Elsevier Editorial System(tm) for Quaternary International
Manuscript Draft

Manuscript Number: QUATINT-D-11-00219R1

Title: Investigating climate at the Upper Palaeolithic site of Kraków Spadzista Street (B), Poland, using oxygen isotopes

Article Type: MIS 3 in Central Europe

Keywords: Woolly mammoth; Dansgaard-Oeschger; enamel; carbonate; palaeotemperature; Palaeoclimate

Corresponding Author: Mr Alexander John Edward Pryor, MPhil

Corresponding Author's Institution: University of Cambridge

First Author: Alexander John Edward Pryor, MPhil

Order of Authors: Alexander John Edward Pryor, MPhil; Rhiannon E Stevens, PhD; Piotr Wojtal, PhD; Alina Krzemińska; Tamsin C O'Connell, PhD

Abstract: Between 50,000 and 20,000 years ago, Europe experienced a series of rapid climate change events known as the Dansgaard-Oeschger cycles, which may have made areas of northern Europe more attractive for occupation by early modern humans at certain times than at others. This paper investigates when humans were occupying northern Europe in relation to these climatic changes at the archaeological site of Kraków Spadzista Street (B), by applying oxygen isotope analysis of mammoth tooth enamel carbonates (δ18O and δ13C) found at the site. The new isotopic data suggest that mean annual temperatures at Kraków Spadzista were 4-9oC colder than present and, based on comparisons with previously published isotopic data for mammoth in Europe, we argue that the Kraków assemblage most likely formed during a cold Dansgaard-Oeschger event. This suggests modern humans were able to occupy and survive in this area of northern Europe during the harsh cold phases that affected Europe at this time.

Investigating climate at the Upper Palaeolithic site of Kraków Spadzista Street (B), Poland, using oxygen isotopes

Alexander J. E. Pryor[a] (corresponding author), Rhiannon E. Stevens[b], Piotr Wojtal[c], Alina Krzemińska[d] and Tamsin C. O'Connell[a, b]

[a] Department of Archaeology, University of Cambridge, Downing Street, Cambridge, CB2 3DZ, United Kingdom. T: +44 (0) 1223 333538. F: +44 (0) 1223 333536. ajep2@cam.ac.uk, tco21@cam.ac.uk.

[b] McDonald Institute for Archaeological Research, University of Cambridge, Downing Street, Cambridge, CB2 3ER, United Kingdom. res57@cam.ac.uk, tco21@cam.ac.uk.

[c] Institute of Systematics and Evolution of Animals, Polish Academy of Sciences, Sławkowska 17, 31-016 Kraków, Poland. wojtal@isez.pan.krakow.pl.

[d] Department of Science Education, Communication and Mediation, Institute of Biology, Pedagogical University of Cracow, Podbrzezie 3, 31-054 Kraków, Poland, sulymo@gmail.com.

ABSTRACT

Between 50,000 and 20,000 years ago, Europe experienced a series of rapid climate change events known as the Dansgaard-Oeschger cycles, which may have made areas of northern Europe more attractive for occupation by early modern humans at certain times than at others. This paper investigates when humans were occupying northern Europe in relation to these climatic changes at the archaeological site of Kraków Spadzista Street (B), by applying oxygen isotope analysis of mammoth tooth enamel carbonates ($\delta^{18}O$ and $\delta^{13}C$) found at the site. The new isotopic data suggest that mean annual temperatures at Kraków Spadzista were 4-9^{o}C colder than present and, based on comparisons with previously published isotopic data for mammoth in Europe, we argue that the Kraków assemblage most likely formed during a cold Dansgaard-Oeschger event. This suggests modern humans were able to occupy and survive in this area of northern Europe during the harsh cold phases that affected Europe at this time.

Key words:

Woolly mammoth, Dansgaard-Oeschger, enamel, carbonate, palaeotemperature, palaeoclimate.

1. INTRODUCTION

The manner in which anatomically modern humans (AMH) responded to the harsh glacial conditions 50-20ka is one of the key questions concerning the Upper Palaeolithic occupation of Europe. According to current evidence, AMH evolved in Africa some time prior to 100-150ka, before spreading out to colonise areas of northern Eurasia after approximately 50ka (Mellars, 2004). This brought modern humans into contact with cold glacial climates and arctic tundra landscapes, possibly for the first time in the history of the species. Yet although early AMH had evolved in warm African climates and therefore lacked specific morphological adaptations to the cold, archaeological sites in Europe have indicated that some of the earliest AMH in Europe were able to colonise regions further north than the native Neanderthals reached in over 200ka (e.g. Mamontovaya Kurya in NW Russia; Pavlov et al., 2001). This suggests that AMH were more capable of surviving in colder environments than Neanderthals, and has focused attention on the technological and cultural adaptations of modern humans that allowed them to live in areas and climates where the Neanderthals apparently could not (e.g. van Andel and Davies, 2003).

AMH occupation sites across the North European Plains and areas north of the Trans-European mountain barrier (formed by the Alps, the Carpathians and the Bohemian Massif) are central to addressing this topic. Oxygen isotope data from the Greenland ice cores have revealed a series of eleven rapid cold-warm oscillations during the period 50-20ka, known as the Greenland Interstadial (GI) events, or Dansgaard-Oeschger (D-O) cycles. These oscillations would potentially have made the northern plains more attractive during the warm periods than during the cold phases, and suggest climate may have been an important factor in determining when the North European Plains were occupied. Moreover, population fell dramatically across this region during the cold Late Glacial Maximum (LGM) period 24-18ka (e.g. van Andel and Davies, 2003; Terberger and Street, 2002), and it is therefore relevant to ask whether the earlier short cold D-O events may have triggered similar population responses by AMH. Questions such as this may be addressed by assessing the climatic context to dated human occupations in northern Europe in the context of D-O climatic variability.

The Kraków Spadzista Street site complex is situated in the modern city of Kraków, Poland, and provides a rare example of human occupation of the Northern Plains in the cold period approaching the LGM (c.24ka ^{14}C yr BP). The largest of the sites is Kraków Spadzista Street (B), where a big accumulation of lithics and mammoth bones was recovered (Wojtal and Sobczyk, 2005), and the site is crucial for understanding how AMH groups were using the northern zone at this time. Given the D-O climatic variability, however, it remains unclear whether the site represents a cold-period occupation, or whether the site was occupied during an unusually warm period related to a warm D-O event.

Oxygen isotope analysis of woolly mammoth remains (*Mammuthus primigenius*) is now an established methodology for assessing past climates (e.g. Ayliffe et al., 1992; Genoni et al., 1998; Ukkonen et al., 2007; Tütken et al., 2007; Iacumin et al., 2010; Arppe and Karhu, 2010; Skrzypek et al. 2011). Working within this context, this study aims to reconstruct the climatic background at Kraków Spadzista Street (B) through oxygen isotopic analysis of mammoth tooth remains found at the site, and relate the results to the question of human occupation of the northern Plains and the D-O cycles. Previous oxygen isotopic analyses of four samples of mammoth tooth enamel from the Spadzista site cluster have given preliminary indications of a 1.5-2.7‰ depletion in local precipitation compared with modern values (Arppe and Karhu, 2010). These suggest climatic conditions were colder than present, but still relatively mild for a glacial period. We test this hypothesis here with a focused analysis of the Kraków Spadzista (B) material.

2. BACKGROUND TO KRAKÓW SPADZISTA STREET (B)

The following description is based on recent reanalyses at the site (Wojtal and Sobczyk, 2005; Wojtal, 2007), which was originally excavated in the 1970s (Kozłowski et al., 1974). The Kraków Spadzista Street site complex is situated in the western suburbs of the modern city of Kraków, on a rocky prominence bounded by a steep downward slope to the north, and large depressions to the east and west (Figure 1). The resulting promontory lies 50m above the wide floodplain of the Rudawa River, and is accessible only from the southern side via a hummock of land connecting it to the main slope of the Saint Bronisława hill (250-259m). This conspicuous location in the landscape, with excellent views across the river valley, repeatedly drew groups to this spot, creating a series of stratified deposits of multiple occupations across a deep time span. The largest of the sites is Kraków Spadzista (B), where the remains of at least 86 individual mammoth were found concentrated across a relatively small area (c. 150m^2), in association with a Gravettian lithic assemblage characteristic of the Kostenki-Avdeevo cultural facies. Other archaeological finds included a bone scraper, a notched mammoth rib, and a few examples of cut-marked bones. A few fragments of burned bones were also recovered, although solifluction had destroyed any potential evidence for hearths. The faunal assemblage contained all parts of the mammoth skeleton, including smaller elements such as hyoid and sesamoid bones, suggesting that the animals died at the location. This, together with large numbers of stone tools probably used as knives and spear points, has led to the interpretation of the site as a mammoth butchery location and possible kill site, although the cause of death for the mammoth individuals remains ambiguous (Wojtal and Sobczyk, 2005; Wojtal, 2007). Seven radiocarbon dates are available for the site clustering around 23-24ka ^{14}C yr BP, equating to 27-29.4ka cal yr BP (Table 1). The site therefore dates to the start of the climatic cooling at the beginning of oxygen isotope stage 2, around the time of GI events 4 and 3 (Figure 2).

3. OXYGEN ISOTOPES IN TOOTH ENAMEL AS A PALAEOCLIMATIC PROXY

Oxygen isotope ratios in the tooth enamel of large mammals closely reflect the isotopic content of ingested water, consumed by drinking and through the intake of water in food (Longinelli, 1984; Luz et al., 1984; Bryant and Froelich, 1995; Kohn, 1996). Ingested waters are, in turn, primarily controlled by the isotopic content of local precipitation, which in continental environments is determined by near-surface air temperature (e.g. Dansgaard, 1964; Rozanski et al., 1993). Studies have shown that both phosphates and carbonates in biogenic materials may undergo diagenetic changes, with phosphates more susceptible to change in organic environments and carbonates more susceptible to exchange in inorganic solutions (Zazzo et al., 2004). However enamel is resistant to diagenesis and retains information that can be used in palaeoclimatic analyses (e.g. Ayliffe et al., 1994; Koch et al., 1997; Kohn et al., 1999). Oxygen isotope ratios in tooth enamel can therefore be used as indicators of past climate, an application that has been used widely in recent years (Hoppe, 2004; Navarro et al., 2004; Nelson, 2005; Zanazzi and Kohn, 2008; García García et al., 2009). When interpreting isotopic signatures, however, it is also important to consider influences that may modify the isotopic composition of ingestion waters prior to their consumption by animals. These include changing seasonality of rainfall (Rozanski et al., 1993), and the evaporative enrichment of surface and leaf waters, which is primarily controlled by ambient aridity rather than ambient temperature (Dongmann et al., 1974; Gibson and Reid, 2010). Surface waters c.7‰ higher in $\delta^{18}O$ are known from cold arid environments (Gibson and Reid, 2010), while enrichment of leaf waters can be much greater, elevating $\delta^{18}O$ by over 20‰ relative to surface water in some instances (Dongmann et al., 1974).

