig. 3.3d) portrays winter climate variability at KC that is not attributable to ice-sheet retreat, greenhouse gases, or insolation. We use this detrended $\delta^{18}O$ time series to test the hypothesis that continental Eurasian climate was coupled with that of the North Atlantic sector at suborbital timescales by a common synoptic-scale mechanism.

Stalagmite $\delta^{18}O$ in KC was previously shown to reflect the $\delta^{18}O$ value of precipitation ($\delta^{18}O_p$) during the winter half year (Oct–Mar), when the AO, NAO and Scandinavian Pattern (SCA) project most strongly onto regional surface temperatures (Fig. 3.2). Locally, the $\delta^{18}O_p$ signal is controlled via a ‘continental effect’ by the strength and position of wintertime westerlies in the North Atlantic and European sectors, which modulate moisture source to the cave site and air temperature along storm tracks. Hence the positive (negative) phase of the AO/NAO (SCA), signifying enhanced zonal flow, results in warmer air temperatures and higher $\delta^{18}O_p$ near KC (Baker et al., 2017). This atmospheric control strongly links the local KC $\delta^{18}O$ signal to North Atlantic winter climate, making our stalagmite record an excellent test of the major forcings hypothesized to explain quasi-periodic fluctuations in North Atlantic paleoclimate. If climatic fluctuations were associated with persistent shifts in synoptic-scale atmospheric circulation, then the detrended KC $\delta^{18}O$ series should exhibit statistically robust phasing with warm and cold anomalies in the North Atlantic Ocean. Alternatively, we would expect to see a direct thermal forcing of KC $\delta^{18}O$ if TSI were the dominant driver of suborbital climate variability over the
continental interior. Finally, we will consider how the presence and absence of the Laurentide and Scandinavian ice sheets affected the climatic coupling of continental with oceanic climate. If the hypothesis is correct that meltwater input and surface salinity amplified minor solar forcing, then the relationship of NA proxy records with KC $\delta^{18}$O should be fundamentally different between the Early and Late Holocene.

3.3 METHODS

3.3.1 Stable-isotope time series

Stalagmites KC-1 (34.5 cm) and KC-3 (13 cm) were collected in growth position from a dead-end room in Kinderlinskaya Cave (KC; 54.1°N 56.9°E), located in the western flank of the southern Ural Mountains of Russia (Fig. 3.1). A total of 940 carbonate powders were drilled on a stage at 0.5-mm resolution and analyzed for $\delta^{18}$O and $\delta^{13}$C by phosphoric-acid reaction at 70°C using a Kiel IV carbonate device attached to a ThermoElectron Delta V Plus mass spectrometer at the Las Vegas Isotope Science (LVIS) laboratory, University of Nevada, Las Vegas. Isotopic values have been corrected to internal and external standards and are reported herein as per mil (‰) deviations from the Vienna Pee Dee Belemnite (VPDB) standard. Age models for KC-1 and KC-3, constrained by 29 U-Th disequilibrium ages, were constructed using iscam software written for Matlab (Baker et al., 2017). According to this model, the composite $\delta^{18}$O time series (Fig. 3.3) continuously covers the interval from 11.75 ka to present with an average 12.5-year sampling resolution and 36-year age uncertainty (2-σ).

3.3.2 Detection of millennial-scale cyclicity in KC $\delta^{18}$O
We utilized RedFit software (Schulz and Mudelsee, 2002) to identify whether prominent peaks and troughs in the detrended $\delta^{18}$O series correspond to a periodic climatic rhythm, as is observed in the proxy archives cited herein. The analysis applies a simple Fast Fourier Transform (FFT) to $\delta^{18}$O data and fits a first-order autoregressive process (AR1) to estimate statistical significance against a red-noise background. For time series that exhibit persistence (non-stochastic process), the latter step avoids overestimating the significance of spectral peaks, whose amplitude exponentially diminishes with increasing frequency. Holocene cyclicity was further analyzed by a wavelet toolbox in Matlab, after interpolating $\delta^{18}$O data onto 12.5-year time steps (average sampling resolution). This wavelet analysis constrains the specific intervals over which spectral peaks are significant.

3.3.3 Estimating North Atlantic Sea-Surface Temperature Gradients

We have reconstructed spatial SST gradients between key marine sites along the major branches of the NAC for comparison with KC $\delta^{18}$O (see discussion for justification). The western branch of the NAC is represented by a diatom-based reconstruction of SST from core LO09-14 (58.94°N 30.41°W), located along the IC on the Reykjanes Ridge, Irminger Sea (Berner et al., 2008). The eastern branch of the NAC is represented by planktonic foraminiferal reconstructions of SST in two cores (Hald et al., 2007): MD95-2011 (66.97°N 7.63°E) and M23258 (75°N 14°E), which are located along the NwASC and WSC on the Vøring Plateau and western Barents Sea margin, respectively (Fig. 3.1).

Data from all three cores overlap in the interval 0.65–11.13 ka, for which the sampling resolution varies from 48–52 years. Therefore, we chose 50-year intervals from 0.65 to 11.15 ka ($n = 211$) as the common time series on which to linearly interpolate data from each core, which
was necessary to estimate a SST gradient. We calculated two gradients (LO09-14 – M23258, defined as ΔSST-1; and LO09-14 – MD95-2011, defined as ΔSST-2) by subtracting SST at the relatively warmer Irminger Sea location from the higher latitude sites, so that negative values indicate a steeper thermal gradient between colder Nordic Seas and/or a warmer subpolar North Atlantic (Fig. 3.4).

To account for possible bias introduced by the arbitrary start point (0.65 ka) of our common time series, both SST datasets were varied systematically by ±75 years (the average 14C analytical uncertainty in the respective age models) before calculating the difference between interpolated values. Therefore, each data point in Figure 3.4b-c represents the mean of 22,802 simulations allowed by the original age models, for which the 1-σ uncertainties are denoted by vertical shading. Finally, to be consistent with the detrending process applied to KC δ18O, we also detrended the SST gradients in Figure 3.4b-c (dashed lines) before statistical comparison to our record. This step had negligible impact on the testing of our hypothesis, but does have paleoclimatic significance (see discussion for details and justification).

3.3.4 Monte Carlo simulation for test of statistical covariance with KC δ18O

We have developed a statistically rigorous method to compare KC δ18O with our reconstructed North Atlantic SST gradients. First, we interpolated the higher resolution δ18O data onto the same 50-year time steps used for plotting SST gradients (n = 211). This interpolation was necessary to calculate a Pearson correlation coefficient (r), which measures covariance between equally spaced time series according to a least-squares linear regression. However, the associated confidence level (p) assumes a stochastic process, in which each value is independent of adjacent values in the time series. This assumption is invalid for time series that exhibit
persistence (e.g. climate trends), resulting in overestimation of confidence levels that requires additional correction, as described below.

Persistence in the KC $\delta^{18}O$ time series was measured by the lag-1 autoregressive coefficient (AR1). We then designed a Matlab script that employed a Monte Carlo method to simulate 100,000 red-noise time series with equal persistence (fitted by the same AR1 coefficient). The script further calculated the Pearson correlation coefficient between each red-noise time series and KC $\delta^{18}O$ and plotted these values on a histogram. Taking the mean and standard deviation of the resulting normal distribution, we converted $r$ values to Z scores, after which the confidence level ($p$) was calculated by the probability integral of a normal distribution with a standard deviation equal to 1:

$$p(Z) = \frac{1}{\sqrt{2\pi}} \int_{-Z}^{Z} e^{-\frac{Z^2}{2}} dZ$$

### 3.4 Results

#### 3.4.1 Suborbital $\delta^{18}O$ variability recorded by KC stalagmites

After detrending KC $\delta^{18}O$, isotopic anomalies up to ±1‰ are evident throughout the Holocene (Fig. 3.3d). However, the magnitude of anomalies decreases after the beginning of the Late Holocene at 4.2 ka, when it varies less than ±0.4‰. Negative centennial-scale $\delta^{18}O$ anomalies are centered at 4.3 ka, 5.1 ka, 6.6 ka, 7.1 ka, 8.2 ka, and 11 ka, of which the two most prominent coincide with the boundaries of the Middle Holocene (4.2–8.2 ka; Walker et al., 2012). Positive centennial-scale $\delta^{18}O$ anomalies are centered at 4.1 ka, 4.8 ka, 5.6 ka, 7.8 ka, 9.8 ka, and possibly at 11.7 ka. The duration of anomalies also tends to decrease toward the Late Holocene, with the broadest trends occurring from 11–9.8 ka and 9.8–8.2 ka.
Spectral analysis of KC $\delta^{18}O$ using the FFT method in RedFit identified four periodicities—2.3 ka, 1.4 ka, 1.0 ka, and 0.7 ka—significant at 95% confidence, of which the first three have frequently been documented in Holocene records by the same method (Wanner et al., 2011). However, only the 2.3-ka cycle exceeds the “false alarm” level estimated by the software’s Monte Carlo simulation of red-noise spectra (Fig. 3.5a), implying that the remaining cycles are likely not robust features of Holocene climate variability at our study site. Wavelet analysis of KC $\delta^{18}O$ also identified a significant ($p < 0.01$) spectral peak near 2.3 ka, but it is restricted to the first half of the Holocene (Fig. 3.6). This finding is consistent with the observed decrease in $\delta^{18}O$ variability toward the Late Holocene. The spectral peak at 0.7 ka is present only during the interval 4-5 ka, which appears anomalous in our record. Finally, the 1.4-ka and 1.0-ka cycles are strongest during the Middle Holocene but never exceed 95% confidence, according to the wavelet analysis.

3.4.2 Covariance between SST gradients and KC $\delta^{18}O$

Our reconstructed SST gradients between the western and eastern branches of the NAC are plotted in Figure 4b-c. Although the LO09-14 – M23258 (hereafter $\Delta$SST-1) gradient is shallower during the Early Holocene relative to the rest of the record, it exhibits common millennial features with the LO09-14 – MD95-2011 (hereafter $\Delta$SST-2) prior to 5 ka. For example, both reconstructions indicate a steeper gradient near 6.7 ka, 8.4 ka, and 11 ka and shallow or reverse gradients near 6 ka, 7.9 ka, and 9.8 ka. Visually, these centennial-scale features correspond almost perfectly to the suborbital $\delta^{18}O$ variability recorded in KC stalagmites prior to 5 ka (Fig. 3.4d). The relationship breaks down after ~5 ka, suggesting that during the
Early-Middle Holocene, colder (warmer) surface conditions in the Irminger Sea (Barents Sea) corresponded to higher $\delta^{18}O$ values of winter half-year precipitation at KC.

After detrending each $\Delta$SST time series (Fig. 3.7a–b), the covariance of KC $\delta^{18}O$ (Fig. 3.7c) with $\Delta$SST-1 ($r = 0.384$) and $\Delta$SST-2 ($r = 0.376$) is almost identical over the common interval (11.15–0.65 ka). Running correlations from the beginning of the record show that the $r$ value increases with the exclusion of Late Holocene data (e.g., for 5.0–11.15 ka, $r = 0.523$). However, the significance of the correlation does not increase, due to the loss of sample size (degrees of freedom). Results of the Monte Carlo simulation are plotted in Figure 3.7d–e and show a normal distribution of $r$ values between KC $\delta^{18}O$ and red-noise series fitted to the same AR1 coefficient. Based on this distribution, an $r$ value of 0.384 corresponds to a Z-score of 2.76, for which $p = 0.006$. Therefore, we reject the null hypothesis at 99.4% confidence that covariance of KC $\delta^{18}O$ with SST gradients in the subpolar North Atlantic Ocean is random.

3.5 DISCUSSION

3.5.1 Air circulation control on $\delta^{18}O$ of precipitation at Kinderlinskaya Cave

Our analysis (Fig. 3.7) confirms that suborbital variability in the $\delta^{18}O$ of winter half-year precipitation at Kinderlinskaya Cave exhibits statistically robust phasing with summer SST gradients between the subpolar North Atlantic (Reykjanest Ridge) and the Nordic seas (Vøring Plateau, Barents Sea) during the Early and Middle Holocene. What then was the synoptic-scale coupling mechanism between continental Eurasian and North Atlantic climates? Over the modern instrumental period, October–March surface air temperature and $\delta^{18}O_p$ near the cave site are positively correlated with enhanced zonal flow across the northeastern North Atlantic and western Eurasia (Fig. 3.2). Recent studies have also linked summer SST in the Irminger Sea with
the NAO index and documented opposite phasing with SST in the Vøring Plateau during the Late Holocene (Miettinen et al., 2012; Miettinen et al., 2010). We therefore consider the strength of wintertime westerlies as the synoptic-scale mechanism by which the oceanic and continental realms were linked during the Early–Middle Holocene.

Stronger westerlies enhance wintertime heat advection from the North Atlantic to our study site and cause an equatorward shift in moisture source and storm tracks (Hurrell et al., 2003), resulting in higher temperature and δ¹⁸O_p (Baker et al., 2017). Conversely, atmospheric blocking in the North Atlantic and Scandinavian sectors enhances northwesterly flow to the cave site, depressing temperature and δ¹⁸O_p (Bueh and Nakamura, 2007). To quantify this relationship further, we analyzed GNIP data from the two stations nearest our cave site (Table 3.1). Winter (DJF) months with the highest δ¹⁸O_p values—exceeding 1-σ from the station mean—averaged -14.2 ± 0.7‰ (Kirov) and -12.2 ± 0.3‰ (Saratov), whereas months with the lowest δ¹⁸O_p values averaged -21.5 ± 0.7 (Kirov) and -20.2 ± 1.1‰ (Saratov). These data indicate that winter δ¹⁸O_p may be influenced by atmospheric circulation between high-δ¹⁸O and low-δ¹⁸O winter months. To test this idea, we subtracted the average GPH spatial structure during high-δ¹⁸O_p months from that of low-δ¹⁸O_p months to map circulation anomalies over the North Atlantic and our study area (Fig. 3.8). We found that high δ¹⁸O_p near the cave site is linked to stronger Azores and Siberian highs, as well as enhanced cyclonic circulation in the northeastern Atlantic and Mediterranean. These features are characteristic of the teleconnection indices correlated to higher surface temperatures locally (Fig. 3.2). Observed interannual δ¹⁸O_p variability associated with modes of atmospheric circulation analogous to the AO, NAO, and SCA (7.3–8.0‰) is substantially greater than the documented Holocene variability in KC stalagmites (<1‰). Suborbital variability in stalagmite δ¹⁸O can thus readily be explained by the slight dominance of
one mode over centennial- to millennial-scale intervals. However, this shift in mean circulation would require a persistent external forcing.

3.5.2 Dynamic link between North Atlantic SST gradients and wintertime westerly strength

Regional SST in the North Atlantic is strongly linked to predominant air circulation via mechanisms such as wind-curl-driven surface advection, latent air-sea heat exchange, gyre rotation, and vertical upwelling (Cassou et al., 2004; Gámiz-Fortis et al., 2011; Schlichtholz, 2014; Visbeck et al., 1998). The positive NAO in particular imprints a characteristic tripole ‘horseshoe’ pattern described by a warmer than average Gulf Stream and a cold patch south of Greenland (Czaja and Frankignoul, 2002; Flatau et al., 2003; Gastineau and Frankignoul, 2015). In turn, regional anomalies in evaporative heat flux modify the overlying air column, for example by expansive heating over warm surface waters and geopotential damping associated with reductions in latent heat downwind of the cold patch (Gastineau et al., 2012; Kushnir et al., 2002; Rodwell et al., 1999). Due to this interaction, the meridional structure of positive NAO-driven SST anomalies enhances the geopotential height gradient between the subtropical high and subpolar low belts, strengthening westerly winds over the North Atlantic sector and allowing for persistence in a stochastic system. Because the geopotential height forcing is relatively weak (~20 m/K) and internal variability is high in the North Atlantic climate system, the signal-to-noise ratio remains low in modeled and observed datasets (Rodwell et al., 1999). In theory, however, the observed centennial-scale perturbations to Holocene SST (1–3°C) could have caused one circulation mode to dominate slightly.

The modern relationship between SST in the ‘cold patch’ south of Greenland and the NAO index is consistent with the longest available instrumental reconstruction of NAO
circulation (Luterbacher et al., 2002). A high-resolution (2-year), 230-year reconstruction of summer SST at core Rapid 21-12B on the Reykjanes Ridge (along the Irminger Current) documented decadal-scale variability up to 1°C that was highly anticorrelated to the NAO index (Miettinen et al., 2010). The authors suggested that stronger westerly winds associated with the NAO+ phase weakened the western branching of the NAC toward the Irminger Sea, which allowed the cold EGC to extend southward and decrease SST at the core site. Concomitantly, the NAO+ mode strengthens poleward heat advection along the eastern branch of the NAC into the Nordic seas, which should result in opposite phasing between surface temperature in the Irminger and Nordic seas. This hypothesis was confirmed by analysis of Late Holocene (2.8 ka–Present) SST reconstructions from Rapid 21-COM along the Reykjanes Ridge and CR 948/2011 on the Vøring Plateau (Miettinen et al., 2012). Wavelet coherency analysis of the two reconstructions showed antiphasing significant in the 200–450-year and 640–960-year bands, confirming that the SST pattern could persist over multicentennial time scales. This observation justifies our choice of core locations for estimating SST gradients and corroborates our hypothesis that the opposite behavior of the NAC branches could be related to NAO-analogous changes in the strength of westerly winds in the North Atlantic sector.

3.5.3 Coherence between NA SST gradients and KC climate in observational data

We further test the hypothesis that air temperature at our study site is directly linked to NA SST anomalies by analyzing observed SST at cores LO09-14 and M23258 alongside LST at Kinderlinskaya Cave over the instrumental period (1880–2016 C.E.), using the NASA GISTEMP dataset (Hansen et al., 2010). The SST gradient between core sites (ΔSST-1) decreased by ~2°C since 1880, due to long-term warming (cooling) in the Barents (Irminger) sea,
and decadal-scale antiphasing is apparent, for example, in the interval 1880–1900 C.E (Fig. 3.9a). Surface temperature at KC almost perfectly tracks ΔSST-1 over the observed period (Fig. 3.9b), supporting our interpretation of the Holocene records. Because this signal captures anthropogenic warming, however, we also detrended the decadally smoothed time series. Although the response is non-linear, decadal to multidecadal variability in LST at KC appears to be in phase with that of the SST gradient.

Decadal variations in both time series are linked by a common atmospheric signal. The observed SST gradient closely tracks the winter NAO index from 1948–2016 C.E. (Fig. 3.9c), supporting our attribution of proxy data to the dynamic forcing. As a broader measure of wintertime westerly strength, we also calculated the GPH gradient (500 hPa) between 30°N–60°N to demonstrate coherence between the observed SST gradient and meridional baroclinicity over the North Atlantic sector. Finally, spatial correlation between the SST gradient and GPH at 500 hPa (Fig. 3.9d) reveals a pattern similar to that, which explains winter δ¹⁸O_p and air temperature at Kinderlinskaya Cave.

3.5.4 Antiphasing of KC δ¹⁸O and ΔSST with Holocene TSI variability

Because the 2.3-ka spectral peak in KC δ¹⁸O exceeds the false-alarm level (Fig. 3.5a) and is very near the 2,500-year solar cycle (Vonmoos et al., 2006), we test whether climate variability in our record was coherent with reconstructed SST gradients and TSI specifically in these bands. Using Analyseries software, we applied Gaussian filters to the time series for each wavelength (Fig. 3.5b). At least for the interval 11–5 ka, KC δ¹⁸O is almost perfectly in phase with ΔSST-1 (within age-model uncertainty), corroborating the results of our Monte Carlo analysis. Conversely, both time series exhibit strong antiphasing with TSI variability in the 2.3-
ka spectral band. From this observation, we conclude that enhanced solar output did not directly increase surface temperature at KC (as would be indicated in anomalously high $\delta^{18}$O values) or the high-latitude marine sites. Rather, lower TSI is associated with enhanced heat transport along the eastern branch of the NAC, stronger westerlies, and warmer winter climate in western Eurasia, suggesting that at centennial and millennial timescales, radiative forcing by TSI is less influential on western Eurasian surface temperature than atmospheric and ocean circulation dynamics. The antiphasing of TSI and temperature can be explained, however, if we consider that radiative forcing by TSI could have indirectly influenced winter surface temperature. For example, enhanced meltwater output from the LIS and SIS, plausibly initiated by higher TSI, would have produced salinity anomalies that dampened surface advection along the eastern branch of the NAC or slowed the AMOC system entirely. The mitigating effect of excess meltwater on AMOC strength has been observed today in response to anthropogenic warming (Rahmstorf et al., 2015) and has been modeled for various scenarios (Blaschek et al., 2014). Because of the demonstrated link between the NAC and continental interior climate, we propose that even small changes in TSI could have been amplified through perturbation of the North Atlantic system, which transports heat to high-latitude Eurasia during winter.

3.5.5 Holocene proxies of wintertime westerlies and North Atlantic poleward heat transport

If our hypothesis is correct that SST forcing of wintertime westerlies linked suborbital variability in KC $\delta^{18}$O and North Atlantic SST gradients, then these patterns should be evident in additional Holocene proxy data from the North Atlantic sector (Fig. 3.10). For example, Early Holocene warming (11–9.8 ka) and cooling (9.8–8.2 ka) anomalies (superimposed on the orbital-scale trend associated with ice-sheet retreat and GHGs) in KC $\delta^{18}$O is similarly exhibited by SST
off the western Svalbard coast (Fig. 3.10a; Aagaard-Sorensen et al., 2013). Poleward heat advection along the Norwegian coast (Fig. 3.10b)—estimated by the SST gradient through cores Troll 8903, MD95-2011, T79-51/2, T-88-2, M23258, and MD99-2304 (Fig. 3.1)—also peaks at 9–10 ka between minima at 11 ka and 8.2 ka. Stronger surface heat advection into the Barents and Arctic seas during the Early Holocene (Hald et al., 2007) likely explains why ΔSST-1 is shallower than ΔSST-2 over the same interval (Fig. 3.4). Beyond the Early Holocene, however, the highest latitude proxy sites show negligible coherence with KC δ¹⁸O, with the possible exception of warm conditions near 5 ka.

Variability in Atlantic Water inflow to the Vøring Plateau, interpreted from coccolithophore abundance in MD95-2011, strongly covaries with KC δ¹⁸O over the Early and Middle Holocene (Fig. 3.10c). The authors identified a quasi-stationary period of 2.5 ka in coccolithophore data and opposite phasing with ice exports to the northwestern Icelandic coast (Giraudeau et al., 2010), concurrent with our findings. The Icelandic drift ice anomaly (Fig. 3.10d) especially covaries with our datasets for the intervals 4–6 ka and 9–11.7 ka, indicating that a stronger EGC coincided with enhanced cyclonic circulation in the northeastern Atlantic. Giraudeau et al. (2010) explained the behavior in surface advective currents by wintertime atmospheric forcing analogous to the modern NAO, which was corroborated by reconstructions of winter precipitation in Norway (Bakke et al., 2008; Bjune et al., 2005; Fig. 3.10h) and wind strength over Iceland (Jackson et al., 2005).

Return NADW current strength in the AMOC system has been interpreted from sortable-silt data in cores MD2251 (Hoogakker et al., 2011) and NEAP-15K (Bianchi and McCave, 1999) south of Iceland (Fig. 3.1). Reconstructed ISOW strength (Fig. 3.10e–f) is somewhat inconsistent between these cores, but exhibits common features with KC δ¹⁸O at 7–10 ka (Fig. 3.10e) and 4–6
ka (Fig. 3.10f). Enhanced zonal atmospheric flow over western Eurasia is thus associated with both surface and deepwater components of AMOC during the Early–Middle Holocene. These findings demonstrate a regionally coherent portrait of AMOC variability, wintertime westerly strength, and continental Eurasian climate at Kinderlinskaya Cave. Finally, we note that $\delta^{18}O$ anomalies in the GISP2 ice-core from central Greenland (detrended series from 10.3 ka to present; Schulz and Paul, 2002) align well with our record from 10.3–4 ka (Fig. 3.10i), suggesting a common forcing on the $\delta^{18}O$ of winter precipitation in Greenland and $\delta^{18}O$ anomalies in the southern Urals.

3.5.6 Anomalous perturbations at 4–5 ka

The large-amplitude oscillations in KC $\delta^{18}O$ from 4–5 ka are not explained by our hypothesized link to behavior of the NAC, because none of the three SST reconstructions record major perturbations in this interval. Although positive $\delta^{18}O$ anomalies near 4.8 ka are consistent with several proxy datasets in Figure 3.10, the strong negative peak centered at 4.3 ka seems anomalous in our record. Cooling at 4.4–4.2 ka has been documented, for example, in Greenland and Iceland (Andrews, 2009; Geirsdóttir et al., 2013; Giraudeau et al., 2010; Jouzel et al., 2007) and may correspond to Bond Event 3 in the North Atlantic IRD stack (Bond et al., 2001). However, coincident cooling at our study site with the subpolar North Atlantic would imply a fundamentally different mechanism of hemispheric change than for Early–Middle Holocene events. Because the ‘4.2 ka event’ is also marked by aridity in the Mediterranean (Drysdale et al., 2006; Staubwasser and Weiss, 2006) and southeast Asia (Shao et al., 2006), it may be related to a shift in the Intertropical Convergence Zone, given the near ubiquitous onset of drought in low
latitudes and cooling in the northern midlatitudes (Walker et al., 2012). At present, we cannot confidently attribute the 4.3 ka shift in KC δ¹⁸O to a particular forcing.

3.5.7 Implications for climate projections under anthropogenic warming

The North Atlantic ‘cold patch’ south of Greenland has been uniquely resilient to anthropogenic surface warming, in part because accelerated melting of the Greenland Ice Sheet enhanced freshwater forcing through the Labrador Straight provoked a coincident slowdown in AMOC (Rahmstorf et al., 2015). However, this slowdown does not seem to have impacted the rate of warming along the eastern branch of the NAC and coincides with a transition from predominantly negative to positive NAO conditions (Luterbacher et al., 2002). A single-point correlation map of SST at LO09-14 from 1880–2016 C.E. shows opposite temperature variability with most of the globe, but especially the northeastern Atlantic and western Eurasia (Fig. 3.11). This antiphasing is similar to centennial-scale warming observed in KC δ¹⁸O during two Early Holocene events (Fig. 3.12), when LO09-14 SST simultaneously decreased and wintertime westerlies strengthened. In both Early Holocene scenarios, however, the trends persisted only for 2–3 centuries, at which point cooling over western Eurasia coincided with a reorganization of major current strength in the North Atlantic Ocean.

Centennial-scale, Early Holocene variability in KC δ¹⁸O and North Atlantic proxy data may thus provide a paleo-analog for the anomalous rates of high-latitude warming and glacial melt observed in response to anthropogenic forcings (Noël et al., 2017; Rahmstorf et al., 2015). If this comparison is valid, continued warming should reach a dynamic threshold, at which point feedbacks in North Atlantic circulation could significantly alter climate trends in Eurasia. In a recent synthesis of climate model forecasts, Hansen et al. (2016) suggest that positive feedbacks
in the cryosphere and ocean dynamics may have been underestimated. Accounting for the heightened sensitivity, their model projects a flattening or reversal of winter warming over western Eurasia by 2070–2080 C.E., which would enhance the extremity of cold events and winter drought. Although the external radiative forcing is different (TSI vs. GHG), the modeled temperature response and mechanism are described well by Early Holocene proxy data. Our conclusions from this study are therefore relevant to regional temperature evolution and climate dynamics under future anthropogenic warming.

3.6 CONCLUSIONS

Suborbital Holocene climate variability in the North Atlantic realm is well documented by oceanic and terrestrial proxies, but its dynamic relationship with the climate of the continental interior has not been thoroughly investigated, due to a paucity of high-resolution data. By detrending our previously published δ18O record from Kinderlinskaya Cave, Russia, we have isolated multidecadal to millennial-scale oxygen-isotope variability up to 1‰ from the Holocene trend. We interpret positive (negative) oxygen-isotope anomalies to signify intervals of exceptionally warm (cold) winter climate, which are not attributable to forcing by glacial extent, greenhouse gases, or insolation. Spectral analysis of the detrended time series shows statistically significant periodicities (p < 0.05) at 2.3 ka, 1.4 ka, and 1.0 ka, which are very close to the three major rhythms exhibited by Holocene paleoclimate proxies of temperature, precipitation, oceanic current strength, salinity, and sea ice (Bianchi and McCave, 1999; Bond et al., 1997; Debret et al., 2009; Mayewski et al., 2004; Wanner et al., 2011). However, wavelet analysis revealed that the 1.4 ka and 1.0 ka cycles are likely not robust Holocene features and that the 2.3-ka cycle only exceeds statistical confidence at p < 0.01 during the Early–Middle Holocene.
Through comparison of δ¹⁸O anomalies at Kinderlinskaya Cave with paleoclimate records from Greenland, the North Atlantic, and northern Europe, we demonstrate a regional coherence of winter surface temperature in the southern Ural Mountains with surface and deepwater components of AMOC, NAO-like shifts in the strength of wintertime westerlies, and the δ¹⁸O of precipitation in Greenland. The strongest similarities are observed between KC δ¹⁸O and SST in the Irminger Sea (core LO09-14), Vøring Plateau (core MD95-2011), and western Barents Sea (core M23258). Because SST at the Nordic locations exhibits opposite phasing with SST in the Irminger Sea during the Early–Middle Holocene, we defined two North Atlantic SST gradients from southwest to northeast at 50-year resolution from 0.65–11.13 ka, which we interpret to reflect relative strength of the eastern and western branches of the NAC. Regressing KC δ¹⁸O against the SST gradients showed a moderately strong correlation (r = 0.384), for which statistical significance (p = 0.006) was estimated using a Monte Carlo approach. Relatively warm (cold) winter climate intervals at KC thus coincide with a dampened (enhanced) SST gradient between the Irminger and Nordic seas in the North Atlantic, associated with strengthening (weakening) of the eastern branch of the NAC. Based on modern observed and modeled relationships, we propose that the strength of wintertime westerly flow into northern Eurasia (analogous to the AO/NAO) was modified by the spatial structure of North Atlantic SST, thereby coupling Holocene winter climate variability in the southern Urals to that of the North Atlantic realm at multidecadal to millennial timescales.

The link between oceanic and continental climate was strongest prior to the disintegration of the Laurentide Ice Sheet, which could indicate that millennial-scale fluctuations in North Atlantic current strength were amplified by glacial meltwater inputs. This scenario plausibly explains the antiphasing of KC δ¹⁸O and TSI in the 2.3-ka spectral band, which contradicts a
direct solar forcing of continental winter climate. If higher solar output enhanced meltwater from
the LIS, then concomitant weakening of the eastern branch of the NAC would have dampened
poleward heat transport and zonal atmospheric flow during winter, resulting in lower air
temperatures and δ¹⁸O_p at our study site. This finding is relevant to understanding regional
climate change under continued anthropogenic warming, which is significantly modified by
feedbacks in the high-latitude oceans and cryosphere. Because our record supports the projected
response of northern Eurasian climate in response to rapid melting of the Greenland Ice Sheet, it
provides an important Holocene analogue for 21st century forecasts.
Table 3.1: Mean $\delta^{18}O_p$ for winter months (1980–2000) at Kirov and Saratov GNIP stations

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*Bold indicates monthly $\delta^{18}O_p$ is >1σ from station mean.
Figure 3.1: Topography and bathymetry of the North Atlantic sector. Major warm (red) and cold (blue) surface currents indicated by solid arrows: North Atlantic Current (NAC), Irminger Current (IC), Norwegian Atlantic Slope Current (NwASC), Norwegian Atlantic Current (NwAC), North Cape Current (NCaC), West Spitsbergen Current (WSC), East and West Greenland Current (EGC/WGC). Iceland-Scotland Overflow Water (deepwater return current; ISOW) indicated by dashed black arrow. Holocene records, cited herein, from selected marine cores (yellow circles), Greenland Ice Sheet Project (GISP2), Folgefonna Glacier (FG), and Kinderlinskaya Cave (yellow star) are plotted for reference.
Figure 3.2: Coefficients of determination between mean monthly air temperature (Ufa, Russia) and atmospheric teleconnections: North Atlantic Oscillation (NAO), Arctic Oscillation (AO), North Sea–Caspian Pattern (NCP), and Scandinavian Pattern (SCA). Atmospheric data span the NCEP/NCAR reanalysis period (1948–2016 C.E.). Values higher than dashed line are significant at $p = 0.01$. 
Figure 3.3: Detrending of KC δ¹⁸O to isolate suborbital climate variability. Original time series (B) was detrended according to a best-fit 2nd-order polynomial (red dashed line) to remove Holocene signal driven by glacial retreat (A) and atmospheric carbon dioxide (C). Residual anomalies in KC δ¹⁸O (D) interpreted as suborbital winter climate variability at KC resulting from other forcings. Bold blue line in (D) represents a 250-year LOESS smoothing.
Figure 3.4: Summer SST gradients and residual KC $\delta^{18}O$. (A) Holocene SST reconstructed from three marine core sites in the Irminger Sea, Vøring Plateau, and Barents Sea. (B) and (C) Calculated SST gradients between the subpolar North Atlantic and Nordic seas (shaded area denotes ±1-σ uncertainty); dashed lines indicate regressions used for detrending each series. (D) KC $\delta^{18}O$ anomalies. Calibrated radiocarbon dates for marine cores in (A) denoted by filled diamonds; U-Th ages (±2-σ) in KC denoted by black diamonds.
Figure 3.5: Spectral analysis of Holocene KC δ¹⁸O anomalies and comparison with millennial-scale variability in calculated SST gradients and TSI. (A) Spectral amplitude in KC δ¹⁸O anomalies estimated using RedFit software. Spectral peaks exceeding 95% confidence are labeled. (B) Suborbital variability in KC Δδ¹⁸O, TSI, and ΔSST-1 isolated through application of Gaussian filters in the 2.3-ka band. For visual comparison, each time series was normalized to standard-deviation units (Z-score).
Figure 3.6: Wavelet analysis of KC δ¹⁸O anomalies, interpolated at the average sampling resolution (12.5 years). Bold line envelops intervals during which periodicities are significant at 99% confidence. Cone of influence demarcated by light shaded area.
Figure 3.7: Correlation of ΔSST-1 and ΔSST-2 with KC δ¹⁸O anomalies using a Monte Carlo analysis to estimate significance. (A) Holocene SST gradient between the Irminger Sea and western Barents Sea after detrending according to a best-fit polynomial. (B) Holocene SST gradient between the Irminger Sea and Vøring Plateau after detrending from a linear regression. (C) KC δ¹⁸O anomalies. (D) Correlation coefficients between (C) and simulated Holocene time series with equal persistence. (E) Histogram of r values, showing normal distribution from which the p value (0.006) is calculated.
Figure 3.8: Difference in mean geopotential height (500 mb) between winters characterized by high-$\delta^{18}$Op and low-$\delta^{18}$Op at Kirov (A) and Saratov (B) GNIP stations (red dots). Red and blue contours represent positive and negative anomalies, respectively. Contours are interpolated from a 2.5° x 2.5° grid; contour interval is 20 meters.
Figure 3.9: Analysis of SST between nodes defining ΔSST-1 and LST near KC during the instrumental period (1880–2016 C.E.). (A) Observed mean annual SST at core sites LO09-14 and M23258, used to calculate ΔSST-1. (B) Comparison of observed ΔSST-1 and LST at KC (decadally smoothed), before and after removing the signal from anthropogenic warming. (C) Decadally smoothed ΔSST-1 against the NAO index and meridional GPH gradient. (D) Map of relevant sites and gradients. Surface temperature data are from the NASA GISTEMP archive (2016; accessed from http://data.giss.nasa.gov/gistemp/); atmospheric data are from the NCEP/NCAR reanalysis (2016; accessed from https://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.html).
Figure 3.10: Comparison of suborbital variability in KC $\delta^{18}O$ anomalies with Holocene paleoclimate records from the North Atlantic sector. (A) Eastern Fram Strait SST; (B) T gradient estimated from 6 cores along the Nordic branch of the North Atlantic Current; (C) Coccolithophore abundance as a proxy for Atlantic Water inflow; (D) detrended quartz and plagioclase content along the Iceland shelf as a proxy for drift ice along; (E) mean sortable silt grain size as a proxy for Northeast Atlantic Deepwater formation; (F) mean sortable-silt grain size as a proxy for Iceland-Scotland Overflow Water; (G) detrended $\delta^{18}O$ from Kinderlinskaya Cave; (H) reconstructed winter precipitation from Folgefonna glacier ELA variations (dashed line indicates glacier absent); (I) central Greenland ice-core (GISP2) $\delta^{18}O$. 
Figure 3.11: Single-point correlation map of SST at core LO09-14 (Irminger Sea) with global land and surface temperatures (Land and Ocean Temperature Index; LOTI). Surface temperature data are from the NASA GISTEMP archive. Dashed line indicates that the correlation with grid point nearest LO09-14 is significant at \( p = 0.01 \).
Figure 3.12: Centennial-scale warming and cooling events during the Early Holocene as paleo-analogues for the regional response to modern anthropogenic warming. Observed LST at KC during the winter half year (Oct–Mar) depicted as solid red line. Early Holocene events are plotted relative to 9.8 ka and 7.85 ka for temporal alignment of trends. Secondary vertical axis is scaled to the gradient 0.5‰/°C, typical of 20th-century northern Eurasian precipitation, as a first-order approximation of Holocene temperature change at KC.
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Baker, J.L., Nikitin, M.Yu., Kuznetsov, V.Yu., Maksimov, F.E., Levchenko, S.B.,
Grigoriev, V.A., and Lachniet, Matthew S.