4. MAMMOTH TOOTH ENAMEL GROWTH AND ECOLOGY

4.1. Tooth Growth and Structure

Proboscidean teeth form at the rear of the jaw and are forced progressively forwards into the space already occupied by older teeth, pushing them distally out of the mouth (Maschenko, 2002). Simultaneously the older teeth already in wear become increasingly worn down, eventually becoming dislodged, and are either swallowed or drop out of the mouth (Haynes, 1991: appendix A). Each individual molar is composed of a series of parallel-arranged cones, consisting of a dentine core enclosed with a thick enamel coating, collectively referred to as a 'laminae' or 'molar plate' (Ferretti, 2003). From M2 onwards, these molar plates form in a sequence, beginning towards the mesial end of the tooth, becoming progressively later in time towards the dorsal end of the tooth (Maschenko, 2002). New enamel is therefore being grown continuously throughout the lifetime of the animal, with each molar plate corresponding to a slightly different time period during the life of the animal.

4.2. Water Intake

The climatic signal produced from tooth enamel is affected by both the length of time the enamel took to grow, and the range of drinking sources encountered by individual animals as they moved around. Precise information on enamel mineralisation patterns is not available for mammoth or modern elephants, but assuming similar vertical growth rates along the molar plates to those observed in horses (3-4cm per year), each individual lamina would average several years of water intake (Hoppe, 2004; Hoppe and Koch, 2006). Based on modern elephant populations, various authors have estimated dietary requirements for adult mammoth of c.100-300kg of food (e.g. Haynes, 1991; Maschenko, 2002) and 100-300 litres of water per day. Mammoth were obligate drinkers, and at least two thirds of their total water intake would have come from fresh drinking water as opposed to water included in food (Koch et al., 1989; Ayliffe et al., 1992). Both the proportion of drinking water to food water and the large total volume of water required by mammoth imply that their teeth will give a good indication of local environmental waters, averaging a wide range of sources over a long period of time.

4.3. Movement and Mobility

Mammoth mobility patterns have been extrapolated from modern elephant ranges, suggesting daily movements of around 7-12km when a group had young calves, while annual territories may have been around 200-300km in diameter (Haynes, 1991). Modern elephants are highly territorial, and it is extremely difficult to make them leave their family territory unless there are exceptional circumstances. Nevertheless, periodic migrations may occur over long distances when food is scarce (Haynes, 1991). Strontium analyses of mammoth faunal remains from Florida (North America) and Yakutia (northern Russia) suggested mammoth migrations did not exceed a few hundred kilometres, and were at maximum 700km in these areas (Hoppe et al., 1999; Barbieri et al., 2008). This would agree with anecdotal data indicating that before national parks constrained their movements, former African elephant populations migrated over distances of around 500km (Ayliffe et al., 1992).

5. METHOD

Enamel samples were collected from 13 mammoth teeth (all selected as M5 and M6, the last and largest of the teeth grown by mammoth) excavated from Kraków Spadzista Street (B) and curated at the Institute of Systematics and Evolution of Animals, Kraków. Teeth were carefully selected in an attempt to avoid sampling molars from the same individual. Powdered enamel samples were drilled using a diamond-tipped drill piece, and were collected from the maximum available height of the molar plate being sampled, to average the longest period of time possible (Hoppe, 2004; Hoppe and Koch, 2006). Samples were sieved using a 90μm mesh to remove stray dirt and enamel splinters that fell into the sample during the drilling process, and 5-10mg of each sample was then pre-treated for carbonate oxygen isotopic analysis according to the protocol outlined in Balasse et al. (2002). Samples were then reacted with 100% orthophosphoric acid at $90^{o}C$ using a Micromass Multicarb Sample Preparation System. The carbon dioxide produced was dried, and transferred cryogenically into a PRISM mass spectrometer for isotopic analysis, conducted at the Godwin Laboratory in the Earth Sciences Department, University of Cambridge. The carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotopic compositions are reported as δ-values in ‰ relative to the international standard Vienna Pee Dee Belemnite (VPDB), where $\delta = [(R_{sample} - R_{standard})/R_{standard}] \times 1000$ and $R = {}^{13}C/{}^{12}C$ or ${}^{18}O/{}^{16}O$ respectively. Matrix-matched laboratory enamel standards (one modern, one archaeological) were also pre-treated and analysed alongside the Kraków Spadzista (B) samples for comparative purposes. The precision of measurement is better than ± 0.10‰.

Testing of enamel pre-treatment protocols has suggested that differences of c.1‰ or more may be introduced when different methods are used (e.g. Lee-Thorp and van der Merwe 1991; Koch et al. 1997). Three samples from the present sample set were therefore re-analysed following the pre-treatment method applied to the four samples previously reported from the Kraków Spadzista site cluster (Arppe and Karhu 2010).

6. RESULTS

The $\delta^{18}O$ data for 13 enamel samples from Kraków Spadzista (B) fell within a range of 1.7‰, between –10.6‰ and –12.3‰, with a mean value of –11.5‰ ($1\sigma = 0.5$‰) (Table 2). Small differences in $\delta^{18}O$ according to tooth type are visible, with M5 teeth (n=4) tending to be higher than M6 teeth (n=5), while teeth identified as M5/M6 (n=4) fall in between. A Student T-test between the M5 and M6 groups, however, shows that the difference between the means is not significant ($P = 0.137$). The length of enamel sampled varied between 51 and 138mm, and can be used as an indicator of the relative length of time averaged within each sample. There is a weak correlation between enamel length and $\delta^{18}O$ ($r^2 = 0.17$), although it is not significant ($P = 0.167$), and no correlation exists for enamel length and $\delta^{13}C$ ($r^2 = 0.00$). The range in $\delta^{13}C$ results is 1.2‰, varying between –11.7‰ and –10.5‰ with a mean value of –11.0‰ ($1\sigma = 0.3$‰). No differences in $\delta^{13}C$ are apparent between tooth type, with means of –11.1‰ ($1\sigma = 0.3$‰) and –11.0‰ ($1\sigma = 0.3$‰) for M5 and M6 respectively ($P = 0.529$).

The three duplicate analyses comparing the pre-treatment methods employed in this study with those used by Arppe and Karhu (2010) show differences of ≤0.5‰, and suggest no consistent offsets have been introduced between the new sample set and the four presently available values due to pre-treatment processes.

7. DISCUSSION

7.1. Intra-Population Range and Site Taphonomy

The small standard deviation and range of the Spadzista $\delta^{18}O$ data indicate that the water intake of mammoth was isotopically quite homogenous between individuals, suggesting they consumed water from a similar range of sources and experienced similar climates during the period in which their teeth were growing. This is also reflected in the small range and standard deviation of the $\delta^{13}C$ values, which indicate a similar inter-individual dietary intake of C3 plants. Because samples were drilled over the maximum length of enamel available, the isotopic signals produced represent a relatively long-term (several years) regional average of climatic conditions, sampled from a large volume of surface waters and food on a daily basis. The isotopic similarity, observed across a relatively large number of samples at Spadzista, may therefore indicate that the assemblage contains animals that occupied a similar territorial range, that died and accumulated over a relatively short period of time. It is thus possible to speculate that the mammoth individuals belonged to broadly the same population, a supposition that is supported by the tight clustering of the radiocarbon dates at the site (Wojtal and Sobczyk, 2005).

7.2. Comparison with Previous Studies

The isotopic results from Spadzista can be compared with previously published data available for European mammoth remains dated 50-20ka (Ayliffe et al., 1992; Genoni et al., 1998; Arppe and Karhu, 2006; Tütken et al., 2007; Tütken et al., 2008; Ukkonen et al., 2007; Arppe and Karhu, 2010), including four previously published results for the Kraków Spadzista site complex (Arppe and Karhu, 2010)(Appendix A). To facilitate this comparison, the following equations were used to convert all data to calculated phosphate $\delta^{18}O$ values, reported relative to the VSMOW isotopic standard.

$$\delta 18O_{VSMOW} = 1.03091\ \delta^{18}O_{PDB} + 30.91$$ (Coplen et al., 1983)(Equation 1)

$$\delta^{18}O_{phosphate} = 0.98\ (\pm 0.03)\ \delta^{18}O_{carbonate} - 8.5\ (\pm 0.18)$$ (Iacumin et al., 1996) (Equation 2)

Comparisons that require data to be converted cannot be made uncritically, and an assessment of the errors associated with each conversion is required. Equation 1 is a transition between two scales, and errors therefore depend on the measurement analytical error alone (±0.1‰); errors for Equation 2 were calculated using a least squares regression analysis of the original data used to define these equations, and were propagated through the conversions accordingly (Appendix B; Table 2, Table 3).

Where both carbonate and phosphate measurements were available in the literature for a single specimen, we have taken the carbonate values and converted them to phosphate using equation 2 to make the values for these individuals more comparable with those reported in this paper. A summary of the mean isotope values, standard deviations and ranges of the comparative data are given in Table 3, and in Figures 3 and 4, with raw values given in Appendix A. It should also be noted that both previous studies and testing in the University of Cambridge have shown that different enamel carbonate pre-treatment procedures may result in isotopic offsets of up to 1‰ (Lee-Thorp and van der Merwe 1991; Koch et al., 1997). Differences have also been observed between different enamel phosphate pre-treatment protocols (see summary in Arppe and Karhu, 2010). There is currently no way to calibrate data produced using different methods; however, the pre-treatment methods used in each study are listed for comparative purposes (Table 3).

7.2.1. $\delta^{13}C$ Data

The new Spadzista $\delta^{13}C$ values are fully comparable with existing mammoth data from across Europe (Figure 4), which suggest the consumption of C3 plants. Together, these values indicate that mammoth diets were broadly similar across central and northern Europe throughout the period 50-20ka, although some mammoth from Finland/Western Russia, Sweden and Latvia have more negative values.