### 4.1 Abstract

The Holocene annual temperature evolution of the Fennoscandian and Baltic regions is broadly characterized by relatively rapid warming—paced by the retreat of northern hemisphere ice sheets—until the Holocene Climatic Optimum (HCO, ~9–5 ka), followed by 2–3°C cooling until the Pre-Industrial (PI) period. This altithermal and orbitally forced cooling trend is well documented by multiple proxy datasets, but most of these reflect only peak summer climate. The paucity of winter-sensitive paleoclimate archives in this region could therefore mask winter temperature trends and associated dynamics. Herein we analyze the stable-isotope and cation chemistry of a 2-meter section of microdetrital carbonate sediment, classified as meteogenic travertine, which was deposited in a shallow lake setting. The spring-fed lake system formed within a linear depression along a NW–SE-oriented fault, which likely was reactivated during post-glacial isostatic rebound. A decline in strongly covariant $\delta^{13}\text{C}$ and Sr/Ca values of travertine
documents afforestation of the plateau and increasing influence of soil-respired CO₂ over the life of the lake.

Radiocarbon and U-Th dating of peat and travertine, respectively, constrains the age of the travertine deposit to approximately 9.5–6.8 ka and suggests that the depositional rate increased until the lake shoaled locally. Anticorrelation of Mg/Ca with δ¹⁸O likely reflects NAO-like shifts between mild/wet and cold/dry conditions during this interval. We interpret a steady increase in δ¹⁸O from Early to Middle Holocene as a gradual winter warming trend, on which centennial-scale cooling at 8.2 ka is superimposed. Our reconstruction of this interval is consistent with regional proxy data, but analysis of modern carbonate deposition implies that winter warming also continued until the PI period, in contrast to summer climate trends. This finding elucidates the opposing roles of winter and summer forcings for the Mid-Late Holocene temperature evolution of the Baltic Region, similar to that of the continental interior of Eurasia.

4.2 INTRODUCTION

Calcareous tufa and travertine have widely been utilized as indicators of Quaternary environmental and climatic change based on their sedimentological and geochemical characteristics (Andrews et al., 1997; Garnett et al., 2004a; Hennig et al., 1983; Ihlenfeld et al., 2003; Pazdur et al., 1988; Pedley, 2009; Rogerson et al., 2008). They form in a range of freshwater depositional environments, including lacustrine, paludal, riverine, cascade, and spring-slope (Ford and Pedley, 1996; Pedley, 1990), and commonly contain macrophytic vegetation, malacofauna, and pollen to aid paleoenvironmental interpretations (Alexandrowicz et al., 2016; Pentecost and Zhao-Hui, 2008). Because these crystalline deposits record the stable-isotope and elemental chemistry of meteoric waters (Pentecost and Spiro, 1990; Teboul et al.,
and can be dated directly using a combination of radiocarbon and Uranium-Thorium disequilibrium techniques (Garnett et al., 2004b; Sierralta et al., 2010), tufa and travertine are among the most informative terrestrial paleoclimate proxies. Several challenges have been noted, however, which complicate paleoclimatic interpretations and limit the overall research utility of these freshwater carbonates. First, non-equilibrium isotopic exchange during mineral precipitation are common both in high- and low-temperature settings (Ihlenfeld et al., 2003; Kele et al., 2008; Kele et al., 2011), which could obfuscate the interpretation of their stable-isotope and cation chemistry. Secondly, tufa and travertine deposits are generally confined to interglacial periods and, outside of the subtropics, their occurrence has declined since the Middle Holocene (Goudie et al., 1993; Pentecost, 1995). The lack of actively growing carbonate minerals at many extratropical sites precludes the assessment of equilibrium during formative geochemical reactions, for which the reaction kinetics are notably site-specific.

In the classification of freshwater carbonate deposits, definitions of the terms tufa and travertine somewhat overlap (Ford and Pedley, 1996; Pedley, 1990; Pentecost, 1995). Pedley (1990) applies the term tufa to all cool-water carbonates characterized by a porous or spongy texture and possible presence of micro- and macrophytic casts of vegetation. The latter indicates the biomediation of cool-water calcite precipitation in tufa, which was thought to contrast with purely physico-chemical calcite precipitation of travertine from high-temperature springs. Biomediation of calcite precipitation occurs when photosynthetic uptake of CO₂, whether by algae, bacteria, or aquatic vegetation, enhances calcite saturation of the fluid. Because biomediation can be observed in high-temperature settings (Pedley, 2009), however, it is not a diagnostic process between cool-water tufa and hydrothermal travertine. Another possible line of distinction is the well-lithified fabric of travertine (Anzalone et al., 2007), commonly cemented
by diagenetic calcite spar that can be identified petrographically, but cementation depends more on the age and burial of the deposit than its genesis. Finally, tufa and travertine may be distinguished by process of formation and primary source of CO₂. In classic travertine models, CO₂ is brought to the surface by hydrothermal springs along deep faults; hence, the total Dissolved Inorganic Carbonate (DIC) is higher in these settings and the δ¹³C of precipitated calcite is less depleted (Pentecost, 1995). This model contrasts with cool-water tufa formation, in which carbon is sourced primarily from ¹³C-depleted soil-respired CO₂. However, cool-water tufa deposits are commonly associated with structural anomalies, such as faults, which can deliver an additional source of CO₂ to the surface environment via low-temperature springs (Garnett et al., 2004a; Henchiri, 2013; Johnson et al., 2009). Hence, Pentecost terms these unique tufa deposits as meteogene (low-T) travertine and distinguishes them from thermogene (high-T) travertine by the primary CO₂ source and water temperature during formation.

Holocene freshwater carbonates on the Izhora Plateau in northwestern Russia—classified herein as calcareous tufa or meteogenic travertine (Pentecost, 1995)—record deposition in lacustrine, paludal, and riverine environments, but have not been reported outside of Russian literature or investigated for their geochemical properties. Because carbonates are actively forming at several sites, the Izhora Plateau provides a unique opportunity to interpret conventional paleoclimatic proxies in Holocene deposits through the results of controlled experiments documenting modern geochemical processes. This site is also one of the highest latitude occurrences at nearly 60°N, whereas tufa and travertine are most commonly found in lower mid-latitude (southeastern Europe) and subtropical (Eastern Mediterranean) locations. For this reason, along with the Early–Middle Holocene age of most deposits, some researchers have proposed a climatic control on travertine deposition (Dramis et al., 1999; Pentecost, 1996). The
occurrence of travertine on the Izhora Plateau in the absence of hydrothermal springs may challenge this supposition, so we aim to investigate the origin of both Holocene and modern deposits.

4.2.1 Study area

The Izhora Plateau (Fig. 4.1) is an uplifted region (100–150 m asl) south of the Gulf of Finland that is roughly rectangular by area (59°18’–59°46’ N, 28°52’–30°15’ E). Its surface is characterized by isolated hills and linear depressions, the latter of which are filled by streams, ponds, and lakes. Until almost 13 ka, the region was glaciated by the Scandinavian Ice Sheet, after which the environment shifted abruptly from proglacial tundra to boreal forest by 12–10 ka. Both the topographic surface and underlying Ordovician limestone bedrock dip gently to the southeast (<1°), directing streams and groundwater flow. Surface water is generally sourced from high-carbonate-alkalinity springs associated with joints and faults in the limestone bedrock that tend to strike along a NW or NE azimuth. Anticlinal deformation of the bedrock is somewhat common and is expressed as subsurface folds or ‘island’ uplifts (e.g. Duderhof Heights), for which the axes generally trend SW–NE. The most prominent geomorphic feature is a cuesta-like erosional escarpment, called the Baltic-Ladoga glint, which demarcates the northern margin of the Izhora Plateau and divides the watershed. The Baltic-Ladoga glint trends E-W near the Izhora Plateau, but the trend shifts to ~75° below the southern margin of Lake Ladoga to the east, and to the west through Estonia to the Gulf of Finland (Dronov et al., 1996; Krotova-Putintseva and Verbitskiy, 2012).

Meteogenic travertine is actively forming at only a few locations on the Izhora Plateau, for example near the headwaters of the Fabrichnaya River. Most deposits occur in streambeds as
isolated phytocretions and lithified algal mats, especially at small cascades. In contrast, Early–Middle Holocene deposits up to several meters thick have been documented at localities from Gostilitsy and Shingarka (north) to Pudost and Antelevo (east), indicating a significant reduction in the extent of travertine formation during the Late Holocene. In this study, we choose to focus on a 2-meter layer of weakly laminated, microdetrital calcite near the town of Pudost, which we interpret to reflect deposition within a shallow lake environment from approximately 9.4 to 6.8 ka. If correct this interpretation is correct, then stratigraphic variations in stable-isotope and elemental geochemistry should reflect temporal changes in surface-water chemistry, possibly associated with climatic and environmental evolution of the region.

4.2.2 Regional climate and Holocene temperature history of the Peribaltic

Modern climate of the Izhora Plateau is highly seasonal, as the average surface air temperature ranges from -6.7°C (DJF) to 16.4°C (JJA), with an annual average temperature of 4.5°C, during the interval 1834–2016 C.E. The Peribaltic region (including Fennoscandia) is strongly influenced by atmospheric teleconnections that transport heat and moisture from the North Atlantic and Arctic oceans. Instrumental climate data from St. Petersburg, Russia (30–40 km northeast of the Izhora Plateau) indicate a strong dependence of winter surface temperature on the North Atlantic Oscillation (NAO) and Arctic Oscillation (AO) and monthly precipitation on the Scandinavian Pattern (Fig. 4.2). These teleconnections are broadly defined by meridional pressure gradients over the ocean, which determine the zonality of atmospheric flow into northern Europe. More zonal flow produces southwesterly air circulation and directs warm, humid air masses from lower latitudes to our study area, resulting in higher air temperature and enhanced precipitation.
The Holocene paleoclimate history of the region is well documented by multiple proxy techniques, including pollen (Heikkilä and Seppä, 2010), lake isotopes (Heikkilä et al., 2010), glacial extent (Nesje, 2009; Nesje et al., 2001), caves (Sundqvist et al., 2007), and coastal marine deposits (Sejrup et al., 2011). Collectively, these reconstructions show rapid amelioration of periglacial conditions following the Younger Dryas until the Middle Holocene, attributed primarily to retreat of northern hemisphere ice sheets. Until its final collapse at ca. 9 ka, the Scandinavian Ice Sheet (SIS) cooled the adjacent region via an albedo effect, which kept summer temperatures below the Holocene average, despite relatively high greenhouse gas (GHG) concentrations and maximal summer insolation (Renssen et al., 2009). Topography of the SIS and Laurentide Ice Sheet (LIS) also displaced the polar jet stream southward until ca. 7 ka, resulting in colder and drier winters over much of northern Eurasia (Baker et al., 2017; Jin et al., 2011; Mauri et al., 2015). Climatic warming paced by ice-sheet disintegration was amplified by several feedbacks, including a concomitant rise in GHG concentrations, reforestation, a loss of sea ice, and rejuvenation of poleward ocean heat transport via Atlantic Meridional Overturning Circulation (AMOC).

Between 9–5 ka, northern hemisphere climate had equilibrated to the summer insolation maximum, which forced higher sea and land temperatures across the North Atlantic sector and northern Europe (Marcott et al., 2013; Sejrup et al., 2016). This interval, termed the Holocene Climatic Optimum (HCO), was further characterized by enhanced anticyclonic circulation over central Scandinavia, resulting in hotter and drier summers (Antonsson et al., 2008; Harrison et al., 1992; Seppä and Poska, 2004). Following the HCO, most proxy records indicate gradual cooling of 2–3°C until the Pre-Industrial period. This trend is opposite the small rise in GHG concentrations, but consistent with a 27 W/m² decrease in northern hemisphere summer
insolation (NHSI). Therefore, orbital forcing of summer climate and feedbacks from ice-sheet disintegration seem to have been the dominant controls on the Holocene annual temperature evolution of Fennoscandia and the Baltic region.

Warming during the HCO was markedly pronounced in the North Atlantic and Fennoscandian regions, with surface temperature anomalies exceeding 1°C above the hemispheric mean, according to a spatiotemporal reconstruction utilizing proxy data from 74 sites (Sejrup et al., 2016). However, only 24 of these proxy datasets were interpreted to reflect mean annual temperature, with the remaining 50 sites indicative of growing season or peak summer conditions. The paucity of winter records could therefore bias the annual signal and even mask the influence of certain dynamic forcings, for example given the opposite trajectories of summer and winter insolation. From 11 ka to present, summer (JJA) insolation at 60 N latitude decreased by 27 W/m² (6.2%), whereas winter (DJF) insolation increased by 6 W/m² (15%). If winter insolation were a significant forcing on Holocene surface temperature, then long-term winter warming would have mitigated the summer cooling signal following the HCO. Because regional temperature reconstructions rely almost exclusively on summer temperature proxies, evidence of Holocene winter warming could imply that the thermal maximum has been exaggerated by sampling bias.

4.3 METHODS

4.3.1 Sampling of the Pudost travertine deposit

The main section of paludo-lacustrine travertine outcrops within a small quarry (59.62°N 30.04°E) near the town of Pudost, Russia, adjacent to the Izhora River (Fig. 4.3). Weakly laminated microdetrital carbonate sediment unconformably overlies a thin (10–30 cm)
glaciolacustrine, fine-grained till, which itself covers the Ordovician limestone bedrock. The travertine exposure is approximately 200 cm thick within the quarry, although recent soil activity has altered the upper 5 cm. For stable-isotope and elemental analysis (Table B1), we collected sediment into plastic vials from individual laminae at 2-cm intervals from the basal contact to the soil horizon. A triangular section of the travertine outcrop was removed from the quarry for storage at St. Petersburg State University and future analyses. Separate collections were taken for Uranium-Thorium disequilibrium and radiocarbon dating of the material. Microdetrital carbonate sediment is relatively free of organic (woody) material, but contains abundant malacofauna and common phytocretions associated with *Chara* algae.

A ground-penetrating radar (GPR) scan was made in the vicinity of the quarry to assess the homogeneity of outcrop thickness. These data confirmed that thickness did not vary measurably and that we most likely sampled near the lake depocenter. The travertine deposit shoals and pinches out within ~300 meters on either side of the Izhora river, which is most evident in the Pudost south quarry exposure (Fig. 4.3). Hand samples were collected from the south quarry to describe sedimentary facies and to constrain stable-isotope variability from shoreline to depocenter.

The western margin of the Pudost travertine deposit outcrops northwest of Taitsy Bridge, where it transitions gradually from pure microdetrital carbonate to coarser phytoclastic grainstone upstream. Accumulation of microdetrital facies at this site exceeds one meter in thickness, but has been more severely eroded by the modern Izhora River than near the main quarry site. Therefore, we could not sample along a single stratigraphic profile for geochemical analysis or to determine the relative age of the Taitsy Bridge exposure. Finally, a stratigraphic profile near Antelevo (18 km east of Pudost; Fig. 4.1) was described for facies analysis of
travertine deposits downstream. Hand samples were collected to compare overall stable-isotope composition and to date the underlying peat layer, but a stable-isotope profile was not feasible, due to the non-laminar nature of the deposit.