7.2.2. $\delta^{18}O$ Data - Comparison with Previously Published Values for Kraków

The new Spadzista $\delta^{18}O$ data are depleted by a mean value of 2.3‰ relative to previously published results from the four sites in the Kraków Spadzista complex and the Kraków Zwierzyniec site, all located within a few hundred metres of Kraków Spadzista Street (B) (mean calculated $\delta^{18}O_{phosphate}$ = 12.4‰, standard deviation = 0.2‰ n=6, see Table 3). Five of the published results come from teeth found in different archaeological assemblages unconnected to the site B deposits analysed in this study, including samples from Kraków Spadzista sites E and F which are c.1,000 years older, and Kraków Zwierzyniec which is c.1,000 years younger. These dating discrepancies may plausibly explain the differences in the isotopic signals, and it should also be noted that the values recorded at these sites are virtually identical to those measured for two mammoth teeth recovered from a late OIS-5 Mousterian assemblage at the Hallera Avenue Site, Wrocław, Poland (dating constrained between 80.4-51.9ka), which have a mean $\delta^{18}O_{phosphate}$ value of 12.3‰ (calculated from measured $\delta^{18}O_{carbonate}$ values using the method outlined in section 7.2)(Skrzypek et al. 2011). This may suggest that the higher values from Kraków sites (E), (F) and Zwierzyniec are indicating warmer intervals where climates were similar to those experienced in late OIS-5, however the single values available do not allow population means to be determined and further isotopic testing of these sites is necessary to confirm the magnitude and nature of differences between them.

One of the previously published samples comes from Kraków Spadzista Street (B), the same deposits analysed in this study, and is higher by 2.2‰ relative to the new data. Although this isotope result is clearly an outlier for the Spadzista assemblage overall, it was included in all further calculations unless specifically stated; however, no identification of the molar element sampled was possible, which means that weaning effects cannot conclusively be ruled out, and a relatively small crown height of only 1-2cm of enamel was sampled which increases the potential impact of inter-annual variability in the sample. For these reasons, mean values of $\delta^{18}O$ and estimated temperature for the Kraków Spadzista (B) assemblage are quoted below both including and excluding this value for comparative purposes.

7.2.3. $\delta^{18}O$ Data - Comparison with European-Wide Results

The converted $\delta^{18}O_{phosphate}$ values of the Kraków Spadzista Street (B) samples reported in this study are amongst the lowest values presently measured for woolly mammoth from the European Upper Palaeolithic (Figure 3). The only archaeological sites where comparative mammoth $\delta^{18}O$ data are available are Avdeevo and Khotylevo II, two short-term AMH occupation sites from the Russian Plain belonging to the same Kostenkian lithic cultural grouping as Kraków Spadzista Street (B), and dated to a similar period, around 20-25ka ^{14}C yr BP (Abramova et al., 2001). The Kraków site is 1.7‰ lower than the Russian sites, demonstrating a reversal of modern trends observed between Moravia and the Russian Plain today, where the Russian Plain is c.2‰ more negative than Moravia (IAEA data). As the Rayleigh Fractionation effect (which describes the preferential rainout of heavier isotopes, causing a change in $\delta^{18}O$ of successive rainout effects independent of temperature effects) is minimal when considering differences between two continental locations (Rozanski et al., 1993), this modern difference is largely attributable to the difference in mean annual temperature between the regions of c.3^{o}C. Given that sea levels were approximately 80m lower than present at the time the archaeological sites were occupied (Siddall et al., 2003), this increased continentality is likely to have further reduced the impact of Rayleigh fractionation between these two areas. This therefore implies that the human groups which visited Kraków Spadzista c.24ka ^{14}C yr BP experienced a colder climate than that tolerated by occupants of the Russian Plain, despite the fact that the Russian sites were located further north than Kraków Spadzista, and the differences in relative temperature between the sites today. The results are also 0.5-1.0‰ lower than those of mammoths at Niederweningen, the site of a mass death event from Switzerland firmly correlated to a GI event c.45-50ka cal BP by climatic and dating evidence (Tütken et al., 2007; Hajdas et al., 2007). This difference also likely reflects geographic and chronological differences in climate between the two sites.

A substantial (4.5-4.7‰) depletion in ^{18}O of the Spadzista samples is also seen relative to the geographically and temporally dispersed assemblages from Essex (SE England), the North Sea and Germany (see Table 3). This agrees with the spatial pattern of variability observed today, but shows a much larger magnitude of change, probably relating partly to Rayleigh fractionation effects and an increased isotopic gradient in $\delta^{18}O_{precipitation}$ during the last glacial (Kehrwald 2010), and partly to climatic differences.

The remaining data from Denmark, Estonia, Latvia, Lithuania, Sweden and Finland/Western Russia represent isotopic values measured on stray finds redeposited by the Fennoscandian ice sheet and dated between 20-42ka (Arppe and Karhu, 2010). Although based on a small number of data-points, if the sampled mammoth are assumed to have lived in both D-O warm and cold periods, these values will approximate to a long-term average of δ^{18}O in these regions (Arppe and Karhu, 2010).

With the exception of Denmark, spatial patterns in modern rainfall show generally lower δ^{18}O across all these areas relative to Poland, however the mean $\delta^{18}O_{phosphate}$ calculated for the Spadzista samples (10.3‰ including the previously published value; 10.1‰ if it is excluded) is at least 0.7‰ lower than all the other assemblages apart from those in Estonia (10.5‰) and Finland/Western Russia (9.8‰). As was the case compared with Russia, the difference between Kraków and neighbouring regions is opposite to that which would be predicted from modern rainfall patterns. Despite having a relatively large sample-set from Kraków Spadzista Street (B), the standard deviation of the samples (0.7‰; 0.5‰ if outlier is excluded) is also equal to or smaller than any of these mixed assemblages (see Table 3), supporting the view that the Spadzista mammoth assemblage may have formed over a relatively short time period.

The isotopic differences between mammoth assemblages compiled here reflect variability in the isotopic composition of water ingested by proboscideans across the different time periods and areas represented in the sampled teeth. Although some effects of evaporation on the $\delta^{18}O$ signature are possible, these are not considered to be a dominant source of the variation for several reasons: first, the cooler glacial climates would have reduced evaporative influences in comparison with today; second, the water in the river networks that provided a major source of drinking water for mammoth would have been continually replenished from local groundwater reservoirs, meaning their isotopic composition would have been relatively immune to change from evaporative influences (Darling et al., 2006); and, third, because mammoth consumed a relatively large proportion of their water each day by drinking rather than as water consumed through food, the latter being more susceptible to evapotranspiration effects (Dongmann et al., 1974). Evaporation has also been rejected as a primary factor in previous isotopic studies involving mammoth in Europe (e.g. Ukkonen et al., 2007; Tütken et al., 2007, Arppe and Karhu, 2010), and the large body-size of mammoth is likely to have made them less susceptible to the isotopic effects of local humidity and physiological effects (Tütken et al., 2007). Similarly, neither the results reported here, nor those from previous studies, have shown any influence of glacial melt waters in the isotopic samples, which would be very strongly depleted in ^{18}O.

Ruling out these effects allows the differences between the sites to be interpreted as primarily representing temperature differences between the sites and study areas. This implies that the mammoths that died at Kraków Spadzista (B) lived in a relatively cold climate compared with the average conditions experienced by mammoths living elsewhere, probably reflecting Spadzista's geographic position on the narrowest portion of the North European Plain sandwiched between the trans-European mountain barrier and an ice sheet that had already begun advancing towards its maximum extent at the time Spadzista was occupied.

Recent discussions of mammoth $\delta^{18}O$ data have cautioned against making direct associations with stadial/interstadial periods purely on the basis of the isotopic values (e.g. Arppe and Karhu 2010; Ukkonen et al. 2011). Further work is indeed needed to confirm the magnitude of $\delta^{18}O$ fluctuations across Europe associated with the D-O cycles; yet previous discussions have considered single values measured on chronologically and geographically mixed materials, and could not take naturally-occurring population-level diversity into account (c.2-3‰ in the Spadzista and Niederweningen mammoth populations). In contrast, the new Spadzista data allow this variability to be investigated and a mean value for the assemblage as a whole to be calculated, vastly increasing the reliability of the climatic reconstruction that is possible from the isotopic data for the Spadzista region.

The radiocarbon dates for the Kraków Spadzista (B) assemblage place it around the time of GI events 3 and 4, two rapid warm-cold oscillations that occurred within a period of less than 2,000 years (Figure 2). We argue here that in the context of the new data reported in this paper, the deposit at Spadzista appears to have formed during a D-O cold event, most likely Greenland stadial 4 based on the radiocarbon dates (see Figure 2). This interpretation would be consistent with the more positive $\delta^{18}O$ mammoth data reported from Niederweningen that was assigned to a D-O warm event (Tütken et al., 2007). It also fits with the geographically and temporally dispersed samples from Latvia, Lithuania and Sweden, as these show a large standard deviation and range in their values (Table 3), and likely incorporate individuals that lived during both warm and cold D-O periods (Arppe and Karhu, 2010). This would explain the larger range in their $\delta^{18}O$ values, and the overlap in isotopic values with the Spadzista mammoth. It is notable in this regard that the two assemblages isotopically most similar to Kraków, in both mean values and ranges, are those from Finland/Western Russia and Estonia. Based on their similarity it could be argued that these assemblages are also producing a discrete climatic signal, with all sampled individuals indicating either a warm D-O, or alternatively a cold D-O event. However, these assemblages are based on geographically and temporally dispersed samples and assigning individual mammoth to a D-O cycle will only therefore be possible through further analysis of isotopic and climatic data specific to these regions, which is beyond the scope of this paper.

7.3. Estimates of Drinking Water

Modern studies have provided quantitative relationships that allow $\delta^{18}O_{enamel}$ to be related to the isotopic composition of water ingested by animals in their diet, which can be used as an approximation of isotopes in groundwater, and precipitation (e.g. Ayliffe et al., 1992; Delgado Huertas et al., 1995). Because mammoth are extinct, it is necessary to use the conversion from $\delta^{18}O_{enamel\ phosphate}$ to $\delta^{18}O_{drinking\ water}$ calculated for elephants (Ayliffe et al., 1992), the closest living relative of mammoth. This equation was published with the errors quoted here.

$$\delta^{18}O_{enamel\ phosphate} = 0.94\ (\pm\ 0.10)\ \delta^{18}O_{drinking\ water} + 23.3\ (\pm\ 0.7) \qquad \text{(Equation 3)}$$

The $\delta^{18}O_{drinking\ water}$ values estimated from the Kraków Spadzista (B) mammoth $\delta^{18}O_{enamel\ phosphate}$ data using Equation 3 have a mean value of –13.8‰ relative to VSMOW (1σ = 0.8‰; Table 2), substantially lower than that of modern precipitation in Kraków which has a weighted mean average of –9.2‰ (1σ = 0.8‰)(IAEA station in Kraków for 1975-2002). These estimated $\delta^{18}O_{drinking\ water}$ values are also 1‰ to 3.6‰ lower than the very long-term average values of –10.2‰ to –12.8‰ measured on water from palaeo-aquifers around Kraków, representing water that accumulated over thousands or tens-of-thousands of years, including precipitation from both the D-O warm and cold events (Rozanski et al., 1993; Zuber et al., 2004). These data indicate that the Spadzista mammoths died at the site during a period that was colder than average for this area during the glacial period, highlighting again that the Spadzista molars exhibit some of the most depleted $\delta^{18}O$ signals yet measured in European fauna.