4.3.2 Surface water sampling

To assess geographic and seasonal variability in the δ¹⁸O and δD of surface waters across the Izhora Plateau, we systematically collected from rivers, ponds, and springs between December 2011 and August 2013. Water samples were collected in 5-mL glass vials with no airspace and sealed with electrical tape to prevent evaporative alteration of the stable-isotope signatures. Winter and summer collections were taken from the spring-fed Izhora River, which flows southeast along the linear depression in which the Pudost travertine was deposited. Spring and summer collections were made near our modern-analogue site (Shingarka Quarry) from the Fabrichnaya River, which flows north to the Imperial Summer Palace (Peterhof) along the Gulf of Finland, but originates to the northwest of Pudost within the same linear structural depression. Finally, we sampled from the Suma River, located on the western margin of the Izhora Plateau.

Four ponds were sampled along the linear structural depression, including the Pudost main quarry (partially filled, because it cuts below the water table) and the Shingarka Quarry. Because no lake exists on the modern Izhora Plateau that is comparable in size to the Pudost travertine deposit, these samples allow us to compare the δ¹⁸O and δD values of a stable body of water with those of springs and rivers, particularly during the peak of summer evaporation. Most springs across the Izhora Plateau are associated with NW-SE and NE-SW trending structural features (depressions, folds, and faults) that cross cut the underlying carbonate bedrock. We
sampled five springs along the structure associated with the Pudost travertine to assess stable-isotope variability between Gatchina (southeast) and Kipen (northwest).

4.3.3 Stable-isotope analysis

For all carbonate samples, $\delta^{18}$O and $\delta^{13}$C were determined at the Las Vegas Isotope Science (LVIS) lab by phosphoric-acid reaction at 70°C in a Kiel IV automated carbonate preparation device coupled to a ThermoElectron Delta V Plus mass spectrometer. Both $\delta^{18}$O and $\delta^{13}$C were calibrated to internal and external standards, through which precision was determined to be better than 0.08‰ and 0.06‰, respectively, based on long-term means of an internal reference (USC-1). All isotopic values of carbonate materials are reported herein as per mil (‰) deviations from the Vienna Pee Dee Belemnite (VPDB) standard (Tables B1 and B2).

Samples of sedimentary microdetrital tufa (5–10 mg) were sorted under a binocular microscope prior to analysis to isolate fine-grained mineral precipitates from malacofaunal shell material and algal phytocretions. We then subsampled microdetrital material from four individual vials ten times each to constrain intralamellar isotopic variability. This variability slightly exceeded analytical uncertainty at 0.1–0.15‰ for $\delta^{13}$C and 0.08–0.2‰ for $\delta^{18}$O. Therefore, we used the mean of duplicate samples for the stable-isotope profiles of the main travertine section. Gastropod shell material from three layers was also analyzed for $\delta^{13}$C and $\delta^{18}$O to determine isotopic offsets between the two pathways of carbonate precipitation. These three samples show consistent offsets for both stable-isotope values: +0.5‰ for $\delta^{18}$O and -4‰ to -5.5‰ for $\delta^{13}$C (Table B2).

Surface and spring water samples were analyzed for $\delta^{18}$O and $\delta$D at UNLV on a ThermoElectron high-temperature conversion elemental analyzer (TC/EA) using a continuous
flow pyrolysis technique. The TC/EA was fitted with a GC PAL auto-sampler equipped with a 10-μl syringe. Water samples were reacted at 1450°C in a ceramic column lined with glassy carbon and packed with glassy carbon fragments to reduce H₂O injections to CO and H₂ gases. The gases were carried by high-purity helium through a gas chromatograph at 90°C, where they were separated prior to isotopic analysis by the Delta V mass spectrometer via a Conflo-III open split. All δ¹⁸O and δD values were corrected by four internal standards that have been calibrated to VSMOW, SLAP, and GISP standards. Final data are the mean of at least five repeat injections and analysis per sample to ensure a minimal memory effect. δ values are reported as per mil (‰) deviations from Vienna Standard Mean Ocean Water (VSMOW), with precisions better than ±0.2‰ for δ¹⁸O and 2‰ for δD.

4.3.4 Major cation analysis

Determinations of Mg/Ca and Sr/Ca ratios in local springs and along the main section of the Pudost travertine were made using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES; Perkin Elmer Optima 1200 DV) at Cornell College in Mt. Vernon, IA. For travertine samples, 3-5 mg of microdetrital carbonate was dissolved using ICP-grade, 6 M nitric acid and diluted up to 10 ml with nanopure water. Four stock standard solutions were prepared at concentrations bounding that of diluted carbonate solutions: 40, 100, 200, and 400 mg/L for Ca; 0.5, 1, 5, and 10 mg/L for Mg; and 0.1, 0.5, 1, and 5 mg/L for Sr. Additionally, we prepared two blank solutions from diluted nitric acid for instrument calibration. The ICP-OES was re-calibrated using blanks and standard solutions after each set of ~15 unknown sample solutions to account for instrumental drift. Analytical precision (2-σ) with respect to volumetric concentration was determined to be 4.06% for Ca, 1.18% for Mg, and 3.88% for Sr, based on 6
analyses of standard solutions. However, because Mg and Sr were normalized to Ca concentration, the 2-σ uncertainties of final data are lower: 2.46% for Mg/Ca and 2.1% for Sr/Ca.

4.3.5 SEM analysis of Holocene and modern carbonate structures

Imaging of Holocene travertine and modern mineral precipitates was performed using a JEOL scanning electron microscope (model JSM-5610) at the Electron Microanalysis and Imaging Laboratory (EMiL) at the University of Nevada, Las Vegas. All samples were pretreated with a gold coating using a sputter method (30-45 seconds) to enhance contrast under the electron beam and to allow for accurate chemical mapping and quantitative analysis. The latter was used to distinguish calcite precipitates from microdetrital silicates and organic material.

4.3.6 Geochronology and age model

The age of microdetrital carbonate material from the main quarry section at Pudost was constrained by analysis of eight samples along the profile using the \(^{230}\text{Th}/^{234}\text{U}\) disequilibrium method (Table 4.1). Specific activities of \(^{230}\text{Th},^{232}\text{Th},^{234}\text{U},\) and \(^{238}\text{U}\) for age determination were measured by an ORTEC Alpha Duo alpha spectrometer at St. Petersburg State University. Separation of uranium and thorium isotopes from carbonate material was carried out by leaching with nitric acid (the L/L technique described by Maksimov et al., 2012). The U-Th disequilibrium method assumes that 1) during precipitation of calcite, incorporation of \(^{230}\text{Th}\) (detrital thorium) was negligible, and 2) following crystallization, the mineral remained an isotopically closed system with respect to U and Th. Because U-Th ages of material from Pudost
follow stratigraphic order and yield duplicate results within analytical uncertainty at two intervals, we deem it unlikely that age determinations were compromised by an isotopically open system. To correct for any incorporation of $^{230}$Th during calcite crystallization, the concentration of $^{232}$Th is measured in the same sample. Due to its long half-life (14.05 Ga), $^{232}$Th is effectively stable over Quaternary timescales and can be used as a proxy for initial ‘detrital thorium’ (Garnett et al., 2004b). However, the activities of $^{232}$Th were below the detection limit of 0.005 cts/min/g in all carbonate samples from Pudost, precluding the application of a detrital-$^{230}$Th correction. Therefore, we stress that the results reported in Table 4.1 are theoretical maximum ages, for which the potential detrital $^{230}$Th correction (assuming $^{230}$Th activities up to the instrumental detection limit) could range up to 1.0 kyrs in the oldest sample (No. 864) to 2.2 kyrs in the youngest sample (No. 541).

An age-growth model for the Pudost travertine was constructed from the eight U-Th dates using a segmented linear fit, which suggests a doubling of the depositional rate from Early to Middle Holocene (Fig. 4.4). The linear fit is divided at 146 cm depth, because we attribute a corresponding negative peak in the $\delta^{18}$O time series to the well-documented 8.2-ka cooling event. Anchoring of the age model at 8.2 ka slightly alters the estimated range of Holocene deposition, but not beyond analytical uncertainty. Moreover, the anchor improves the statistical fit of the age model to U-Th data and is justified below by a comparison of Pudost $\delta^{18}$O to regional paleoclimate records.

4.3.6.1 Radiocarbon Dating

The ages of three samples of woody material from a peat layer near the town of Antelevo were determined by the radiocarbon method. Sample preparation and analysis was performed
according to the techniques described by Arslanov (1987; 1993) at St. Petersburg State University using a Perkin Elmer Quantulus 1220 ultra-background liquid-scintillation spectrometer radiometer. Uncalibrated radiocarbon ($^{14}$C) dates are reported in Table 2 as years B.P. (Before Present, where Present = 1950 C.E.), along with 2-$\sigma$ analytical uncertainties. All ages were calibrated to calendar years using OxCal online software according to the IntCal13 radiocarbon calibration curve (Reimer et al., 2013); calibrated ages are reported in Table 4.2 and referenced herein as years B2K.

4.4 RESULTS

4.4.1 Stable-isotope variability in the Pudost travertine

Stratigraphic variations in $\delta^{18}$O and $\delta^{13}$C along the Pudost main quarry section are shown in Figure 4.5. Each data point represents the arithmetic mean and standard deviation of duplicate analyses from each 2-cm interval. Due to a step in the quarry that split the stratigraphic section, the interval from 94–98 cm was sampled twice (once from each exposure) to align the sections. Therefore, the final stable-isotope profile is comprised of a total of 206 analyses from 103 intervals along the 200-cm section. Assuming the constraints from our age model, the averaging sampling resolution from 9.5–6.8 ka is approximately 27 years, which is sufficient to resolve centennial-scale isotopic trends.

The $\delta^{13}$C of microdetrital sediment decreases from -7‰ at the base of the section to approximately -9‰ in the upper half. This negative trend in $\delta^{13}$C is sharper toward the base, resulting in a concave-upward pattern in the stratigraphic profile that reaches equilibrium by 120 cm depth (ca. 7.8 ka). Above 150 cm depth, $\delta^{13}$C variability is less pronounced and ranges from -8.2‰ to -9.2‰. However, a distinct peak in $\delta^{13}$C occurs at 142 cm, which coincides with the ‘8.2
ka event’, followed by a 1‰ negative shift that reaches a minimum value of -9.21‰ at 124 cm, or 7.75 ka. Though less prominent, another peak and trough pair can be resolved between 100 cm and 50 cm depth in the profile (7.5–7.0 ka).

In contrast to δ¹³C, the δ¹⁸O of microdetrital sediment increases steadily throughout the profile, from -13‰ at the base to -11.5‰ VPDB in the upper half of the section. Below 80 cm depth, δ¹⁸O variability is considerably less than toward the top of the section, with the exception of a prominent 0.5‰ negative excursion from 136–150 cm depth. Based on preliminary age constraints from U-Th ages and regional paleoclimate records, we correlated this excursion to the ‘8.2 ka event’, and, following the assumption of contemporaneity, we used it to anchor the final age model. Above 136 cm depth, δ¹⁸O sharply increases by 0.7‰ toward a small peak centered at 124 cm depth (~7.75 ka). The remainder of the record is characterized by δ¹⁸O variations of ±0.5‰ around an upward linear trend, with the most prominent deviations at 50 cm (~7 ka; +0.5‰) and 26 cm (~6.8 ka; -0.5‰). While the total range of δ¹⁸O values in the Pudost profile is 1.83‰, the linear trend is closer to 1.25‰, or from -12.75‰ at 9.5 ka to -11.5‰ at 6.8 ka.

4.4.2 Major-cation variability in the Pudost travertine

Stratigraphic variations in Mg/Ca and Sr/Ca along the Pudost main quarry section are plotted alongside stable-isotope data in Figure 4.5. These data are comprised of a total of 103 analyses at 2-cm resolution (overlapping at 94-98 cm), resulting in the same temporal resolution as for δ¹⁸O and δ¹³C. The stratigraphic trend in Sr/Ca is very similar to that of δ¹³C, because the highest ratios (~3x10⁻⁴) at the base of the section decrease in a concave-upward pattern to about half that value (1.6x10⁻⁴) within the upper 10 cm of the section. Although minor peaks and troughs in δ¹³C and Sr/Ca generally align, the signal-to-noise ratio for the latter dataset is not
sufficient to resolve centennial-scale trends (e.g. the ‘8.2 ka event’) with statistical confidence. The long-term trend, however, seems to indicate a major shift in Sr systematics over the life of the lake system, so we explore hypotheses related to changes to groundwater chemistry, aquifer source, water-rock interactions, or kinetic effects during calcite precipitation below.

The Mg/Ca ratio of microdetrital travertine ranges from 0.016 to 0.021, which is considerably less variation than for Sr/Ca. However, the signal-to-noise ratio is much higher (the lag-1 autoregressive coefficient for Mg/Ca is only 0.3, compared to 0.96 for Sr/Ca), and there are no discernable Holocene trends for Mg/Ca. Still, centennial-scale peaks and troughs are evident in the dataset. For example the interval from 125–150 cm depth (centered around 8.2 ka) is characterized by a higher ratio (by 0.0015) than in the 10-cm intervals that surround it.

4.4.3 Surface hydrology of the Izhora Plateau

Stable-isotope analysis of rivers, ponds, and springs across the Izhora Plateau (Table 4.3) revealed limited variability (~1.5‰ for δ¹⁸O) between sampling sites and seasons. For example, the average δ¹⁸O value for all sites is -12.6±0.6‰, but the majority of data are within uncertainty of -13.0‰, with only a few summer collections yielding less depleted values (up to -11.5‰). The same pattern is exhibited by δD values, for which the majority of data group near the average value of -89‰, whereas a few summer collections yielded less depleted values (up to -82‰). It is notable that the less ¹⁸O-depleted summer collections are also characterized by lower d-excess values, indicative of a different moisture source—in this case, precipitation originating from low-latitude Atlantic or Mediterranean waters rather than the Arctic (Kurita, 2004, 2011). Summer isotopic enrichment of surface waters is not associated, however, with the type of collection (e.g. pond vs. spring) and therefore cannot be attributed to evaporation. Instead, the
sites exhibiting higher $\delta^{18}$O and $\delta$D values are geographically isolated to the west/northwest or southeast of Pudost, near the edges of the linear structural feature. In the vicinity of the Pudost quarry, stable-isotope data are invariable across seasons and collection type.

We have defined a Local Meteoric Water Line (LMWL) using monthly GNIP data from 1980–1990 collected at the Leningrad Station (IAEA/WMO database, 2016; http://www.iaea.org/water) and precipitation events from 2012–2013 (Table 4.4). Surface-water collections plot along the LMWL (Figure 4.6), but $\delta^{18}$O and $\delta$D are depleted by 1.2‰ and 4‰, respectively, relative to the average annual values (dashed lines) of available GNIP data. Assuming the 1980–1990 decade is characteristic of more recent precipitation, the lower observed isotope values suggests that the surface hydrology of the Izhora Plateau is heavily weighted toward winter precipitation. For example, the average $\delta^{18}$O value of our data (-12.6‰) can be explained if 90% of spring and surface water originates from winter half-year precipitation (October–March; $\delta^{18}$O = -12.83‰), or similarly if 66% originates from peak winter precipitation (DJF; $\delta^{18}$O = -13.94‰), with equal contributions from other seasons. This winter bias in groundwater composition is common in vegetated temperature localities (Baker et al., 2017; Göktürk et al., 2011), and is explained by unequal infiltration of meteoric water into shallow aquifers. During the warm season, enhanced evapotranspiration recycles a significant fraction of rainfall back into the atmosphere, limiting summer contributions to the aquifer.

We further analyzed the major cation chemistry in six springs on the Izhora Plateau (Table 4.5), using collections made simultaneously in August 2013. The Mg/Ca ratio is nearly ubiquitous between springs (0.47–0.50), except in the sample from Duderhof Heights, which is a minor outlier (Mg/Ca = 0.57). Whereas the other five localities are associated with faulted depressions, Duderhof Heights is a set of linear hills comprised of folded stratigraphy that are
raised above the Izhora Plateau. Hence, it is geomorphologically unique among our sampling sites. In the remaining springs, the average Mg/Ca ratio (0.48) is approximately 25 times larger than that of the Pudost travertine. If the Early Holocene travertine precipitated from a solution with modern spring-water chemistry, the resulting partition coefficient ([Mg/Ca]_{calc}/[Mg/Ca]_{sol}) would be 0.04. This value is within the range of experimental calcite precipitation (Oomori et al., 1987) but corresponds to unrealistically high water temperatures (40–50°C). Therefore, modern Mg/Ca ratios in Izhora springs must be significantly lower than during the Early Holocene. Comparing the Mg/Ca of modern phytocretions to that of local springs yields a partition coefficient of 0.018, which is more consistent with the ambient water temperature of ~7–12°C.

Ratios of Sr/Ca in Izhora springs are far more variable, ranging from 0.0004–0.0015. Again, the Duderhof Heights spring is considered an outlier, along with the sample from Krasnoye Selo (4 km north of Duderhof Heights). These springs, located on the northern margin of the plateau, exhibit much higher Sr/Ca values (0.0014–0.0015) than in the vicinity of Pudost (0.0005). Still, samples from south of Pudost (Korpikovo; Sr/Ca = 0.0008) and at the northwestern edge of the faulted depression (Kipen; Sr/Ca = 0.0010) are relatively high. This variability could be due to the respective solubility of SrCO₃ along groundwater pathways or simply variations in bedrock chemistry. Comparing the Sr/Ca of modern phytocretions (0.0018) to spring waters yields partition coefficients ranging from 0.12–0.40, consistent with experimental determinations below 25°C (Pingitore and Eastman, 1986).