7.4. Estimates of Temperature

The $\delta^{18}O$ in modern precipitation in Kraków has been shown to change by 0.64 ± 0.05‰ per degree of temperature change (Duliński et al., 2001). This is consistent with the long-term $\delta^{18}O_{precipitation}$/temperature relationship measured on glacial waters from palaeo-aquifers in the Kraków region, of 0.67 ± 0.17‰ per degree (Zuber et al., 2004), but the correlation between modern $\delta^{18}O_{precipitation}$/temperature is weak ($R^2$ = 0.39; n=265), and there are no data across the $\delta^{18}O_{precipitation}$ range required here (c.– 13‰ to –15‰). Interpreting the archaeological data using the local dataset would therefore require significant extrapolation of the relationship, greatly increasing the errors associated with the results (McKillup, 2005). Palaeo-temperature at Spadzista was therefore estimated using the general equation for Europe calculated by Rozanski et al. (1992), which is better constrained across the range of $\delta^{18}O$-values of relevance in this paper and provides a first-order estimate of temperature for the Spadzista samples. The error on the precipitation/temperature coefficient is taken from Rozanski et al., (1992), and the error on the y-intercept was calculated using a least squares regression analysis (Appendix B):

$$\delta^{18}O_{rainfall} = 0.59\ (\pm\ 0.08)\ T_{average} - 14.24\ (\pm\ 0.5) \qquad \text{(Equation 4)}$$

The resulting mean annual temperature (MAT) estimates for Kraków Spadzista Street (B) vary between $-1.0^{o}C$ ($\pm 2^{o}C$) and $+4.3^{o}C$ ($\pm 1.7^{o}C$) with a mean of $+0.7^{o}C$ ($1\sigma = 1.3^{o}C$). This is $4^{o}C$ to $9^{o}C$ cooler than present MAT at Kraków ($8.2^{o}C$), implying conditions similar to those now experienced in northern Scandinavia and north-western Russia. If only data from this study are used, the range of MAT estimates for Kraków Spadzista Street (B) narrows to between $-1.0^{o}C$ ($\pm 2^{o}C$) and $+2.1^{o}C$ (± 1.8), translating to $6^{o}C$ to $9^{o}C$ cooler than present MAT at Kraków. As expected, the new temperature estimates are $2\text{-}3^{o}C$ cooler than those proposed for the higher $\delta^{18}O_{enamel}$ values previously measured at the nearby assemblages of Kraków Spadzista (E), (F) and Kraków Zwierzyniec (Arppe and Karhu 2010). They are also cooler than the $+4.3^{o}C$ ($\pm 2.1^{o}C$) proposed for interstadial mammoth at Niederweningen (Tütken et al. 2007).

No pollen or malacozoological data are available for the Kraków Spadzista Street (B) assemblage (e.g. see Alexandrowicz 2007), yet the new palaeoenvironmental data may be compared with results from a pedological analysis that identified evidence for strong solifluction processes and traces of an ice wedge filled with cultural sediments in the layer immediately below the cultural materials (Kalicki et al. 2007), consistent with a generally cold climatic context for the assemblage. Yet colder temperatures have been estimated from nearby Bełchatów (SW Poland), where MATs for the period 24-26 ^{14}C BP has been estimated as $-4^{o}C$ to $-10^{o}C$ on the basis of ice wedge casts and coleoptera remains (Kasse et al. 1998), while Jary (2009) collates evidence of ice wedges across southern Poland to suggest continuous permafrost and MATs of $\leq -6^{o}C$ for the LGM period. Other MAT estimates for stadial periods between 50-20ka across northern Europe have also typically been made on the basis of frost wedges associated with pollen or chironomid assemblages, and cluster within the same –4°C to –10°C range, for example at Grouw, Netherlands (–4.5°C; Kasse et al. 1995), Reichwalde, Germany (–4°C to –8°C; Bohncke et al. 2008), and Niederlauzit, Germany (–8°C; Bos et al. 2001). While the relative values of the new isotopic data support the interpretation of Kraków Spadzista (B) as one of the coldest mammoth assemblages yet analysed isotopically in Europe, the temperatures predicted from these data therefore appear warmer than the stadial-period temperatures estimated from other local proxy data.

7.5. Humans and Climate at Kraków Spadzista Street (B)

The measured isotopic values describe climate during the period of tooth enamel growth, and therefore correspond to climate shortly before the animal died. As the faunal remains at Kraków Spadzista are related to human butchery and possibly hunting activities (Wojtal and Sobczyk, 2005), this implies that the isotopic signal estimates climate to within a few years of when humans visited the site. The climates were clearly very cold, yet if the interpretation that the Kraków Spadzista mammoth died during a D-O cold event is correct, this implies that humans were not excluded from the North European Plains region by the cold D-O climates. This fact is crucial for understanding occupation patterns and strategies during the Upper Palaeolithic in the context of the D-O cycles, and further investigation is required at other sites to determine if Kraków Spadzista Street (B) is a special case, or part of a more general pattern of northern occupation during the colder periods.

AMH may have occupied Kraków Spadzista and southern Poland throughout the year, or exploited resources and hunting territories across the northern zone seasonally and returned south for the winter period. Both these strategies would still have required sophisticated clothing, and other technological and behavioural adaptations to make this area habitable for humans at this time (e.g. Hoffecker, 2005). This has implications for AMH technological and behavioural adaptations, and suggests AMH were already adapted to ‘arctic’ conditions before the onset of the full LGM. This agrees with the fact that humans were occupying areas inside the Arctic Circle up to 10ka before the occupation at Kraków Spadzista (e.g. Pavlov et al., 2001; Pitulko et al., 2004), and were not excluded from northern Europe during the LGM period that followed the occupation at Kraków Spadzista (e.g. Street and Terberger, 1999).

8. CONCLUSION

Our results indicate that accumulation of the mammoth assemblage at Kraków Spadzista Street (B), and therefore human activity, took place in the context of an extremely cold climate, $4^{o}C$ to $9^{o}C$ colder (6-$9^{o}C$ cooler excluding outlier) than present climate in the vicinity of Kraków today. The isotopic values produced from the mammoth teeth at Kraków Spadzista Street (B) are amongst the lowest measured for European mammoth, and the most likely interpretation of these data is that these mammoth lived during a D-O cold event. This indicates that humans were not excluded from northern areas during these relatively short periods of extreme cold that preceded the LGM.

9. ACKNOWLEDGEMENTS

The authors grateful to Mike Hall and James Rolfe from the Godwin Laboratory (University of Cambridge), and Catherine Kneale for technical and laboratory support in processing the isotopic samples reported here. We also thank the Royal Anthropological Institute and the trustees of the Emslie Horniman Fund for their generous funding towards this research, John Lister for guidance in the mathematical propagation of errors, and to Nisha Doshi and the anonymous referees for comments on earlier drafts of the manuscript. AJEP and RES gratefully acknowledge the University of Cambridge and the Royal Society respectively for funding support.

CAPTIONS

Figure 1 – Map of sites mentioned in this study: 'X' indicates geographically and temporally discrete archaeological and palaeontological assemblages; circles indicate individual samples, and geographically and/or temporally mixed assemblages (Appendix A). Shading indicates areas above 500m. Numbers refer to codes given in Appendix A.

Figure 2 – Plot of Radiocarbon dates alongside the NGRIP ice core δ^{18}O record, generated using the radiocarbon calibration program OxCal v.4.1.3 (Bronk Ramsey 2009); r.5 Atmospheric data from Reimer et al. (2009). Site codes as described in Table 1. Kraków Spadzista Street (B) is represented as a compilation of the seven dates shown in Table 1.

Figure 3 – Calculated $\delta^{18}O_{\text{enamel phosphate}}$ (VSMOW) values of woolly mammoth in European assemblages. Numbers indicate sample size within each assemblage.

Figure 4 – Mammoth δ^{13}C data (PDB) in different European assemblages. Numbers indicate sample size within each assemblage.

Figure 5 - Calculated $\delta^{18}O_{\text{enamel phosphate}}$ data shown by latitude, including the chronologically and spatially discrete archaeological assemblages (open shapes), and the chronologically and spatially mixed assemblages (closed shapes). The mixed assemblages fall into two separate groups: Scandinavian and northern Europe (50-20ka BP); and NW Europe (late Pleistocene).

Table 1 – Radiocarbon dates for sites in the Kraków Spadzista Street site complex and at Kraków Zwierzyniec. All samples are AMS dates unless otherwise stated. Calibrated using OxCal (Reimer et al., 2009).
Site code: KS = Kraków Spadzista Street sites B, C2, E and F; KZ = Kraków Zwierzyniec
†: 1 = Mammoth bone; 2 = Mammoth molar; 3 = Carbonised bone
* = Conventional radiocarbon date

Table 2 – δ^{18}O and δ^{13}C results from Kraków Spadzista Street (B).
†: Converted using equations 1 and 2.
‡: Converted using equation 3.
♦: Converted using equation 4.
*: Previously published sample for Kraków Spadzista Street (B) (Arppe and Karhu 2010)

Table 3 - Summary of woolly mammoth oxygen isotopic data available for Europe. Data based on carbonate results where possible, converted to phosphate values relative to VSMOW using Equations 1 and 2. Data based on phosphate results are indicated in the 'Pre-treatment' column. Raw data given in Appendix A.
†: Dates taken from cited publications unless otherwise stated
‡: Only samples of pre-LGM age were included from the cited references, falling within the age range given.
*: δ^{13}C data taken from Arppe 2009.