4.5 Discussion

4.5.1 Facies interpretation of meteogenic travertine deposits from the Izhora Plateau
Precipitation of calcite in freshwater, spring-fed streams is observed today in several isolated locations on the Izhora Plateau. Near the sources of the Suma River (western margin) and Fabrichnaya River (northern margin), calcite phytocretions form around aquatic plants and on algal mats within the streambed (Fig. 4.7). Most phytocretions are broken up by the stream flow and comprise the coarse detritus fraction downstream, rather than being preserved in situ, as in marginal paludal environments (Ortiz et al., 2009; Pedley, 1990). Carbonate structures associated with algal mats tend to form at vertical breaks in the streambed (Fig. 4.7b). They are characterized by porous aggregations of predominantly cylindrical phytocretions (commonly precipitated around Chara algae), which are cemented together at the base of the mat (Fig. 4.7c-d). Less than 1 km from the source of the Fabrichnaya River, an artificial shallow pond has filled an abandoned quarry pit along the stream (Fig. 4.7a), which was mined for Holocene travertine as a building material. Using anchored glass plates, we confirmed that microdetrital carbonate sediment also forms actively within this pond—which may serve as the closest modern analogue to Early–Middle Holocene deposition at Pudost (below)—but at a rate significantly lower than that estimated for Holocene deposits.

The largest Holocene freshwater carbonate deposits of the Izhora Plateau are found along a NW-SE trending linear depression, which extends ~34 km from north of Gostilitsiy (59.80°N 29.68°E) to the town of Miyza-Ivanovka (59.67°N 30.16°E). Our main site of investigation near the town of Pudost (Fig. 4.1) is an elongated lenticular body of freshwater carbonate sediment that extends approximately 4 km from Pudost to the northwest along the modern Izhora River (Fig. 4.3). Formation thickness reaches two meters near the river, whereas the maximum width of the formation—difficult to trace due to lack of exposure—is likely less than 600 m. The sedimentary composition of the formation is almost ubiquitously microdetrital calcite, which
contains some mollusk shell fragments, sparse intact gastropod shells, *Chara* phytocretions, and rare ostracod shells. Using SEM imaging, we confirmed that non-carbonate detritus is almost non-existent and organic material is uncommon in the Pudost deposit. These observations are supported by ICP-OES data, from which we estimated the acid-insoluble fraction to be 7–11% by weight for all samples (Fig. 4.5). Individual grains, which vary in size up to ~300 μm diameter, are ooid-like aggregates of microcrystalline calcite approximately 3–8 μm across (Fig. 4.8).

In outcrop, the Pudost deposit can be described as porous, pseudo-laminar carbonate sand that is moderately cemented. Based on the formation geometry, sedimentary features, and mass fraction of calcite, we interpret the Pudost main quarry section as reflecting deposition within a shallow lacustrine environment. This interpretation is further supported by the presence of pioneer species of freshwater pulmonate gastropods from the families Lymnaeidae and Planorbidae (Strong et al., 2008; Table 4.6). Today, these organisms inhabit shallow lacustrine and paludal environments and can withstand seasonal changes in water level, including desiccation. We found no sedimentary evidence, however, of lake desiccation within the main stratigraphic profile. On the other hand, the presence of *Chara* algae throughout the Pudost section and in other exposures indicates a stable open water body less than 5 m depth. The absence of phytocretions associated with vascular aquatic plants and moss is also consistent with open water.

Although the elongated deposit parallels the modern Izhora River, sedimentary material is found at least two meters above the current water table and up to ~300 meters distance from the river bank, suggesting a Late Holocene shift in surface hydrology from paludo-lacustrine to riverine. For a small lake body to pool along the paleo-Izhora River, a natural dam must have cut
off the stream flow during the Early–Middle Holocene upstream from the main quarry section near Pudost. Because paludo-lacustrine facies are not observed east of the plunging anticline adjacent to Miyza-Ivanovka (Fig. 4.3), we suggest this structure as a hypothetical natural barrier, which allowed the stable water body to form in the vicinity of Pudost. The sharp bend around the structure today could reflect a point of break though that led to shoaling of the paleo-lake (below). However, access to Holocene exposures of the deposit is limited between the Pudost south quarry and the anticlinal structure. Therefore, we have mapped out the paleo-lake boundary with a degree of uncertainty (Fig. 4.3), pending additional field studies.

An exposure of the Pudost travertine in the south quarry, closer to the margin of the deposit, exhibits a wider range of facies and evidence of lake shoaling. The lower two thirds of the 1.5-meter section is comprised of pseudo-laminar, microdetrital carbonate sediment, identical to that observed the main section. This uninterrupted sequence of open lacustrine facies between sites supports the notion that the ancient lake system did not dry out for extended intervals during the Early–Middle Holocene. Overlying microdetrital sediment is a distinct layer with algal bioherm structures, phytoclastic grainstone, and in situ phytocretions of vascular aquatic plants typical of marshes (e.g. sedge). These features are characteristic of paludal and riverine facies of meteogenic travertine (Arenas et al., 2000; Pedley, 1990), such as those observed in the modern Fabrichnaya River and quarry pond. Paludal and lacustrine facies are divided by a mildly undulated, unconformable surface, which suggests channel erosion and downcutting prior to subsequent deposition. Because algal bioherms and in situ phytocretions require stagnant or weakly flowing water to form, these structures likely developed during paludal and marshland phases of the shoaling lake system. Phytoclastic grains could have been deposited during intermittent riverine intervals or were carried into the paludal environment during high flow.
stages. Based on the age of the uppermost lacustrine deposits, the regressive phase of the Pudost lake system occurred after 6.8 ka.

Near Taitsy Bridge at the northwestern edge of the Pudost deposit (Fig. 4.3), relatively pure microdetrital carbonate sediment is intercalated with a thin (~20 cm) layer of peat that is not observed in other sections. The peat bed contains both silt and carbonate sediment, along with abundant wood fragments. Given the abrupt, but conformable stratigraphic transition to and from the peat bed, we interpret it to reflect a regressive phase of the lake, during which organic rich delta-like deposits prograded into the lake body. At present, however, the age of the peat bed is unknown, so it is not possible to correlate it with the main stratigraphic section at Pudost. Upstream from the Taitsy Bridge exposure (within 500 m), microdetrital carbonate sediment transitions into organic-rich calcarenite, characteristic of channel deposition. Therefore, this locality was most likely the inlet to the paleo-lake system.

Although the transition from lacustrine to paludal and riverine facies is not observed in the Pudost main quarry section, it is plausible that the uppermost layers were eroded during incision of the modern Izhora River. This scenario would explain, for example, the abundance of broken phytocretions in Holocene riverine deposits up to 20 km downstream from Pudost (see below). In either case, we may conclude that an elongated, open lake system formed by approximately 9.5 ka and persisted at least until 6.8 ka. After 6.8 ka, the lake shoaled abruptly, perhaps in response to a breakthrough of the natural dam, and transitioned to a paludal environment with intermittent stream phases, in which precipitation of calcite continued. In more recent Holocene history, the freshwater carbonate formation was eroded by incision of the modern Izhora River, which now stands more than a meter below the 6.8-ka depositional surface.
Immediately downstream from Pudost—adjacent to the town of Miyza-Ivanovka—the Izhora River bends sharply around a southwest plunging anticlinal ridge (Fig. 4.3). This structure alters the course of the river from its southeast azimuth (130°) to the northeast (45–55°), after which its course alternates between these azimuths that reflect the predominant strikes of structural dislocations across the Izhora Plateau. Approximately 20 km east of the Pudost section, near the town of Antelevo, we find additional evidence of Early Holocene freshwater carbonate formation. Along the bank of the Izhora River, a 4-meter vertical exposure reveals at least four stages of a shoaling lacustrine/paludal environment. Absent from the section is the microdetrital carbonate facies that characterizes the Pudost deposit. Instead, the basal layer of glacio-lacustrine till is overlain by 2 m of intercalated organic-rich silt and woody peat, the top of which was dated by the radiocarbon method to 8.61 ± 0.12 ¹⁴C kyr BP (9.73 ± 0.27 ka B2K; Maksimov et al., 2015). Within the peat layers are preserved pine (*Pinus*) and alder (*Alnus*), which had recovered in the region following deglaciation by ~12–11 ka (Wohlfarth et al., 2007). The organic-rich silt contains abundant malacofauna (Nikitin and Kiyashko, 2009), including freshwater lacustrine bivalves (Family Euglesidae) and pulmonate gastropod species (*Cingulipsidium nitidum*, *Conventus conventus*; Nikitin and Kiyashko, 2009). Additional gastropod species typical of lakes and marshes are found throughout the overlying sediments (Table 4.7).

The basal peat and silt transition abruptly to an organic-rich, silty marl (~1 m thick) with abundant phytocretion clasts, possibly sourced from the Pudost deposit. Organic content diminishes up section as carbonate content increases. Overlying the silty marl is a layer comprised mainly of *in situ* phytocretions of aquatic plants, including shoreline paludal species of sedge (possibly *Scirpus*). Finally, the section is capped by a soil horizon with abundant
pulmonate gastropod shells, indicating a fully terrestrial environment. We therefore interpret the Antelevo section to represent an Early Holocene oligotrophic lake that progressively shoaled into a marshland and eventually a terrestrial forested landscape. Intensive carbonate formation accompanied the early intervals of the regressive phase, which coincides with the Middle Holocene shoaling of the Pudost lake system. Correlation of the two deposits is supported by a U-Th age of 8.0 ± 0.4 ka, using a $^{230}$Th/U isochron method, for phytocretions in the upper carbonate-rich section at Antelevo (Maksimov et al., 2015). Additionally, phytocretions from this layer in the Antelevo section have a $\delta^{18}$O value of -11.7 ± 0.2‰, which aligns with samples in the Pudost profile (Fig. 4.5).

4.5.2 Meteogenic travertine as a marker for post-glacial structural deformation

Three dominant facies of meteogenic travertine have been described from the Izhora Plateau: riverine, characterized by either coarse calcarenite, filamentous phytocretions associated with Chara algae and encrusted microbial mats, or allochthonous phytoclastic grainstone; paludal, identified by in situ phytomorphs of sedge; and lacustrine, comprised mainly of microdetrital calcite grains in a pseudo-laminar deposit. Their occurrence is strictly limited, however, to linear depressions or streambeds following a rectangular drainage pattern. Linear depressions are always associated with near-vertical faults that cross cut the Ordovician limestone bedrock and strike along one of two azimuths: 305–315° and 40–50° (Nikitin and Medvedeva, 2011), so that Izhora stream segments can follow an almost linear course for greater than 10 km along fault lines. Structural dislocations also manifest as a systematic network of joints, which accounts for the rectangular drainage pattern of Izhora streams and provides pathways for CO$_2$-rich groundwater to supply springs across the plateau. It is the high carbonate
alkalinity of these springs, combined with photosynthetic uptake of CO₂ by algae and aquatic plants, which allows for freshwater calcite precipitation (Pentecost, 1996). Therefore, meteogenic travertine deposits are natural markers of structural dislocations on the Izhora Plateau (Nikitin and Medvedeva, 2011).

What, then, is responsible for structural deformation of the Izhora Plateau? The compressional stress field in our study area derives principally from tectonic strain associated with divergence at the Mid-Atlantic Ridge boundary (Fjeldskaar et al., 2000; Ojala et al., 2004). This factor likely explains the predominant azimuths of the conjugate fault network on the Izhora Plateau (305° and 45°), for which the principal stress is within 20° of perpendicular to the mid-ocean ridge. However, the tectonic stress field should have been present at least since the Late Mesozoic and explains only the orientation of faulting, rather than its recent activity. A structural survey of Fennoscandia determined that plate-tectonic stress alone could not explain the level of Holocene paleoseismicity and accounts for less than 10% of vertical uplift in the region (Ojala et al., 2004). Instead, the postglacial reactivation of faults in the Baltic region mainly resulted from isostatic rebound following disintegration of the Scandinavian Ice Sheet at 10.5–9.3 ka (Fjeldskaar et al., 2000). Melting of the ice sheet further reduces normal (vertical) stress on the bedrock, allowing the principal (horizontal compressional) stress to cause failure along planes of weakness. In Finland alone, 89 landslide deposits are associated with postglacial fault movements, which caused earthquakes up to 7.7 in magnitude during the Late Glacial and Early Holocene (Ojala et al., 2017).

Isostatic rebound across the Izhora Plateau—though significantly less than in central Fennoscandia—is estimated to be 100–200 meters, most of which occurred during the Late Glacial and Early Holocene intervals (Mörner, 1978). This magnitude of uplift may have been
sufficient to cause the reactivation of a preexisting fault and joint network, which altered the surface hydrology and hydrochemistry of the plateau by providing flow paths of highly alkaline groundwater to surface springs. Because the precipitation of freshwater calcite was facilitated by the supply of this groundwater to spring-fed rivers, ponds, and lakes via dislocations, then the proposed mechanism of structural deformation explains 1) the timing of initial travertine formation, which coincides with collapse of the Scandinavian Ice Sheet and afforestation of the plateau; 2) the waning of travertine formation from the Middle Holocene to present (Goudie et al., 1993); 3) downcutting of the Izhora River since 6.8 ka, due to continued uplift and/or less active springs; and 4) the very limited geographic occurrence of meteogenic travertine along structural dislocations.

4.5.3 Early–Middle Holocene trends in $\delta^{13}$C and Sr/Ca

From 9.5–6.8 ka in the Pudost section, both $\delta^{13}$C and Sr/Ca of microdetrital sediment steadily decrease throughout the lower half of the profile toward the relatively stable values observed in the upper half (Fig. 4.5). Minor peaks and troughs in the time series also tend to align, resulting in a statistically significant ($p < 0.05$) 30-point running correlation throughout the section (Fig. 4.9). For this reason, we hypothesize that a common mechanism controlled temporal variations in the carbon-isotope signature and strontium concentration of precipitated calcite. This hypothesis is difficult to test, due to the complex controls on $\delta^{13}$C and strontium levels both in surface waters and in mineral precipitates (Andrews et al., 2004; Pentecost and Spiro, 1990; Pentecost and Zhao-Hui, 2008; Rogerson et al., 2008; Zavadlav et al., 2017). However, there are a limited number of factors that could account for covariation between $\delta^{13}$C and Sr/Ca but not with other geochemical markers (Fig. 4.9).
The $\delta^{13}C$ of freshwater calcite depends principally on the $\delta^{13}C$ of bicarbonate ions in solution ($\delta^{13}C_{\text{DIC}}$), temperature of the reaction, and the influence of kinetic fractionation (non-reversible reactions). We choose to ignore the temperature dependence of carbon-isotope fractionation, because it is negligible (<1‰) across the natural range of surface waters (0–25°C; Dreybrodt, 2008). Mechanisms of kinetic fractionation, on the other hand, can heavily influence the $\delta^{13}C$ of travertine and tufa deposits, especially when associated with hydrothermal springs (Kele et al., 2011) or flow through narrow/shallow channels (Liu et al., 2010; Lojen et al., 2009). Emerging spring water can be oversaturated with respect to calcite, for example, due to storage under higher pressure and temperature. During the transition to surface conditions, isotopically light CO$_2$ preferentially exsolves from the solution, enriching the Dissolved Inorganic Carbonate (DIC) reservoir in $^{13}C$ by up to ~6‰. This mode of $^{13}C$ enrichment is easily identified by progressively higher $\delta^{13}C$ values downstream from the spring source. Because we do not observe measurable $\delta^{13}C$ variability along the flow path, whether in modern precipitates or Holocene deposits, we suggest that it is not a likely control on $\delta^{13}C$ in the Pudost section.

A similar mode of kinetic fractionation results from photosynthetic uptake of isotopically light CO$_2$ in the water column. In small water bodies with high residence time, isotopic enrichment could impact the whole DIC reservoir and all minerals that precipitate from it, but this likely was not the case for the Holocene lake at Pudost, due to constant inflow from the paleo-Izhora River. We can determine the degree of kinetic fractionation from photosynthetic uptake by measuring $\delta^{13}C$ both in microdetrital calcite and mollusk shells (Andrews et al., 1997; Garnett et al., 2006), because the latter are precipitated from ingested water. Similar to mollusk bearing lacustrine tufa deposits in the British Isles, we observe a +5–6‰ offset of sedimentary $\delta^{13}C$ relative to shell material from the same layer. This offset is explained by the fact that $\delta^{13}C$
is kinetically enriched only in microreservoirs surrounding the algae or plants, and it is within these microreservoirs that calcite precipitation proceeds (Liutkus, 2009; Rogerson et al., 2008). Based on these data and the ooid-like structure of microdetrital sediment, we may conclude first that travertine formation at Pudost was biomediated, and secondly that microdetrital calcite is enriched by \(-5\%\) compared to the lake DIC. The latter is important for evaluating the sources of carbon to the DIC, which may have varied during the Holocene.

The carbon-isotope composition of lake DIC \(\delta^{13}C_{\text{DIC}}\) is a weighted average of \(\delta^{13}C\) from major carbon sources: soil-respired \(\text{CO}_2\) \((-23\%\text{e} \text{ to } -27\%\text{e})\), atmospheric \(\text{CO}_2\) \((-6.7\%\text{e})\), dissolved bedrock \((-0.5\%\text{e})\), and possibly deep-sourced fluids (endogenic \(\text{CO}_2\), -5\%e; Crossey et al., 2009). Of these, the \(\delta^{13}C\) value of bedrock, atmospheric \(\text{CO}_2\), and endogenic \(\text{CO}_2\) are assumed to be constant. The \(\delta^{13}C\) of soil-respired \(\text{CO}_2\) can vary in response to environmental factors (humidity, temperature, nutrient availability) and the relative abundance of C3 vs. C4 plants (Brüggemann et al., 2011). Because the greatest soil-\(\delta^{13}C\) variability associated with environmental changes is seasonal (on the order of 5\%e), decadal averages would be relatively stable. Regional pollen records provide no evidence that C4 plants were abundant at any point during the Holocene (Wohlfarth et al., 2007). We thus conclude that temporal \(\delta^{13}C\) variations in carbonate deposits were due mainly to the relative contribution of carbon sources over the lifetime of the Holocene lake.

Given the range of \(\delta^{13}C\) in the Pudost section \((-7\%\text{e} \text{ to } -9\%\text{e})\) and the observation that sedimentary \(\delta^{13}C\) was enriched by \(-5\%\text{e}\) relative to lake DIC measured in gastropod shells, \(\delta^{13}C_{\text{DIC}}\) likely varied between \(-12\%\text{e}\) and \(-14\%\text{e}\). Similarly, the \(\delta^{13}C_{\text{DIC}}\) of -15.42\%e in springs (Table 4.5) is 4.5\%e lower than the \(\delta^{13}C\) of recent phytocretions (-10.92\%e). These values are at the low end for freshwater systems but still within the range of biomediated tufa deposits from
forested sites in Europe and the British Isles (Andrews et al., 1997), where soil-respired CO₂ contributes up to 50% or more carbon to the DIC reservoir. Because the partial pressure of soil CO₂ is up to 1-2 orders of magnitude greater than atmospheric levels, the latter has a negligible influence on δ¹³C_DIC. For our study site, therefore, we interpret the measured δ¹³C_DIC values as being predominantly controlled by relative soil productivity, which drives bedrock dissolution until calcite saturation is attained (Dreybrodt and Scholz, 2011). This constraint leaves two competing hypotheses to explain the Early–Middle Holocene trend in δ¹³C: 1) there was an increase in forest density and/or soil productivity while contributions from endogenic CO₂ remained stable; or 2) there was a diminished contribution from endogenic CO₂ while forest density and/or soil productivity remained stable.

We can test between these hypotheses by considering Sr/Ca data. The Sr/Ca in freshwater carbonate deposits can be increased by higher aquifer residence times, prior calcite precipitation in the epikarst, lower pH of infiltrating waters (associated with increased soil-CO₂ production), and higher rates of calcite precipitation. The final relationship results from the kinetic exclusion of Sr²⁺ in the CaCO₃ lattice due to its much larger ionic radius relative to Ca²⁺ and Mg²⁺, whereas the first three result from the lower solubility of SrCO₃ relative to CaCO₃. It is unlikely that aquifer residence time or prior calcite precipitation can explain long-term Sr/Ca variability, because either process would result in covariation between Sr/Ca and Mg/Ca, which is not observed (Fig. 4.9). Though a systematic decrease in calcite precipitation rate could explain the downward trend in Sr/Ca, this conclusion is not warranted by any other data and even contradicts our growth-age model.

A steady decline in forest cover and/or soil production could explain the decrease in Sr/Ca, if lower contributions from soil-respired CO₂ led to a reduction in the total dissolution of
bedrock SrCO₃. However, this scenario is directly contradicted by the coincident decrease in δ¹³C, the lack of a similar trend in Mg/Ca values, and palynological evidence of forest development and stability after 9 ka (Wohlfarth et al., 2007). A more parsimonious interpretation is that the Holocene development of soil cover steadily increased contributions to δ¹³Cₐ from soil-respired CO₂, which explains decreasing δ¹³C from Early Holocene to modern encrustations (Figs. 4.5 and 4.10), while concomitant changes to the acidity of infiltrating meteoric water shifted the site of bedrock dissolution to shallower carbonate strata. Because the Sr/Ca ratio in springs across the Izhora Plateau (Table 4.5) varies more widely than the stratigraphic trend in Sr/Ca in the Pudost profile (Fig. 4.5), small changes to the source of Sr dissolved from bedrock could readily explain the range of measured Sr/Ca. In fact, spring water collections exhibit a moderate positive correlation between δ¹³C and Sr/Ca (r = 0.54), with enhanced Sr/Ca values associated with springs in stratigraphically higher strata, supporting a Sr-source control.

4.5.4 Interpretation of δ¹⁸O as a proxy for winter climate using modern analogue data

The paleoclimatic significance of δ¹⁸O in tufa and travertine has been widely discussed, but there is little agreement as to its reliability in reconstructing temperature and δ¹⁸Oₛ histories (Demeny et al., 2010; Kele et al., 2011). One major challenge is that non-equilibrium isotopic fractionation processes are extremely site-specific, depending on the water temperature, residence time, potential for evaporation and atmospheric exchange, mineral precipitation rate, and exsolution of dissolved gases. Additionally, it is commonly not possible to assess equilibrium fractionation of δ¹⁸O between DIC and calcite deposits, since many tufa and travertine deposits are limited to the Early–Middle Holocene. We have attempted to address
these challenges for our study site by analyzing collections from modern springs and actively growing carbonate formations, which provide a modern analogue to earlier deposition.

Stable-isotope analysis of springs, ponds, and rivers yielded a narrow range of $\delta^{18}O_w$ near -13‰, with values up to -11.5‰ at several sites during summer (Table 4.3). We can assess equilibrium fractionation by comparing these data to the $\delta^{18}O$ of recent calcite. Modern Chara phytocretions were collected from the pond and streambed at Shingarka (along the Fabrichnaya River), which is one of the few locations with actively forming carbonate deposits. Additionally, we subsampled microdetrital carbonate material from an anchored glass plate (placed in the streambed on May 5, 2013) after two weeks, two months, and three months to determine $\delta^{18}O$ variability over the growing season. The average and standard deviation for all samples (5 encrustations and 3 subsamples from the plate) was -10.56‰ ± 0.17‰. Such a narrow range in $\delta^{18}O$ is not characteristic of sites where non-equilibrium fractionation dominates the isotopic signal. Finally, we calculated the equilibrium $\delta^{18}O$ of calcite precipitated from waters at Shingarka according to the formula provided by Kim and O’Neill (1997). Given the average $\delta^{18}O_w$ of -11.7‰ (V-SMOW) at Shingarka near the time of collection and the measured water temperature, which ranged from 6.8–12°C (May–August), the expected $\delta^{18}O$ of calcite is -10.30‰ to -11.44‰ (V-PDB). This range envelops the $\delta^{18}O$ of modern carbonate samples (Fig. 4.10), suggesting the absence of measurable kinetic fractionation.

We conclude from modern analogue data and the lack of spatial $\delta^{18}O$ variability in the Pudost travertine that Holocene values were not dominated by non-equilibrium fractionation (>1‰), which is commonly observed in southeastern European and Mediterranean examples (Kele et al., 2011; Pedley, 2009). Intralaminar $\delta^{18}O$ variability is similarly negligible, which should not be the case if evaporation of the Holocene lake continually enriched $\delta^{18}O_{DIC}$.
throughout the growing season. The difference may be attributed to the unique hydrological setting of our site: a shallow aquifer that homogenized seasonal variation in meteoric waters; low residence time in the relatively small, elongated open lake system; a high-latitude setting that mitigated summer evaporation; low-temperature springs near the average annual surface temperature; and proximal spring sources along the faulted depression (i.e. within the lake) that precluded systematic isotopic enrichment along open channels and cascades. Because water temperature does vary by >5°C during the warm season and we cannot determine initial $\delta^{18}O_w$ values, the Pudost travertine is not suitable for paleotemperature reconstruction. However, the $\delta^{18}O$ of calcite deposits should follow temporal variation in the $\delta^{18}O$ of local meteoric water (rain and snow), which is a proxy for relative climatic change (Dansgaard, 1964; Jouzel et al., 2000; Rozanski et al., 1992). Because surface water $\delta^{18}O$ on the Izhora Plateau is heavily biased toward DJF precipitation, we interpret $\delta^{18}O$ variability in the Pudost travertine specifically as a winter climate proxy. If this interpretation is correct, then our study site constitutes the first winter-specific Holocene climate reconstruction from the Fennoscandian and Baltic regions (Sejrup et al., 2016).

4.5.5 Early–Middle Holocene climate inferred from $\delta^{18}O$ and Mg/Ca in the Pudost travertine

At our study site, the $\delta^{18}O$ of meteoric water is positively correlated with air temperature over the instrumental period (Meyer et al., 2015; Rozanski et al., 1992), because both variables increase with higher water temperature at the moisture source, higher air temperature along storm trajectories, and/or lower latitude moisture source (i.e. southwesterly air flow to our site). Dominant air circulation mode plays the largest role, especially during winter, as it determines the relative influence of cold and dry Arctic vs. warm and humid Atlantic air masses. For
example, during the positive and negative modes, respectively, of the AO/NAO and Scandinavian Pattern, southwesterly airflow is enhanced to Fennoscandia, which results in mild, wet winters (Fig. 4.2).

We therefore interpret the 1.25‰ increase in $\delta^{18}O$ to reflect winter warming from Early to Middle Holocene, which may have been associated with an NAO-like shift in predominant air circulation. This interpretation is supported by proxy data from Fennoscandia and the Peribaltic (Fig. 4.11) and is consistent with the winter-climate record from Kinderlinskaya Cave (Fig. 4.11a), as well as Northern Hemisphere proxy stack (Marcott et al., 2013) and climate model reconstructions (Alder and Hostetler, 2015). If we assume the modern $\delta^{18}O$–T relationship of 0.56‰/°C for northern Europe (Rozanski et al., 1992) and account for the T-dependent fractionation of $\delta^{18}O$ during calcite precipitation (0.24‰/°C), then the 1.25‰ shift corresponds to approximately 3.9°C warming. This magnitude is slightly higher than that estimated from Fennoscandian pollen records (2–3°C; Fig. 4.11c-g). However, because our data reflect changes in winter precipitation and pollen composition is most sensitive to growing-season temperature, it is plausible that both estimates are accurate. Likewise, Early Holocene winter warming in the southern Ural Mountains exceeded summer temperature trends by at least a factor of two (Baker et al., 2017).

We have correlated the -0.9‰ excursion in the lower half of the Pudost section to the 8.2 ka cooling event. Attributed to the catastrophic drainage of glacial meltwater from the Laurentide Ice Sheet to the North Atlantic, the climate anomaly is prominent in most proxy datasets from the region. It is notable, however, that in the Pudost travertine and several Baltic records, the event appears as a multicentennial-cooling interval (spanning 8.4–8.0 ka). This pattern contrasts with the Greenland ice-core $\delta^{18}O$ record, in which the onset of cooling at 8.2 ka is relatively
abrupt and lasts only decades (Vinther et al., 2008). One possible explanation for the discrepancy is that poleward heat transport along the North Atlantic Current diminished gradually in response to freshwater input from glacial melt, affecting northern European climate only, whereas the catastrophic drainage of Lake Agassiz and Lake Ojibway caused a basin-wide disturbance affecting Greenland and North America as well.

Apart from the ‘8.2 ka event’, centennial-scale δ^{18}O variability in the Pudost travertine does not appear to correlate with other regional climate anomalies, but we do observe that travertine δ^{18}O is moderately well anticorrelated to Mg/Ca from 8.5 ka to 6.8 ka (Fig. 4.9). The most parsimonious interpretation of this covariation is that temperature was the dominant control on both variables, because the partition coefficient of Mg (D_{Mg}) from DIC to calcite is highly sensitive to temperature when precipitating from low-Mg solutions at moderate to high mineral growth rates (Saunders et al., 2014). Supporting this interpretation is the fact that the D_{Mg} of 0.018 between spring water (Mg/Ca = 0.47–0.50) and recent phytocretions (Mg/Ca = 0.0089) corresponds to a formation temperature of 14°C (Huang and Fairchild, 2001), which is very close to the ambient water temperature (12°C) at the time of sampling. However, higher Mg/Ca and δ^{18}O values are associated with higher water and air temperatures, respectively, from which we would theoretically expect a positive correlation—not the observed negative relationship. Therefore, a common temperature control is not supported by our data.

Still, the use of Mg/Ca as a paleothermometer in freshwater carbonates is not well established and commonly overestimates water T by up to 20°C, because biomediation of calcite precipitation can incorporate detrital carbonate material (especially on biofilms), elevating the measured Mg/Ca in tufa and travertine. More importantly, we must assume that Mg/Ca of the precipitating solution remained constant over the depositional history of the lake, which is highly
unlikely, given that Mg/Ca is also dependent on aquifer residence time in karstic landscapes. Under high precipitation regimes, the aquifer residence time decreases, limiting the time for Mg dissolution to reach saturation with respect to dolomite. Therefore, low (high) Mg/Ca ratios are more likely to reflect wet (dry) climates. According to this interpretation, the anticorrelation between Mg/Ca and $\delta^{18}$O in our dataset reveals centennial-scale oscillations between warm/wet and cold/dry winters, which are consistent with the modern climatological regimes determined by the AO, NAO, and SCA teleconnections. Finally, we note that Mg/Ca and $\delta^{18}$O do not covary during the interval from 9.5–8.5 ka, for which we interpreted a stratigraphic shift in the main site of bedrock dissolution based on Sr/Ca data.

4.5.6 Is Holocene winter temperature masked by a proxy bias in the Peribaltic?

Nearly all reconstructions of regional and Northern Hemisphere (NH) Holocene surface temperature show warming until a Mid-Holocene climatic optimum (~5–9 ka), followed by more gradual cooling until the Pre-Industrial period. However, these reconstructions are known to contain a substantial bias toward proxies that are sensitive to peak summer or growing-season climate (Baker et al., 2017; Liu et al., 2014); hence, NH Holocene surface temperature appears to follow Northern Hemisphere Summer Insolation (NHSI), only modified by glacial extent during the Early Holocene (Marcott et al., 2013; Renssen et al., 2009). Conversely, NH winter surface temperature should have steadily increased throughout the Holocene, due to declining glacial extent, more zonal atmospheric flow, higher greenhouse-gas concentrations, and increasing winter insolation.

At least for continental western Eurasia, winter and summer temperature followed opposite trajectories, and the annual temperature signal was dominated by winter values (Baker
et al., 2017). Did winter climate dynamics also lead to continual Holocene warming in northwestern Russia in a manner not captured by the summer- and annual-T proxies (Sejrup et al., 2016)? We test this hypothesis for the first time using δ¹⁸O data from the Pudost travertine as a proxy for winter climate. Figure 4.12 shows Pudost δ¹⁸O plotted alongside the speleothem-δ¹⁸O winter climate reconstruction from the southern Ural Mountains, as well as two temperature reconstructions representative of the Peribaltic region. Mean annual T at Lake Laihalampi (southern Finland) and mean summer T at Lake Kurjanovas (southern Latvia) were determined from pollen assemblages by a modern-analogue weighted-average partial-least-squares (WA-PLS) method. Although both records exhibit a Holocene Climatic Optimum (HCO) and subsequent cooling, the HCO is far more pronounced in the summer reconstruction from Latvia. The difference in structure could be attributed to a muted or non-existent HCO pattern for winter climate in this region. This position is supported by Pudost δ¹⁸O values, which initially follow the Peribaltic trends, but are higher in modern carbonates than Early–Middle Holocene deposits (Figs. 4.10 & 4.12). Our data suggest continual wintertime warming for our study area along a trajectory that is similar to that of the southern Ural Mountains. The coupling of Holocene temperature between the Ural Mountains and the Peribaltic suggests a common forcing—related to retreat of the northern hemisphere ice sheets—over a wide region. Our conclusion suggests that winter temperature evolution is different than summer-sensitive proxies would suggest, and its inclusion in regional temperature stacks would reduce bias in existing compilations.

4.6 Conclusion

Freshwater carbonate deposition on the Izhora Plateau initiated with the amelioration of periglacial conditions at ca. 9.5 ka, but has significantly diminished in rate and extent since 6.8
ka. Precipitation of calcite was facilitated by photosynthetic uptake of CO₂ from highly alkaline water, which was delivered to surface springs along a conjugate fracture network from shallow aquifers hosted in Ordovician limestone bedrock. Therefore, we classify these deposits as meteogenic (cool-water) travertine. The spatial correlation of riverine, paludal, and lacustrine travertine facies with these structural dislocations could be explained by post-glacial reactivation of joints and faults concomitant with regional isostatic rebound. However, the most active phase of travertine deposition coincides with the Holocene Climatic Optimum, characterized by summer temperatures that were 2–3°C above the Pre-Industrial average, suggesting a combination of climatic and geomorphic factors on travertine genesis.

Herein, we measured stratigraphic trends in four geochemical indicators from a 2-meter section of microdetrital sediment near the town of Pudost, which was deposited in an open-water lacustrine setting. Early–Middle Holocene trends toward lower δ¹³C and Sr/Ca values evidence the increasing influence of soil-respired CO₂, consistent with regional pollen records of forest stability since ~11 ka and data from modern phytocretions. By analyzing oxygen-isotope ratios in modern precipitates and surface waters, we demonstrated that meteogenic travertine likely precipitated in isotopic equilibrium with respect to oxygen, so that the δ¹⁸O of carbonate material reflects the δ¹⁸O of infiltrating meteoric water near the time of deposition. Because winter precipitation supplies the bulk of water mass to the shallow aquifer, we interpret the δ¹⁸O of lacustrine facies at Pudost specifically as a proxy for Holocene winter climate. According to this interpretation, winter surface temperature on the Izhora Plateau increased by up to 3.9°C from 9.5–6.8 ka. This magnitude of warming is comparable to reconstructed summer temperature trends in paleoclimate archives from the Peribaltic. Centennial-scale δ¹⁸O variability likely reflects NAO-like shifts between mild/wet and cold/dry winters. This conclusion is corroborated
by the anticorrelation of $\delta^{18}O$ with Mg/Ca, which we interpret as a direct proxy for aquifer residence time and indirectly of winter precipitation amount.