A - Abramova et al. 2001
1. This study - Sodium hypochlorite (24hrs), 0.1M acetic acid (4hrs)
2. Sodium hypochlorite (3%) + sodium hydroxide (1%) solution (24hrs), 1M acetic acid-calcium acetate buffer (pH 4.75) (24hrs)
3. Sodium hypochlorite (24hrs), 1M acetic acid-calcium acetate buffer (pH 4.75) (24hrs)
4. Sodium hypochlorite (20hrs), 1M acetic acid-calcium acetate buffer (pH 4.75) (20hrs)
P1. Phosphate prep (fluorination of Ag3PO4)
P2. Phosphate prep (modified silica tube graphite reduction)
P3. Phosphate prep (BiPO4 technique)

Appendix A – Raw data used for comparison with the Kraków Spadzista Street (B) results
†: Teeth are labelled as M1 (1st milk tooth) to M6 (final adult tooth) after Haynes (1991), as there are no clear distinctions in proboscideans between deciduous and adult teeth.
*: Dates summarised from information given in cited publications
References: 1. = Tütken et al 2007; 2. = Genoni et al. 1998; 3. = Ayliffe et al. 1992; 4. Tütken et al. 2008; 5. Arppe and Karhu 2010; 6. Arppe 2009; 7. Ukkonen et al. 2007; 8. Arppe and Karhu 2006.

Appendix B – Methods used to calculate and carry forward errors association with data conversions applied in this paper

REFERENCES

Abramova, Z.A., Grigorieva, G.V. and Zaitseva, G.I., 2001. The age of Upper Paleolithic sites in the Middle Dnieper River basin of eastern Europe. Radiocarbon 43, 1077-1084.

Alexandrowicz, S.W., 2007. Assemblages of molluscs at the Palaeolithic site Kraków-Spadzista. Folia Quaternaria 77, 31-36.

Arppe, L., 2009. Isotopic records of terrestrial ice age environments in mammoth bioapatite. Ph.D. thesis No. 204 of the Department of Geology, University of Helsinki.

Arppe, L. and Karhu, J.A., 2010. Oxygen isotope values of precipitation and the thermal climate in Europe during the middle to late Weichselian ice age. Quaternary Science Reviews 29 (9-10), 1263-1275.

Arppe, L.M. and Karhu, J.A., 2006. Implications for the Late Pleistocene climate in Finland and adjacent areas from the isotopic composition of mammoth skeletal remains. Palaeogeography, Palaeoclimatology, Palaeoecology 231 (3-4), 322-330.

Ayliffe, L.K., Lister, A.M. and Chivas, A.R., 1992. The preservation of glacial-interglacial climatic signatures in the oxygen isotopes of elephant skeletal phosphate. Palaeogeography Palaeoclimatology Palaeoecology 99 (3-4), 179-191.

Ayliffe, L.K., Chivas, A.R. and Leakey, M.G., 1994. The retention of primary oxygen-isotope compositions of fossil elephant skeletal phosphate. Geochimica et Cosmochimica Acta 58 (23), 5291-5298.

Balasse, M., Ambrose, S.H., Smith, A.B. and Price, T.D., 2002. The Seasonal Mobility Model for Prehistoric Herders in the South-western Cape of South Africa Assessed by Isotopic Analysis of Sheep Tooth Enamel. Journal of Archaeological Science 29 (9), 917-932.

Barbieri, M., Kuznetsova, T.V., Nikolaev, V.I. and Palombo, M.R., 2008. Strontium isotopic composition in late Pleistocene mammal bones from the Yakutian region (North-Eastern Siberia). Quaternary International 179 (1), 72-78.

Bohncke, S.J.P., Bos, J.A.A., Engels, S., Heiri, O. and Kasse, C., 2008. Rapid climatic events as recorded in Middle Weichselian thermokarst lake sediments. Quaternary Science Reviews 27 (1-2), 162-174.

Bos, J., A. A., Bohncke, S., J. P. , Kasse, C. and Vandenberghe, J., 2001. Vegetation and climate during the Weichselian Early Glacial and Pleniglacial in the Niederlausitz, eastern Germany - macrofossil and pollen evidence. Journal of Quaternary Science 16 (3), 269-289.

Bryant, J.D. and Froelich, P.N., 1995. A model of oxygen isotope fractionation in body water of large mammals. Geochimica et Cosmochimica Acta 59 (21), 4523-4537.

Coplen, T.B., Kendall, C. and Hopple, J., 1983. Comparison of stable isotope reference samples. Nature 302 (5905), 236-238.

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus 16 (4), 436-468.

Darling, W.G., Bath, A.H., Gibson, J.J. and Rozanski, K., 2006. Isotopes in water. In: M. J. Leng (Ed.) Isotopes in palaeoenvironmental research, pp. 1-66. Springer, Dordrecht.

Delgado Huertas, A., Iacumin, P., Stenni, B., Sánchez Chillón, B. and Longinelli, A., 1995. Oxygen isotope variations of phosphate in mammalian bone and tooth enamel. Geochimica et Cosmochimica Acta 59 (20), 4299-4305.

Dongmann, G., Nürnberg, H.W., Förstel, H. and Wagener, K., 1974. On the enrichment of $H_2^{18}O$ in the leaves of transpiring plants. Radiation and Environmental Biophysics 11 (1), 41-52.
Duliński, M., Florkowski, T., Grabczak, J. and Różański, K., 2001. Twenty-five years of systematic measurements of isotopic composition of precipitation in Poland. Przegląd Geologiczny 49, 250-256.
Ferretti, M.P., 2003. Structure and evolution of mammoth molar enamel. Acta Palaeontologica Polonica 48 (3), 383-396.
García García, N., Feranec, R.S., Arsuaga, J.L., Bermúdez de Castro, J.M. and Carbonell, E., 2009. Isotopic analysis of the ecology of herbivores and carnivores from the Middle Pleistocene deposits of the Sierra De Atapuerca, northern Spain. Journal of Archaeological Science 36 (5), 1142-1151.
Genoni, L., Iacumin, P., Nikolaev, V., Gribchenko, Y. and Longinelli, A., 1998. Oxygen isotope measurements of mammoth and reindeer skeletal remains: an archive of Late Pleistocene environmental conditions in Eurasian Arctic. Earth and Planetary Science Letters 160 (3-4), 587-592.
Gibson, J.J. and Reid, R., 2010. Stable isotope fingerprint of open-water evaporation losses and effective drainage area fluctuations in a subarctic shield watershed. Journal of Hydrology 381 (1-2), 142-150.
Hajdas, I., Bonani, G., Furrer, H., Mäder, A. and Schoch, W., 2007. Radiocarbon chronology of the mammoth site at Niederweningen, Switzerland: Results from dating bones, teeth, wood, and peat. Quaternary International 164-165, 98-105.
Haynes, G., 1991. Mammoths, mastodonts, and elephants: biology, behavior, and the fossil record. Cambridge University Press, Cambridge, xi, 413 p.p.
Hoffecker, J., 2005. Innovation and technological knowledge in the Upper Paleolithic of Northern Eurasia. Evolutionary Anthropology: Issues, News, and Reviews 14 (5), 186-198.
Hoppe, K. and Koch, P., 2006. The biogeochemistry of the Aucilla River fauna. In: S. D. Webb (Ed.) First Floridians and Last Mastodons: The Page-Ladson Site in the Aucilla River, 26, Topics in Geobiology, pp. 379-401. Springer, London.
Hoppe, K.A., Koch, P.L., Carlson, R.W. and Webb, S.D., 1999. Tracking mammoths and mastodons: Reconstruction of migratory behavior using strontium isotope ratios. Geology 27 (5), 439-442.
Hoppe, K.A., 2004. Late Pleistocene mammoth herd structure, migration patterns, and Clovis hunting strategies inferred from isotopic analyses of multiple death assemblages. Paleobiology 30 (1), 129-145.
Iacumin, P., Bocherens, H., Mariotti, A. and Longinelli, A., 1996. Oxygen isotope analyses of co-existing carbonate and phosphate in biogenic apatite: a way to monitor diagenetic alteration of bone phosphate? Earth and Planetary Science Letters 142 (1-2), 1-6.
Iacumin, P., Di Matteo, A., Nikolaev, V. and Kuznetsova, T.V., 2010. Climate information from C, N and O stable isotope analyses of mammoth bones from northern Siberia. Quaternary International 212 (2), 206-212.
Jary, Z., 2009. Periglacial markers within the Late Pleistocene loess-palaeosol sequences in Poland and Western Ukraine. Quaternary International 198 (1-2), 124-135.
Kalicki, T., Kozłowski, J.K., Krzemińska, A., Sobczyk, K. and Wojtal, P., 2007. The formation of mammoth bone accumulation at the Gravettian site Kraków-Spadzista B+B1. Folia Quaternaria 77, 5-30.

Kasse, C., Bohncke, S.J.P. and Vandenberghe, J., 1995. Fluvial periglacial environments, climate and vegetation during the Middle Weichselian in the northern Netherlands with special reference to the Hengelo Interstadial. Mededelingen Rijks Geologische Dienst 52, 387-413.
Kasse, C., Huijzer, A.S., Krzyszkowski, D., Bohncke, S.J.P. and Coope, G.R., 1998. Weichselian Late Pleniglacial and Late-glacial depositional environments, Coleoptera and periglacial climatic records from central Poland (Belchatow). Journal of Quaternary Science 13 (5), 455-469.
Kehrwald, N.M., McCoy, W.D., Thibeault, J., Burns, S.J. and Oches, E.A., 2010. Paleoclimatic implications of the spatial patterns of modern and LGM European land-snail shell $\delta^{18}O$. Quaternary Research 74 (1), 166-176.
Koch, P.L., Fisher, D.C. and Dettman, D., 1989. Oxygen isotope variation in the tusks of extinct proboscideans - a measure of season of death and seasonality. Geology 17 (6), 515-519.
Koch, P.L., Tuross, N. and Fogel, M.L., 1997. The Effects of Sample Treatment and Diagenesis on the Isotopic Integrity of Carbonate in Biogenic Hydroxylapatite. Journal of Archaeological Science 24 (5), 417-429.
Kohn, M., 1996. Predicting animal $\delta^{18}O$: Accounting for diet and physiological adaptation. Geochimica et Cosmochimica Acta 60 (23), 4811-4829.
Kohn, M.J., Schoeninger, M.J. and Barker, W.W., 1999. Altered states: effects of diagenesis on fossil tooth chemistry. Geochimica et Cosmochimica Acta 63 (18), 2737-2747.
Kozłowski, J.K., Kubiak, H., Sachse-Kozłowska, E., van Vliet, B. and Zakrzewska, G., 1974. Upper Palaeolithic site with dwellings of mammoth bones – Cracow, Spadzista Street B. Folia Quaternaria 44, 1-110.
Lee-Thorp, J.A. and van der Merwe, N.J., 1991. Aspects of the chemistry of modern and fossil biological apatites. Journal of Archaeological Science 18 (3), 343-354.
Longinelli, A., 1984. Oxygen isotopes in mammal bone phosphate: a new tool for paleohydrological and paleoclimatological research? Geochimica et Cosmochimica Acta 48 (2), 385-390.
Luz, B., Kolodny, Y. and Horowitz, M., 1984. Fractionation of oxygen isotopes between mammalian bone-phosphate and environmental drinking water. Geochimica et Cosmochimica Acta 48 (8), 1689-1693.
Maschenko, E.N., 2002. Individual development, biology and evolution of the woolly mammoth. Cranium 19 (1), 1-120.
McKillup, S., 2005. Statistics explained: an introductory guide for life scientists. Cambridge University Press, Cambridge.
Mellars, P., 2004. Neanderthals and the modern human colonization of Europe. Nature 432 (7016), 461-465.
Navarro, N., Lécuyer, C., Montuire, S., Langlois, C. and Martineau, F., 2004. Oxygen isotope compositions of phosphate from arvicoline teeth and Quaternary climatic changes, Gigny, French Jura. Quaternary Research 62 (2), 172-182.
Nelson, S.V., 2005. Paleoseasonality inferred from equid teeth and intra-tooth isotopic variability. Palaeogeography, Palaeoclimatology, Palaeoecology 222 (1-2), 122-144.
Pavlov, P., Svendsen, J. and Indrelid, S., 2001. Human presence in the European Arctic nearly 40,000 years ago. Nature 413 (6851), 64-67.
Pitulko, V., Nikolsky, P., Girya, E., Basilyan, A., Tumskoy, V., Koulakov, S., Astakhov, S., Pavlova, E. and Anisimov, M., 2004. The Yana RHS Site:

Humans in the Arctic Before the Last Glacial Maximum. Science 303 (5654), 52-56.
Reimer, P.J., Baillie, M.G.L., Bard, E., Bayliss, A., Beck, J.W., Blackwell, P.G., Bronk Ramsey, C., Buck, C.E., Burr, G.S., Edwards, R.L., Friedrich, M., Grootes, P.M., Guilderson, T.P., Hajdas, I., Heaton, T.J., Hogg, A.G., Hughen, K.A., Kaiser, K.F., Kromer, B., McCormac, F.G., Manning, S.W., Reimer, R.W., Richards, D.A., Southon, J.R., Talamo, S., Turney, C.S.M., Van der Plicht, J. and Weyhenmeyer, C.E., 2009. IntCal09 and Marine09 radiocarbon age calibration curves, 0-50,000 years cal BP. Radiocarbon 51 (4), 1111-1150.
Rozanski, K., Araguás-Araguás, L. and Gonfiantini, R., 1992. Relation Between Long-Term Trends of Oxygen-18 Isotope Composition of Precipitation and Climate. Science 258 (5084), 981-985.
Rozanski, K., Araguás-Araguás, L. and Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. In: P. K. Swart, K. C. Lohmann, J. McKenzie and S. Savin (Eds.), Climate change in Continental Isotopic Records, Geophysical Monograph 78, pp. 1-36. American Geophysical Union, Washington DC.
Siddall, M., Rohling, E.J., Almogi-Labin, A., Hemleben, C., Meischner, D., Schmelzer, I. and Smeed, D.A., 2003. Sea-level fluctuations during the last glacial cycle. Nature 423 (6942), 853-858.
Skrzypek, G., Wiśniewski, A. and Grierson, P.F., 2011. How cold was it for Neanderthals moving to Central Europe during warm phases of the last glaciation? Quaternary Science Reviews 30 (5-6), 481-487.
Street, M. and Terberger, T., 1999. The last Pleniglacial and the human settlement of Central Europe: New information from the Rhineland site of Wiesbaden-Igstadt. Antiquity 73 (280), 259-272.
Terberger, T. and Street, M., 2002. Hiatus or continuity? New results for the question of pleniglacial settlement in Central Europe. Antiquity 76 (293), 691-698.
Tütken, T., Furrer, H. and Walter Vennemann, T., 2007. Stable isotope compositions of mammoth teeth from Niederweningen, Switzerland: Implications for the Late Pleistocene climate, environment, and diet. Quaternary International 164-165, 139-150.
Tütken, T., Vennemann, T.W. and Pfretzschner, H.U., 2008. Early diagenesis of bone and tooth apatite in fluvial and marine settings: constraints from combined oxygen isotope, nitrogen and REE analysis. Palaeogeography, Palaeoclimatology, Palaeoecology 266 (3-4), 254-268.
Ukkonen, P., Arppe, L., Houmark-Nielsen, M., Kjaer, K.H. and Karhu, J.A., 2007. MIS 3 mammoth remains from Sweden - implications for faunal history, palaeoclimate and glaciation chronology. Quaternary Science Reviews 26 (25-28), 3081-3098.
Ukkonen, P., Aaris-Sørensen, K., Arppe, L., Clark, P.U., Daugnora, L., Lister, A.M., Lõugas, L., Seppä, H., Sommer, R.S., Stuart, A.J., Wojtal, P. and Zupiņs, I., 2011. Woolly mammoth (*Mammuthus primigenius* Blum.) and its environment in northern Europe during the last glaciation. Quaternary Science Reviews 30 (5-6), 693-712.
van Andel, T.H. and Davies, W., 2003. Neanderthals and modern humans in the European landscape during the last glaciation: archaeological results of the Stage 3 project. McDonald Institute for Archaeological Research, Cambridge, xviii, 265p.
Wojtal, P., 2007. Zooarchaeological studies of the Late Pleistocene sites in Poland. Institute of Systematics and Evolution of Animals, Kraków, 189p.

Wojtal, P. and Sobczyk, K., 2005. Man and woolly mammoth at the Kraków Spadzista Street (B) - taphonomy of the site. Journal of Archaeological Science 32 (2), 193-206.

Zanazzi, A. and Kohn, M.J., 2008. Ecology and physiology of White River mammals based on stable isotope ratios of teeth. Palaeogeography, Palaeoclimatology, Palaeoecology 257 (1-2), 22-37.

Zazzo, A., Lecuyer, C. and Mariotti, A., 2004. Experimentally-controlled carbon and oxygen isotope exchange between bioapatites and water under inorganic and microbially-mediated conditions. Geochimica et Cosmochimica Acta 68 (1), 1-12.

Zuber, A., Weise, S.M., Motyka, J., Osenbrück, K. and Rózanski, K., 2004. Age and flow pattern of groundwater in a Jurassic limestone aquifer and related Tertiary sands derived from combined isotope, noble gas and chemical data. Journal of Hydrology 286 (1-4), 87-112.

Appendix A

Click here to view linked References

Site no.	Site	Element (Where known) †	Country	Age (ka)*	$\delta^{18}O_{phosphate}$ (VSMOW)	$\delta^{18}O_{carbonate}$ (VSMOW)	Converted $\delta^{18}O^{phosphate}$ (VSMOW)	$\delta^{13}C$ (PDB)	Reference
Discreet assemblages									
	Niederweningen	M6	Switzerland	45-50		19.9	11.0	-11.7	1
	Niederweningen	M5	Switzerland	45-50		20.0	11.1	-11.8	1
	Niederweningen		Switzerland	45-50		21.3	12.4	-11.5	1
	Niederweningen		Switzerland	45-50		19.5	10.6	-11.5	1
	Niederweningen	M5	Switzerland	45-50		18.4	9.5	-11.3	1
	Niederweningen	M6	Switzerland	45-50		20.1	11.2	-11.1	1
	Niederweningen	M5	Switzerland	45-50		20.0	11.1	-11.7	1
	Niederweningen	M5	Switzerland	45-50		19.7	10.8	-11.6	1
	Niederweningen	M6	Switzerland	45-50		20.4	11.5	-11.5	1
	Niederweningen	M6	Switzerland	45-50		19.7	10.8	-10.9	1
	Avdeevo		Ukraine	21-23	11.7				2
	Avdeevo		Ukraine	21-23	12.5				2
	Avdeevo		Ukraine	21-23	12.2				2
	Avdeevo		Ukraine	21-23	11.6				2
	Khotylevo		Ukraine	23-25	11.2				2
	Khotylevo		Ukraine	23-25	12.3				2
	Khotylevo		Ukraine	23-25	12.4				2
Mixed/scattered assemblages									
1	Ponders End, Lea Valley, Essex		England	28	14.8				3
	Edmonton, Lea Valley, Essex		England	28	15.2				3
2	North Sea Bed, N Amsterdam		Netherlands	Late Pleistocene	14.9				4
	North Sea Bed, Brown Bank		England	Late Pleistocene	14.7				4
3	Rhine river gravels		Germany	Late Pleistocene	14.1				4
	Rhine river gravels		Germany	Late Pleistocene	15.4				4
	Rhine river gravels		Germany	Late Pleistocene	14.8				4
4	Højballegard, Hånsted		Denmark	19.9		23.9	14.9	-11.7	5, 6
5	Høgebjerg		Denmark	26.4		21.1	12.2	-10.8	5, 6
6	Nymølle, Sjælland		Denmark	34.6		21.0	12.1	-11.5	5, 6
7	Nymølle, Sjælland		Denmark	26		20.6	11.7	-11.3	5, 6
8	Hornbæk		Denmark	22.9		21.1	12.2	-10.6	5, 6
9	Ramsele, Västernorrland	M6	Sweden	41.0		19.9	11.0	-11.3	7
10	Sollefteå, Västernorrland	M6	Sweden	24.8		20.1	11.2	-12.0	7
11	Västansjö, Sättna, Västernorrland	M6	Sweden	29.5		18.9	10.0	-11.0	7
12	Pilgrimstad, Jämtland	M6	Sweden	25.9		19.7	10.8	-11.1	7
13	Bäck, Rättvik, Dalarna	M6	Sweden	31.0		21.0	12.1	-11.4	7
14	Dösebacka, Romelanda, Bohuslän		Sweden	36.0		21.0	12.1	-11.8	7
15	Bårslöv, Skåne	M6	Sweden	33.9		22.0	13.1	-10.8	7
16	Djurslöv, Mölleberga, Skåne	M4	Sweden	26.2		19.7	10.8	-11.3	7
17	Arrie, Risebjär, Skåne	M6	Sweden	40.0		16.5	7.7	-11.9	7
18	Örsjö, Skåne	M4	Sweden	34.5		21.2	12.3	-12.5	7
19	Nilsiä, Syväri		Finland	22.4		17.9	9.0	-12.7	8
20	Helsinki, Töölö		Finland	23.3		18.3	9.4	-13.2	8
21	Salmi, Ladoga		Western Russia	40.0		18.9	10.0	-11.2	8
22	Kirillov		Western Russia	27.9		19.7	10.8	-11.2	8
23	Valga		Estonia	28.8		18.5	9.6	-11.1	5,6
24	Kallaste, Saru		Estonia	38		19.4	10.5	-11.3	5,6
25	Mooste, Kaaru		Estonia	30.6		18.9	10.0	-11.8	5,6
26	Ihasalu		Estonia	41		20.3	11.4	-11.8	5,6
27	Koosa		Estonia	40.9		19.7	10.8	-11.3	5,6
29	Ikšķile, Ogre district		Latvia	40.9		20.8	11.9	-12.4	5, 6
30	Pļaviņas, Aizkraukle district		Latvia	27.9		18.6	9.7	-12.1	5, 6