Our paleoclimate reconstruction using meteogenic travertine deposits from the Izhora Plateau thus constitutes the first winter-sensitive proxy archive for the Peribaltic region (including Scandinavia). Using this dataset, we tested the hypothesis that winter and summer climate followed opposite trajectories during the Holocene, due to differing climate dynamics. Based on the continued upward trend in $\delta^{18}O$ from Mid–Holocene to modern carbonate samples, we conclude that our study area experienced continual winter warming, which is anticipated from a combination of glacial retreat, increasing winter insolation, and a subtle rise in greenhouse-gas concentrations. This trend contradicts regional temperature histories, but the latter are derived almost exclusively from summer-sensitive paleoclimate proxies. Therefore, we offer the first direct evidence that Holocene temperature evolution in Fennoscandia and the Peribaltic is seasonally biased in regional proxy reconstructions to date.
## 4.7 Tables

**Table 4.1: U-Th Disequilibrium Dating Results from the Pudost Main Section**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>DFT (cm)</th>
<th>$^{238}$U (cts/min/g)</th>
<th>$^{234}$U (cts/min/g)</th>
<th>$^{230}$Th (cts/min/g)</th>
<th>$^{230}$Th/$^{234}$U</th>
<th>$^{234}$U/$^{238}$U</th>
<th>Age (ka B2K) ±2-σ *</th>
</tr>
</thead>
<tbody>
<tr>
<td>541</td>
<td>5</td>
<td>0.7970 ± 0.0362</td>
<td>1.1339 ± 0.0462</td>
<td>0.0691 ± 0.0033</td>
<td>0.0609 ± 0.0038</td>
<td>1.4227 ± 0.0672</td>
<td>6.85 ± 0.4</td>
</tr>
<tr>
<td>542</td>
<td>45</td>
<td>0.8579 ± 0.0463</td>
<td>1.2110 ± 0.0590</td>
<td>0.0771 ± 0.0039</td>
<td>0.0637 ± 0.0045</td>
<td>1.4116 ± 0.0783</td>
<td>7.17 ± 0.5</td>
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<tr>
<td>523</td>
<td>95</td>
<td>0.8838 ± 0.0320</td>
<td>1.2243 ± 0.0410</td>
<td>0.0809 ± 0.0042</td>
<td>0.0661 ± 0.0041</td>
<td>1.3853 ± 0.0473</td>
<td>7.44 ± 0.5</td>
</tr>
<tr>
<td>520</td>
<td>95</td>
<td>0.9408 ± 0.0292</td>
<td>1.3226 ± 0.0381</td>
<td>0.0879 ± 0.0036</td>
<td>0.0665 ± 0.0033</td>
<td>1.4058 ± 0.0339</td>
<td>7.48 ± 0.4</td>
</tr>
<tr>
<td>868</td>
<td>155</td>
<td>1.5359 ± 0.0545</td>
<td>2.0996 ± 0.0692</td>
<td>0.1517 ± 0.0073</td>
<td>0.0722 ± 0.0042</td>
<td>1.3670 ± 0.0453</td>
<td>8.17 ± 0.5</td>
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<td>867</td>
<td>165</td>
<td>1.4947 ± 0.0779</td>
<td>2.1377 ± 0.1019</td>
<td>0.1667 ± 0.0070</td>
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<td>1.4302 ± 0.0716</td>
<td>8.83 ± 0.6</td>
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<tr>
<td>866</td>
<td>175</td>
<td>1.5911 ± 0.0481</td>
<td>2.2652 ± 0.0633</td>
<td>0.1803 ± 0.0076</td>
<td>0.0796 ± 0.0040</td>
<td>1.4237 ± 0.0393</td>
<td>9.02 ± 0.5</td>
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<tr>
<td>864</td>
<td>195</td>
<td>1.6536 ± 0.0476</td>
<td>2.4734 ± 0.0649</td>
<td>0.2014 ± 0.0063</td>
<td>0.0814 ± 0.0033</td>
<td>1.4958 ± 0.0583</td>
<td>9.23 ± 0.4</td>
</tr>
</tbody>
</table>

*Ages are not corrected for initial $^{230}$Th, because $^{232}$Th was below instrumental detection (0.005 cts/min/g). $[^{230}$Th/$^{238}$U] = 1 - $e^{-230T}$ + ($Δ^{234}$U$_{measured}$/1000)(λ$_{236}$/λ$_{230}$ - λ$_{234}$), where T is the age and $Δ^{234}$U = ([$^{234}$U/$^{238}$U] - 1) x 1000. Decay constants (λ) are 9.1577 x 10$^{-6}$ year$^{-1}$ for $^{230}$Th, 2.8263 x 10$^{-6}$ year$^{-1}$ for $^{234}$U, and 1.55125 x 10$^{-10}$ year$^{-1}$ for $^{238}$U.*
Table 4.2: Radiocarbon Dating Results for the Antelevo Section

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<th></th>
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<td>9728</td>
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<td>11051</td>
<td>10546</td>
<td>11556</td>
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</table>

* BP = 1950 C.E.

Table 4.3: Surface Water Samples from the Izhora Plateau

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<th>Rivers</th>
<th>$\delta^{18}$O</th>
<th>$\delta$D</th>
<th>Dexcess</th>
<th>Date</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Izhora-01</td>
<td>-13.0</td>
<td>-88.3</td>
<td>15.7</td>
<td>12/18/11</td>
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<td>30.04°E</td>
</tr>
<tr>
<td>Izhora-02</td>
<td>-13.0</td>
<td>-91.0</td>
<td>13.0</td>
<td>6/24/12</td>
<td>59.62°N</td>
<td>30.04°E</td>
</tr>
<tr>
<td>Izhora-03</td>
<td>-13.0</td>
<td>-90.4</td>
<td>13.6</td>
<td>7/31/12</td>
<td>59.62°N</td>
<td>30.04°E</td>
</tr>
<tr>
<td>Fabrichnaya-01</td>
<td>-11.9</td>
<td>-88.5</td>
<td>6.7</td>
<td>4/6/13</td>
<td>59.74°N</td>
<td>29.76°E</td>
</tr>
<tr>
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<td>-11.6</td>
<td>-86.9</td>
<td>5.9</td>
<td>6/2/13</td>
<td>59.74°N</td>
<td>29.76°E</td>
</tr>
<tr>
<td>Suma-01</td>
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<td>-82.6</td>
<td>11.0</td>
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<td>28.85°E</td>
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</table>

**Ponds**

<table>
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<th>Longitude</th>
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**Springs**

<table>
<thead>
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<th>Dexcess</th>
<th>Date</th>
<th>Latitude</th>
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<td>-88.2</td>
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Table 4.4: Precipitation Event Samples from the Izhora Plateau Region

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<tr>
<th>Sample No.</th>
<th>δ(^{18})O</th>
<th>δD</th>
<th>D(_{excess})</th>
<th>Date</th>
<th>Type</th>
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<td>4/20/13</td>
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<tr>
<td>Russia_2</td>
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<td>-10.1</td>
<td>4.3</td>
<td>11/23/12</td>
<td>Snow</td>
</tr>
<tr>
<td>Russia_3</td>
<td>-75.7</td>
<td>-9.7</td>
<td>1.5</td>
<td>9/24/12</td>
<td>Rain</td>
</tr>
<tr>
<td>Russia_4</td>
<td>-65.0</td>
<td>-8.8</td>
<td>5.5</td>
<td>4/30/13</td>
<td>Rain</td>
</tr>
<tr>
<td>Russia_5</td>
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<td>-9.7</td>
<td>0.8</td>
<td>5/15/13</td>
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</tr>
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<td>Russia_6</td>
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<td>3.0</td>
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<td>Rain</td>
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<td>-9.9</td>
<td>2.1</td>
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<td>10.1</td>
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Values of δ¹⁸O and δD are reported in ‰ VSMOW. D_{excess} is reported as the % deviation from the Global Meteoric Water Line (δD = 8•δ¹⁸O + 8‰) at δ¹⁸O = 0‰. Date format is MM/DD/YY.
Table 4.5: Stable-Isotope and Major-Cation Chemistry of Izhora Plateau Springs

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<th>Location</th>
<th>Latitude</th>
<th>Longitude</th>
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<th>Sr/Ca</th>
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Table 4.6: Malacofauna of the Pudost Section

Cl. Gastropoda

Family Lymnaeidae (Rafinesque, 1815)

- *Lymnaea atra* (Schranck, 1803)
- *Lymnaea peregra* (Müller, 1774)
- *Lymnaea palustris* (Müller 1774)
- *Lymnaea ovata* (Draparnaud, 1805)

Family Planorbidae (Rafinesque, 1815)

- *Anisus acronicus* (Ferussac, 1807)
- *Planorbis planorbis* (Linne, 1758)
- *Anisus vortex* (Linne, 1758)
- *Anisus contortus* (Linne, 1758)
- *Anisus spirorbis* (Linne, 1758)
**Table 4.7: Malacofauna of the Antelevo Section**

Cl. Gastropoda  
**Subclass Pectinibranchia**  
Family Bithyniidae (Troschel, 1857)  
  *Bithynia tentaculata* (Linnaeus, 1758)  
  *Bithynia leachii* (Sheppard, 1823)  
Family Valvatidae (Gray, 1840)  
  *Valvata cristata* (Müller, 1774)

Cl. Pulmonata  
**Subclass Pulmonata**  
Family Acroloxidae (Thiele, 1931)  
  *Acroloxus lacustris* (Linnaeus, 1758)  
Family Planorbidae (Rafinesque, 1815)  
  *Anisus sp.*  
Family Lymnaeidae (Rafinesque, 1815)  
  *Lymnaea palustris* (Müller, 1774)  
Family Succineidae (Beck, 1837)  
  *Succinea putris* (Linnaeus, 1758)  
  *Succinella oblonga* (Draparnaud, 1801)

Cl. Bivalvia  
Family Euglesidae (Pirogov et al., 1974)  
  *Tetragonocyclas milium* (Pirogov et al., 1974)  
  *Henslowiana lilijeborgi* (Clessin, 1886)  
  *Cingulipisidium nitidum* (Jenyns, 1832)  
  *Conventus conventus* (Clessin, 1877)
4.8 Figures

Figure 4.1: Digital elevation map of the Izhora Plateau, whose northern edge (59°45' N) is demarcated by the Baltic-Ladoga glint. Investigated sites of Holocene travertine deposition are denoted by yellow circles. Locations of sampled springs are shown as blue diamonds: SR - Suma River; FR - Fabrichnaya River; Ki - Kipen; Sk - Skvoritsiy; TB - Taitsy Bridge; Ko - Korpikovo; KS - Krasnoye Selo; Du - Duderhof Heights; Ga - Gatchina. Faulted linear depression (discussed in text) approximated by red dashed line.
Figure 4.2: Mean monthly temperature and precipitation at St. Petersburg, Russia correlated against the North Atlantic Oscillation (NAO), Arctic Oscillation (AO), and Scandinavian Pattern (SCA) indices over the NCEP/NCAR reanalysis period (1948–2016 C.E.). Historical meteorological data accessed from http://meteo.ru (2016).

Figure 4.3: Schematic overview of the study area in the vicinity of the towns Pudost and Miyza-Ivanovka, which are cut by the Izhora River. The main stratigraphic profile for geochemical analysis was measured in the Pudost Main Quarry (yellow dot), approximately 1 km downstream from the outcrop and sampled springs near Taitsy Bridge (blue dots). Estimated extent of the paleo-lake is shown in blue shading, which can be mapped confidently to the town of Pudost but likely extended to the plunging anticlinal structure east of the railroad (black arrow indicates trend of the fold axis).
Figure 4.4: Age-depth model for the main quarry section of lacustrine sediments near Pudost. Sediment age and depositional rate are constrained by eight U-Th disequilibrium dates. The age-depth relationship (blue line) is anchored at 8.2 ka (purple square), based on our interpretation of $\delta^{18}$O data, which results in a doubling of depositional rate from Early to Middle Holocene.
Figure 4.5: Stratigraphic variations in geochemical data within the main quarry section of lacustrine travertine near Pudost. Lithology of the stratigraphic profile is shown on the left (top to bottom): microdetrital sediment (dotted brick pattern), glacial till (filled oval pattern), and limestone bedrock (empty brick pattern). Horizontal bar widths for $\delta^{13}$C and $\delta^{18}$O represent the standard deviation around the arithmetic mean (bar center) of duplicate analyses for each interval. Individual stable-isotope results are plotted as black dots. Horizontal bar widths for Sr/Ca, Mg/Ca, and CaCO3 wt. % signify the 1-$\sigma$ analytical uncertainty—calculated from repeat analyses of standard solutions of known concentration—around the measured elemental ratio (bar center). Stratigraphic position and age of samples used for U-Th disequilibrium dating are shown on the right.
Figure 4.6: Results from stable-isotope analysis of meteoric water events at St. Petersburg and surface collections from the Izhora Plateau. Stable-isotope values of mean monthly precipitation (blue dots) were accessed from http://www.iaea.org/water and used to calculate a Local Meteoric Water Line (LMWL). Locations and individual results for springs, rivers, and ponds are shown in Table 4.3A. Event samples (yellow dots) were collected as rain or snow during all months from May 2012–August 2013 (Table 4.3B). Dashed lines indicate mean $\delta^{18}$O and $\delta$D values of GNIP data.
Figure 4.7: Site of modern freshwater carbonate formation near the source of the Fabrichnaya River. (A) Shingarka quarry pond. (B) Algal mat, collected from the stream bed, encrusting calcite phytocretions. (C) Cascade located ~1 km downstream from the resurgence point of the Fabrichnaya River. (D) Broken phytocretions comprising coarse detritus fraction of the stream.
Figure 4.8: Scanning Electron Microscopy (SEM) image of a typical micro detrital grain from the Pudost main quarry section.
Figure 4.9: Covariation of geochemical data measured in microdetrital sediment from the Pudost main quarry section. (A) δ¹³C vs. Sr/Ca. (B) δ¹³C vs. δ¹⁸O. (C) δ¹⁸O vs. Mg/Ca. Blue shaded area shows the running correlation coefficient (r) for 30-sample intervals. Note inverted y-axis in (B) and (C).
Figure 4.10: Cross plot of $\delta^{18}$O and $\delta^{13}$C data from the Pudost main section (blue dots) and modern precipitates from the Fabrichnaya River and quarry pond (purple diamonds). Blue bars indicate the range of calcite $\delta^{18}$O values (in ‰ VPDB) estimated for precipitation in isotopic equilibrium with water at 6.8 to 12°C, assuming a solution $\delta^{18}$O value of -11.7‰ (VSMOW).
Figure 4.11: Comparison of select paleoclimate records from the Peribaltic region and western Russia: a) speleothem $\delta^{18}O$ (with 250-year LOESS smoothing) from Kinderlinskaya Cave, southern Ural Mountains; b) $\delta^{18}O$ in lacustrine facies of travertine, Pudost main quarry (this study); c) lake water $\delta^{18}O$ at Lake Saarikko, Finland; d) pollen-reconstructed temperature anomalies at Lake Kurjanovas (eastern Latvia), Lake Laihalampi (southern Finland), and Lake Flarken (southern Sweden); e) lake $\delta^{18}O$ at Lake Igelson, Sweden. Blue shading denotes the temporal extent of 8.2-ka cooling.
Figure 4.12: Reconstructed Holocene climate evolution from selected sites, representative of mean annual (Lake Laihalampi, Finland), summer (Lake Kurjanovas, Latvia), and winter (Pudost, Russia, and Kinderlinskaya Cave, Russia) surface temperature. Pudost δ¹⁸O data generally follow Peribaltic climate evolution, except for the Late Holocene, assuming that modern and Holocene data both reflect oxygen-isotope values of peak winter (DJF) precipitation. Data from Pudost are well correlated to speleothem δ¹⁸O from Kinderlinskaya Cave—a continental proxy for winter surface temperature over western Russia.
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APPENDIX A

SUPPLEMENTARY MATERIAL FOR CHAPTER 2: HOLOCENE WARMING IN CONTINENTAL WESTERN EURASIA DRIVEN BY GLACIAL RETREAT AND GREENHOUSE FORCING

A.1: SUPPLEMENTARY TABLES

Table A1  U-series data for stalagmites KC-1 & KC-3
Table A2  Stable-isotope data for stalagmite KC-1
Table A3  Stable-isotope data for stalagmite KC-3

A.2: SUPPLEMENTARY FIGURES

Figure A1  Study area and cave microclimate
Figure A2  Assessment of isotopic equilibrium between cave waters and speleothem calcite
Figure A3  Climatograph and stable isotopes in precipitation at the study area
Figure A4  Single-point correlation maps of mean monthly T and $\delta^{18}O_p$ near the cave site versus mean monthly geopotential height (GPH)
Figure A5  Model reconstructed Holocene surface temperature at study site
Figure A6  Growth-age model for KC-1 and KC-3

A.3: REFERENCES
Table A1: U-series data for stalagmites KC-1 & KC-3

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A.2. **SUPPLEMENTARY FIGURES**

A.2.1 Study Site

Figure A1: Study area and cave microclimate. Location and horizontal schematic (upper panel) of Kinderlinskaya Cave. Microclimate of collection room (lower panel) relative to local surface air temperature. Daily surface temperature (purple line) was accessed via [http://meteo.ru](http://meteo.ru). Solid black line segments represent average temperature of subzero days (cold-season ventilation period).

Kinderlinskaya Cave (KC; 54.15°N 56.85°E) is situated approximately 6 km east of the western edge of the Ural Mountains in Bashkortostan, Russia and is the longest cave in the region. The well-developed soil horizon over the cave occurs in Carboniferous siliciclastic regolith, which overlies the Devonian limestone in which KC was formed. Vegetative cover is
predominantly oak forest, with admixtures of birch and some pine. Local topographic relief is less than 500 m, and the entrance to KC (~240 m AMSL) is situated 94 meters above the Zilim River. Stalagmites KC-1 and KC-3 were collected in July 2012 and July 2013, respectively, from the dead-end Brook Room (Location 1; upper-right panel). A recent cave survey (Yu.V. Sokolov and A.I. Smirnov, personal communication) measured the altitude of the Brook Room to be 20 m higher than the cave entrance (114 m above the Zilim River), from which we calculated a local epikarst thickness of ~125 meters.