28	Jaunpils, Tukums district	Latvia	40.7	21.1	12.2	-12.5	5, 6
31	Veselava, Cēsis district	Latvia	25.8	19.6	10.7	-12.7	5, 6
32	Jonava region, Turžėnų	Lithuania	21.4	20.6	11.7	-11.2	5,6
33	Kaunas region, river Jiesia 2	Lithuania	41.4	18.0	9.1	-11.7	5,6
34	Kaunas region, river Jiesia 3	Lithuania	42.3	20.8	11.9	-11.3	5,6
35	Telšiai region, Pilsūdai	Lithuania	33.7	19.2	10.3	-11.1	5,6
36	Skermentiskiu	Lithuania	?	21.2	12.3	-11.8	5,6
37	Kraków Spadzista (C2)	Poland	23.8	21.1	12.2	-10.9	5, 6
38	Kraków Spadzista (E)	Poland	24.7	21.4	12.5	-10.7	5, 6
39	Kraków Spadzista (F)	Poland	24.6	21.2	12.3	-11.3	5, 6
40	Kraków Zwierzyniec	Poland	?	21.5	12.6	-11.6	5, 6
	Kraków Zwierzyniec	Poland	22.8	21.6	12.7	-11.1	5, 6

Appendix A – Raw data used for comparison with the Krakow Spadzista Street (B) results

†: Teeth are labelled as M1 (1st milk tooth) to M6 (final adult tooth) after Haynes (1991), as there are no clear distinctions in proboscideans between deciduous and adult teeth.

*: Dates summarised from information given in cited publications

References: 1. = Tütken et al 2007; 2. = Genoni et al. 1998; 3. = Ayliffe et al. 1992; 4. Tütken et al. 2008; 5. Arppe and Karhu 2010; 6. Arppe 2009; 7. Ukkonen et al. 2007; 8. Arppe and Karhu 2006.

APPENDIX B: Calculation of errors

The $\delta^{18}O$ carbonate data were converted, where necessary, from the PDB isotopic scale to the VSMOW scale and then to a $\delta^{18}O$ phosphate value, a drinking water $\delta^{18}O$ value and finally to a temperature value using the following equations:

Equation 1: (Coplen, Kendall, & Hoppe, 1983)

$$\delta^{18}O_{VSMOW} = 1.03091\ \delta^{18}O_{PDB} + 30.91$$

Equation 2: (Iacumin et al. 1996)

$$\delta^{18}O_{phosphate} = 0.98\ (\pm 0.03)\ \delta^{18}O_{carbonate} - 8.5\ (\pm 0.18)$$

Equation 3: (Ayliffe, Lister, & Chivas, 1992)

$$\delta^{18}O_{enamel\ phosphate} = 0.94\ (\pm 0.10)\ \delta^{18}O_{drinking\ water} + 23.3\ (\pm\ 0.7)$$

Equation 4: (Rozanski, Araguás-Araguás, & Gonfiantini, 1992)

$$\delta^{18}O_{rainfall} = 0.59\ (\pm\ 0.08)\ T_{temperature\ average} - 14.24\ (\pm\ 0.5)$$

These data conversions are based on a linear equation form of Y = MX + B. For a given value of Y, the error (y) equals the sum of the errors in each of terms M (m), X (x) and B (b), and errors were carried forward at each conversion stage. Several of these equations were published without calculated errors on the slope coefficient (M) and y-axis intercept (B) terms. Least-squares regression analysis was used to calculate standard errors on these terms before using standard formula to sum the errors at each stage. Errors are reported to 1 significant figure throughout.

The following equation was used to calculate the carbonate $\delta^{18}O_{VSMOW}$ error:

$$y=M*x$$

where x = the measurement error on the mass spectrometer and M = 1.03091, the slope coefficient for Equation 1**.**

The following equation was used to calculate the phosphate $\delta^{18}O_{VSMOW}$ error:

$$\sqrt{(\mathrm{m}.(X - X_o))^2 + (x.M)^2 + (b)^2}$$

Where X_o = the mean of the values used to derive the equation. X_o is introduced in order to move the data used to generate the equation along the X-axis towards the origin, with the purpose of counteracting a lever effect resulting from the data lying at least 14‰ away from the y-axis. This has no effect on the r^2 value, the coefficient of the equation (M) or its error value (m), but alters the y-intercept (B) and its associated error (b), which is now much better constrained as it falls in the middle of the range of known values. The data used to generate $\delta^{18}O_{drinking\ water}$ values was also shifted along the X-axis for the same reason.

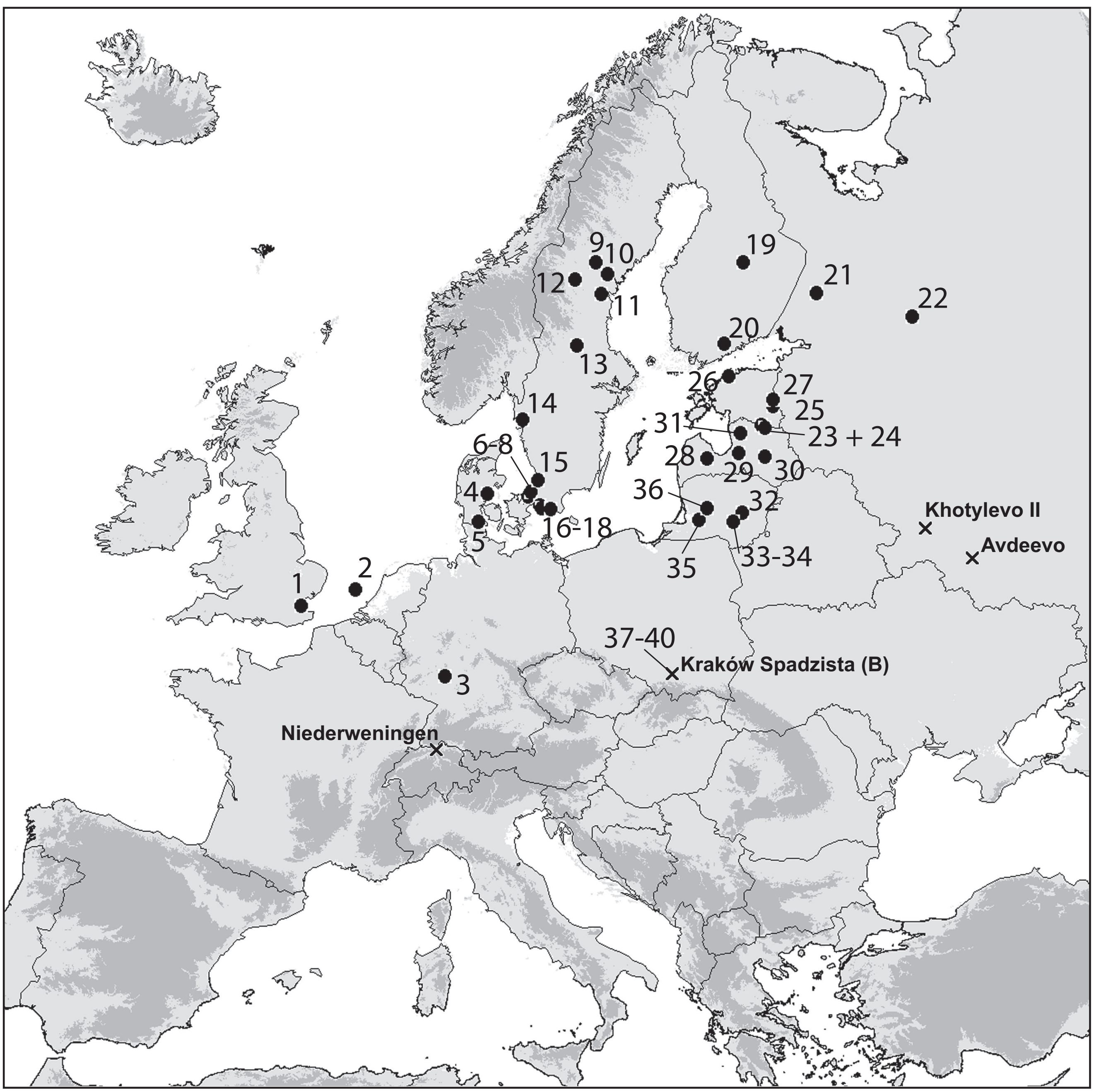
To calculate the $\delta^{18}O_{drinking\ water}$ and temperature values, equations 3 and 4 were rearranged:

$$(X - X_o) = \frac{Y - B}{M} \quad \text{and} \quad X = \frac{Y - B}{M} \quad \text{respectively.}$$

The following equation was used to calculate the $\delta^{18}O_{drinking\ water}$ and temperature errors:

$$\sqrt{(\frac{y}{M})^2 + (\frac{b}{M})^2 + (\frac{(Y - B).m}{M^2})^2}$$

Figure



1
2
3
4
5
6-8
9
10
11
12
13
14
15
16-18
19
20
21
22
23 + 24
25
26
27
28
29
30
31
32
33-34
35
36
37-40
Khotylevo II
Avdeevo
Kraków Spadzista (B)
Niederweningen

Figure 2 (colour for web)