Three HOBO data loggers were installed in 2012/2013 to monitor hourly changes in temperature (T) and relative humidity (RH) within the cave: two in well-ventilated passages near the entrance and one in the Brook Room. The first two datasets (not plotted) revealed that near the cave entrance, T (0–1°C) and RH (100%) fell by up to 8°C and 30% during cold-season ventilation, when outside air temperature was below 0°C. In the Brook Room, RH remained at 100% and T was stable, with two exceptions. In early winter of 2013 and 2014, T rose abruptly by almost 1°C toward a new equilibrium value. We interpret these shifts to be caused by winter ventilation of the cave system, because their timing coincides with the first week of surface air temperatures significantly below 0°C. Additionally, the rise in cave room T was directly proportional (slope = 0.8) to the rise in average surface air temperature of days below 0°C during the monitoring period.

This link will be assessed further in future studies, but we tentatively conclude that interannual winter T variability directly affects air T in the Brook Room. The rapid response of cave microclimate to surface conditions does not compromise our isotopic record; rather, it reinforces its strength as a high-resolution proxy. Additionally, interannual atmospheric
variability is likely averaged at decadal scales in our record due to smoothing of the isotopic signal in the epikarst and due to the sampling resolution for isotopic analysis.

A.2.2 Stable-isotope analysis of cave and meteoric waters

Figure A2: Assessment of isotopic equilibrium between cave waters and speleothem calcite. Range of observed $\delta^{18}O_w$ in locally sourced springs (purple markers) alongside Local Meteoric Water Line (LMWL) for the southern Volga Basin (green dashed line). Orange dashed line indicates predicted equilibrium $\delta^{18}O_w$ for the measured $\delta^{18}O_c$ of -10.9‰ VPDB and cave room temperature (6.2°C) at time of KC-3 collection in July 2013.

To constrain isotopic fractionation between $\delta^{18}O_w$ and stalagmite $\delta^{18}O_c$, we sampled six locally sourced springs near the cave site. Spring water $\delta^{18}O$ and $\delta$D show good overlap with a Local Meteoric Water Line (LMWL) defined by GNIP data from Saratov, Russia (51.57°N 46.03°E). Cave dripwater was also retrieved from soda-straw stalactites above each collected
stalagmite, but these small samples evaporated during transport and storage, rendering their isotopic values unusable. We consider the spring water data to be representative of cave waters sourced from the same well-mixed epikarst.

Given the measured tip value of $\delta^{18}$O in KC-3 (-10.9 ± 0.1‰ VPDB, n = 3) and cave room temperature at the time of collection (6.2°C, July 2013), we calculated a corresponding equilibrium $\delta^{18}$O$_w$ value of -14.02 ± 0.1‰ VSMOW according to the relationship defined by Coplen et al. (2007) This value falls within uncertainty of spring water $\delta^{18}$O$_w$ and is only 0.5‰ from the mean, which is an acceptable offset for assessment of isotopic equilibrium in European speleothems (McDermott et al., 2011). Still, it is important to note that isotopic fractionation depends on temperature of the drip water, which may not fully adjust to cave-air temperature during peak flow rates (e.g. in response to spring snowmelt). As an additional constraint, we estimated the temperature of the epikarst (4.8°C) from the average measured ground temperature down to 160 m in borehole RU-Salavat-1790 (53.67°N, 58.50°E; Huang et al., 2000), located 120 km east of Kinderlinskaya Cave. Assuming a dripwater T of 4.8°C shifts the predicted $\delta^{18}$O$_w$ value to -14.33‰ VSMOW, which is even closer to the mean $\delta^{18}$O$_w$ of locally sourced springs.
Figure A3: Climatograph and stable-isotopes in precipitation at the study area. Climate graph of the study area (top), showing mean monthly precipitation and temperature (bold lines), with 1-σ deviations (dashed lines). Observed mean monthly δ18O_p (bottom) from the two nearest GNIP stations and estimated δ18O_p of the study area (thick dashed line). Measured δ18O_p of local springs (blue dashed line) is significantly lower than the annual average (green dashed line), but within the range of δ18O_p during the winter half year (Oct-Mar; shaded region).

We constructed a climate graph of the study area from monthly air temperature and precipitation data (1888–2015) at Ufa, Russia, located 130 km WNW from KC. Comparison to additional datasets from Sterlitamak (80 km SSW) and Tukan (54 km ESE) confirmed that observations at Ufa are characteristic of the region. The climate near KC is highly continental, with mean temperatures ranging from -14.1°C in January to 19.4°C in July. Precipitation is
relatively stable around the mean of 47 mm/month, but monthly means are lower during March–April and highest in June.

Limited GNIP data from the Kirov and Saratov stations, northwest and southwest of KC, provide upper and lower constraints on monthly $\delta^{18}O_p$. Geostatistical modeling of $\delta^{18}O_p$ in Eurasia (Bowen and Wilkinson, 2002; Butzin et al., 2014) suggests that the isotopic composition of meteoric waters near the cave site should fall approximately halfway between the two stations, so we took the mean value as a first-order estimate of monthly $\delta^{18}O_p$ at KC. From this estimate, we calculated a precipitation-weighted annual mean of -12.1‰ (VSMOW). Since this value assumes no evapotranspiration prior to infiltration, we employed a simple mass-balance calculation to conclude that the $\delta^{18}O_w$ of springs results from relatively higher epikarst recharge (~86% of total infiltration) during the winter half year (Oct–Mar).
A.2.3 Atmospheric controls on air temperature and δ¹⁸Oₚ at KC

Figure A4: Single-point correlation maps of mean monthly T and δ¹⁸Oₚ near the cave site versus mean monthly geopotential height (GPH): (A) mean DJF T at Ufa (red circle) vs. mean DJF GPH (500 hPa); (B) same as (A), but for Oct–Mar; (C) mean δ¹⁸Oₚ of winter (DJF) months at Kirov (red dot) vs. mean GPH (500 hPa); same as (C), but at the 1000-hPa level. Monthly data were compared to the NCEP/NCAR Reanalysis dataset at 2.5°x2.5° resolution for the period 1948–2015. Monthly δ¹⁸Oₚ was available for 24 months ranging from 1980–2000. Plotted values are correlation coefficients (r) between monthly time series. Dashed and dotted contours indicate significance at p = 0.01 and p = 0.001, respectively.
A.2.4 Holocene transient model (FAMOUS) outputs at study site

Figure A5: Model reconstructed Holocene surface temperature at study site. Surface (2-m) air temperature results from the Fast Met Office/UK Universities Simulator (FAMOUS; Smith and Gregory, 2012) from 12 ka to PI, parsed by prescribed forcing and season: (left) annual mean; (middle) winter half year; (right) summer half year. Data are taken from the grid cell that includes our cave site (54°N 57°E) and are smoothed by a 1000-year filter for clarity. Glacial retreat produces warming in all seasons until 7 ka. Greenhouse-gas forcing results in annual warming of ~1°C from 6-7 ka until the PI period. A mixed insolation signal between strong summer cooling and weak or negligible (<1°C) winter T change produces a net annual cooling of less than 1°C across the Holocene. Because the magnitude of radiative forcing by insolation is almost equal between seasons, these data imply that the winter half year is less sensitive to direct orbital forcing.
A.2.5 Growth-Age Model for KC-1 and KC-3

Figure A6: Growth-age model for KC-1 and KC-3. Linearly interpolated age model (dashed lines) for KC-1 and KC-3, using the *iscam* software written for Matlab (Fohlmeister, 2012). Error bars denote 2-σ uncertainties (see methods).

Our age model was constrained primarily by 29 U-Th disequilibrium dates between the two stalagmites. Two ages were rejected from the KC-3 dataset, due to unacceptably low $^{230}\text{Th}/^{232}\text{Th}$ ratios that indicated detrital contamination, but still fall within 2-σ of the final age model. Growth hiatuses were identified by visual interruptions to growth banding, as well as positive stable-isotope anomalies within 1 mm of the hiatus. The KC-3 age model was further constrained by 5 tie points. Tie points at 9.80 ka and 9.55 ka were chosen by visual tuning of prominent $\delta^{18}\text{O}$ anomalies in both records, due to the lack of age constraints in KC-3 for the Early Holocene. The boundaries of the hiatus in KC-3 from 4.84–4.20 ka were also chosen by visual tuning to the KC-1 $\delta^{18}\text{O}$ record. Notably, our choice of tie points is supported by the common growth-rate pattern that results for these intervals (Fig. 2.1a).
Finally, we fixed the tip age of KC-3 to 0 ka, because the stalagmite was located under an active drip at the time of collection and the U-Th age at 0–0.5 mm depth from top is indistinguishable from zero. However, we cannot confirm at present that calcite deposition continued to the present day, and the relatively high detrital thorium content may indicate that stalagmite growth had slowed or previously ceased. For example, extrapolating the growth rate at 4–8 mm results in a tip age of 119 years B2K, which would explain the apparent absence of a 20th-century warming signature in the δ¹⁸O record. Until further analysis resolves this question, we caution against interpreting paleoclimate of the most recent centuries from our record.
A.3 REFERENCES


APPENDIX B

SUPPLEMENTARY MATERIAL FOR CHAPTER 4: HOLOCENE CLIMATIC AND HYDROLOGICAL EVOLUTION OF THE IZHORA PLATEAU (NORTH-WESTERN RUSSIA) RECORDED BY THE STABLE-ISOTOPE AND CATION CHEMISTRY OF METEOGENIC TRAVERTINE DEPOSITS

B.1 SUPPLEMENTARY TABLES

B1 Stable-Isotope and Major-Cation Analysis Results, Pudost Main Section

B2 Stable-Isotope and Major-Cation Analysis Results, Miscellaneous Samples
Table B1: Stable-Isotope and Major-Cation Analysis Results, Pudost Main Section

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CURRICULUM VITAE

Jonathan L. Baker

Profile
Ph.D. candidate in Geoscience. One year experience as a visiting assistant professor at Cornell College, 4+ years experience as a teaching assistant at UNLV, and 5 years experience operating/managing analytical laboratories. Field and laboratory researcher in paleoclimatology, isotope geochemistry, and sedimentology in the western U.S. and Russia. Successfully organized collaborative, interdisciplinary research projects with European geoscientists. Served as a Fulbright student researcher (2012-2013) in the Russian Federation.

Education
UNIVERSITY OF NEVADA, LAS VEGAS – LAS VEGAS, NV
Ph.D. Geoscience, 2011–2018, Dr. Matthew Lachniet, GPA: 3.81
Thesis: Holocene climate evolution of continental western Eurasia constrained by stable-isotope and cation geochemistry of U-Th-dated speleothems and meteogenic travertine

M.S. Geoscience, 2008–2010, Dr. Ganqing Jiang, GPA: 3.69
Thesis: Carbon isotopic fractionation across a Late Cambrian carbonate platform: a regional response to the SPICE event as recorded in the Great Basin, United States

HERZEN STATE PEDAGOGICAL UNIVERSITY – ST. PETERSBURG, RUSSIA
Dr. Ekaterina Shternina

ST. PETERSBURG STATE UNIVERSITY – ST. PETERSBURG, RUSSIA
Visiting Research Associate in Geochemistry, 2012–2013
Dr. Vladislav Kuznetsov and Dr. Erik Tabuns

WEBER STATE UNIVERSITY – OGDEN, UT

Professional Experience
VISITING ASSISTANT PROFESSOR, CORNELL COLLEGE, MT. VERNON, IA — FALL 2015 & 2017
Geology Department Chair: Dr. Rhawn Denniston, rdenniston@cornellcollege.edu
• Designed and taught courses in Advanced Paleoclimatology, Climate Change, Historical Geology, Paleontology, and one Senior Research Thesis
• Faculty advisor for two undergraduate research projects, using ICP-OES analysis to measure cation chemistry in lake sediments and speleothems as a proxy for Holocene hydroclimate
• Jointly presented a senior thesis project at GSA Annual Meeting in Denver, CO (October 2016)
• Advised, interviewed, and evaluated Fulbright Research and ETA candidates on campus
• Delivered three public lectures at Cornell College and Coe College regarding interdisciplinary research in climate science, international studies, and science communication
• Recipient of the Anderson Natural Science Lecturer position for the Fall 2015 Semester
Graduate Assistant, University of Nevada, Las Vegas — August 2008 - Present
Ph.D. Advisor: Dr. Matthew Lachniet, matthew.lachniet@unlv.edu
M.S. Advisor: Dr. Ganqing Jiang, ganqing.jiang@unlv.edu
- Teaching assistant for laboratory sections of Sedimentology/Stratigraphy and Physical Geology, for which I was responsible for all module instruction, leading field trips, and student assessment
- Teaching assistant for online courses in Physical Geography and Physical Geology. Responsible for handling student inquiries, quality checks on course modules, and student assessment
- Research assistant in the Las Vegas Isotope Science Laboratory (4 years total) and the Electron Microanalysis and Imaging Laboratory (1 year). Responsible for daily analysis and routine maintenance, sample preparation, user training, calibration, and data processing/management
- Guest lecturer in Stable-Isotope Geochemistry, Paleoecology, and Global Warming courses
- Two-time committee chair for the annual departmental Geosymposium, a student-led research forum. Successfully raised $4,000+ through private and corporate donations to a silent auction event

Fulbright Research Grant, U.S. Department of State — September 2012–May 2013
Advisor: Dr. Mikhail Nikitin, Department of Geography and Geoecology, Herzen State Pedagogical University, St. Petersburg, Russia, boogiewoogieboy@mail.ru
- Collaborated with geoscientists at Herzen State Pedagogical University and St. Petersburg State University to carry out doctoral research on Holocene lacustrine and cave carbonates
- Sampled speleothems from Kinderlinskaya Cave in the southern Ural mountains over two field seasons and installed data loggers to monitor cave climate and drip rate (active to this day)
- Surveyed Holocene travertine deposits, structural anomalies, and surface hydrology across the Izhora Plateau in northwestern Russia. Monitored the temperature and chemistry of associated springs, along with modern mineral precipitation to measure isotopic exchange. Collected meteoric water samples from individual storm events over a two-year interval
- Translated articles and field guides (Russian-English) for the Peribaltic INQUA conference (2012) hosted in St. Petersburg, Velikiy Novgorod, and Valdai, Russia
- Completed intermediate courses in Russian language at Herzen State Pedagogical University (2 semesters), while teaching English language, TOEFL, and GRE preparation to Russian students through U.S. Embassy-sponsored education centers and tutoring

Field Research Assistant, Weber State University, Ogden, UT — Summer 2007
Advisor: Dr. Jeff Eaton, Department of Geoscience, jeaton@weber.edu
- Paleontology field assistant in Bryce Canyon and Grand Staircase-Escalante National Parks in southern Utah; worked to discover and sample Late Cretaceous microvertebrate sites
- Responsible for prospecting, collecting, identifying, and cataloguing fossil specimens

Skills and Interests
Teaching
- Have enjoyed teaching a wide range of subjects (geology, math, language, and literature) from the high school to university level, to multiple cultures, in both classroom and private settings
- Demonstrated aptitude for teaching geoscience both at introductory and advanced levels
- Successfully taught courses in multiple subdisciplines, including at the edge of my expertise
Eager to lead students through research and presenting at professional scientific meetings
Innovative hands-on teaching style that incorporates technology and invites creative learning

**Research**
- Advanced knowledge of laboratory instrumentation and chemical preparation: mass spectrometry, electron microscopy, ICP, atomic adsorption, sedimentary petrography, wet-lab chemistry
- Successfully designed and implemented geological field projects in the western U.S. and Russia: measuring and describing stratigraphic sections in carbonate rocks, surface and groundwater collections, cave microclimate monitoring, retrieval of secondary cave carbonates
- Advanced user of computer applications related to the presentation of research and data analysis (Office/iWork, Adobe Creative Suite, Grapher, Matlab, some ArcGIS)
- Proficient in Matlab scripting, data management, time-series analysis, and plotting
- Demonstrated success in scientific writing, publishing, and procuring funding for student research

**Science Communication**
- Regular presenter at professional conferences in the Earth sciences (AGU, GSA)
- Science blogger, communicating topics in geology often deemed controversial by the general public (e.g. age of the Earth, evolution, fossil record, climate change)
- Facebook admin for Katharine Hayhoe (Texas Tech University); I assist with the moderation of comments and field questions about climate change from inquisitive followers of the page
- Invited speaker (academic and public forums), specialized in mediating conflicts between science and religious or political ideology—e.g. global warming skepticism, young-earth creationism, etc.

**International Education**
- Semi-fluent in Russian language, with a keen interest in travel and study abroad
- Annually review Fulbright applications for Russian students seeking to study in the U.S.
- Enthusiastic advisor for students applying to programs that facilitate international exchange

**Grants and Awards**
- Anderson Natural Science Lecturer, Endowment Position, Cornell College (2015)
- Graduate and Professional Student Association Research Grant (2014; 2013; 2011)
- Ralph W. Stone Fellowship, National Speleological Society (2013)
- UNLV Geology 101 Teaching Assistant of the Year (2009–2010)
- Nevada Petroleum Society Field Research Grant (2009)

**Research Articles**
Baker, J.L., Lachniet, M.S.L., Chervyatsova, O., Asmerom, Y., and Polyak, V., Submission stage (Quaternary Science Reviews), Suborbital variability in the strength of wintertime westerlies over
continental western Eurasian coupled with poleward heat transport to the northeastern Atlantic Ocean: implications for Holocene reconstructions of NAO and future climate.
Baker, J.L., Nikitin, M.Yu., and Lachniet, M.S.L., Submission stage (Boreas). Holocene warming and winter NAO dynamics recorded by a paludo-lacustrine travertine deposit on the Izhora Plateau, NW Russia.

Meeting abstracts and invited talks
Baker, J.L., Lachniet, M.S., and Kasimtseva, N.V., 2011, From Central America to Central Russia: assessing the impact of climate change through oxygen isotopic records from speleothems, in Proceedings, Geology, Geocology, and Evolutionary Geography, 11th, St. Petersburg: Russia, Herzen State Pedagogical University, p. 43–47.