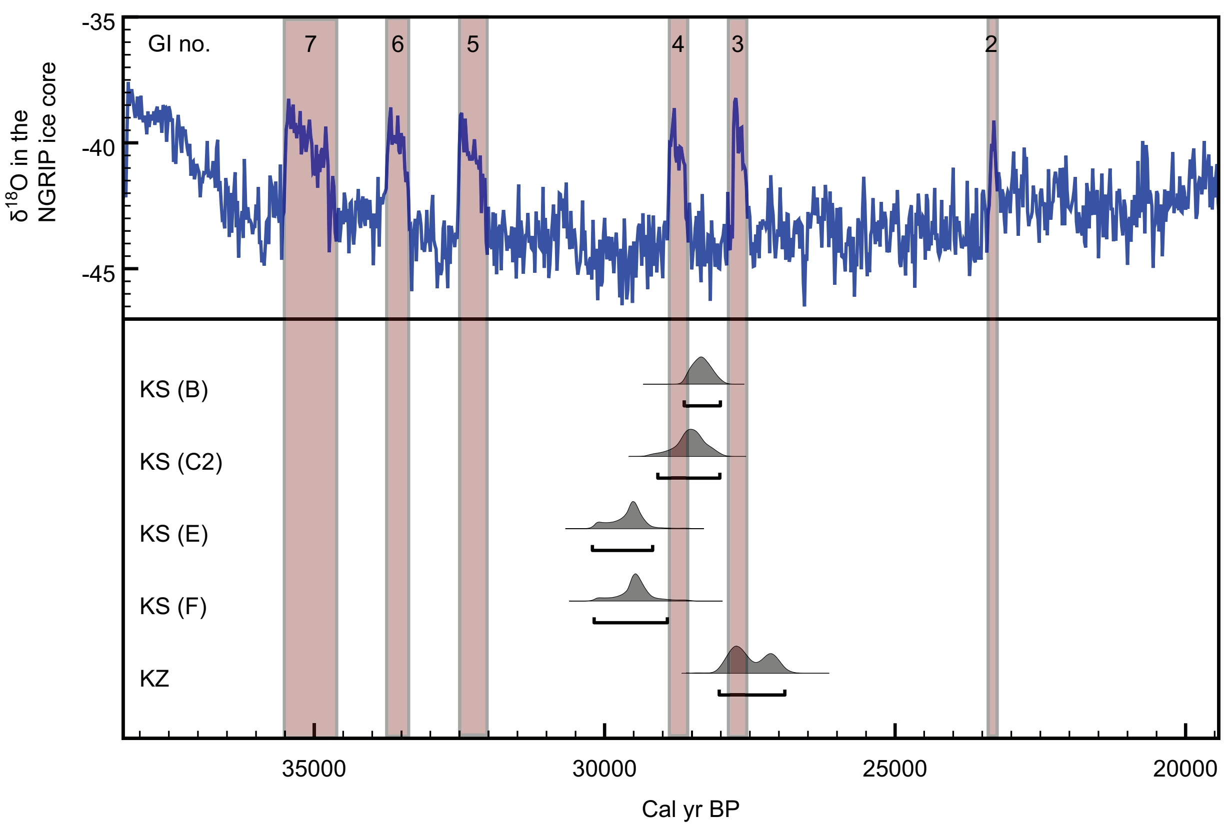


Figure 2 (greyscale for print)

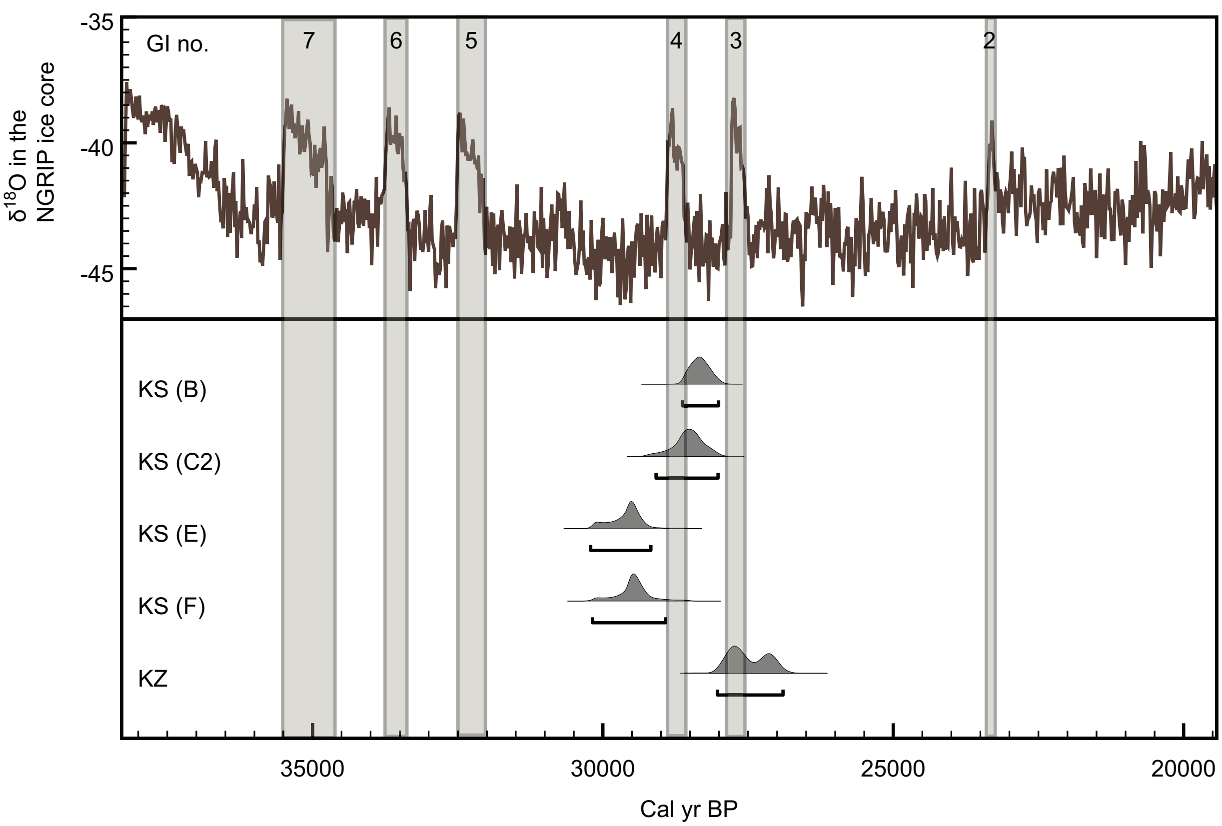


Figure 3

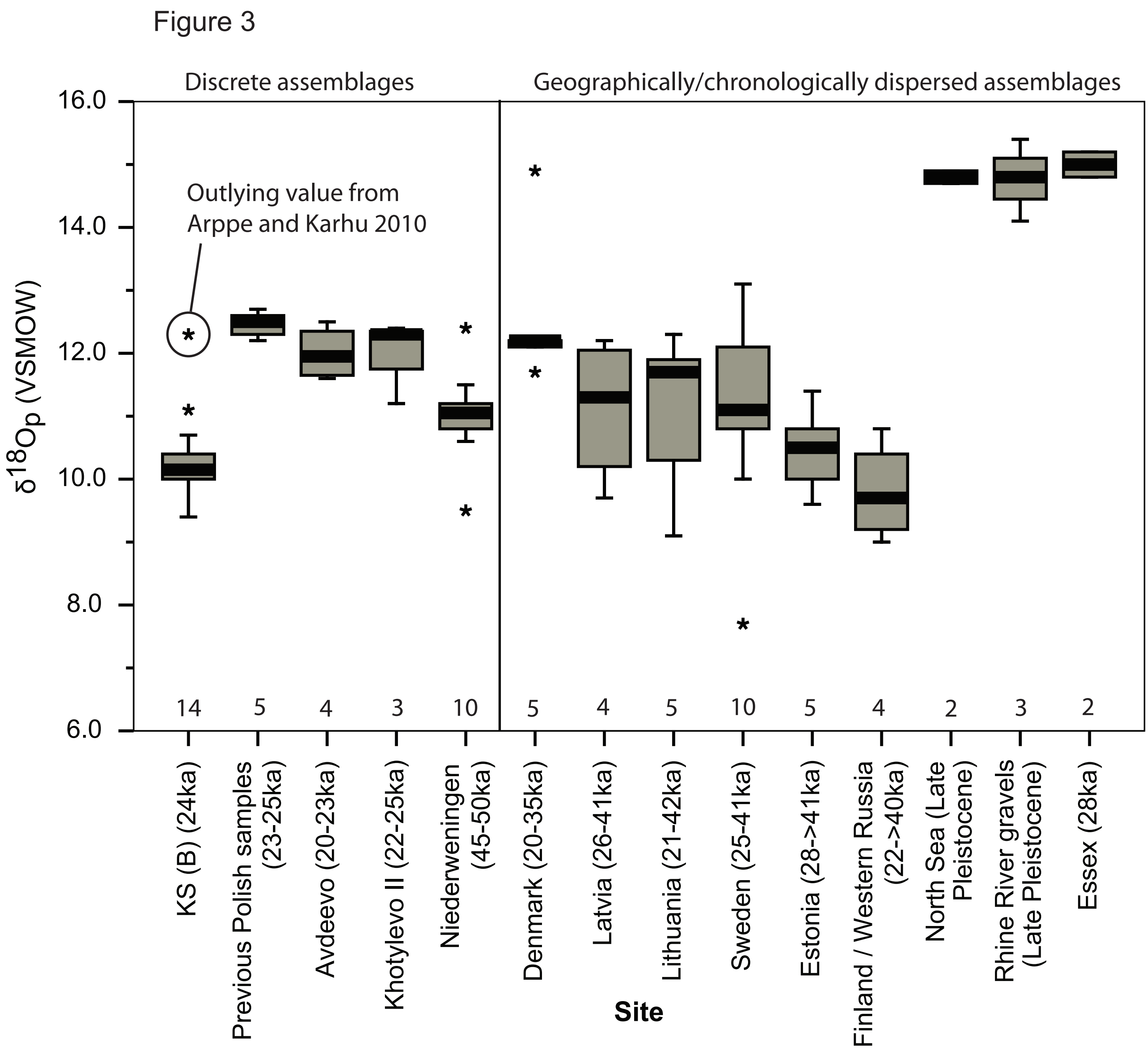


Figure 3
Discrete assemblages
Geographically/chronologically dispersed assemblages
Outlying value from
Arppe and Karhu 2010
δ18Op (VSMOW)
16.0
14.0
12.0
10.0
8.0
6.0
14
5
4
3
10
5
4
5
10
5
4
2
3
2
KS (B) (24ka)
Previous Polish samples (23-25ka)
Avdeevo (20-23ka)
Khotylevo II (22-25ka)
Niederweningen (45-50ka)
Denmark (20-35ka)
Latvia (26-41ka)
Lithuania (21-42ka)
Sweden (25-41ka)
Estonia (28->41ka)
Finland / Western Russia (22->40ka)
North Sea (Late Pleistocene)
Rhine River gravels (Late Pleistocene)
Essex (28ka)
Site

Figure 4

Figure 4

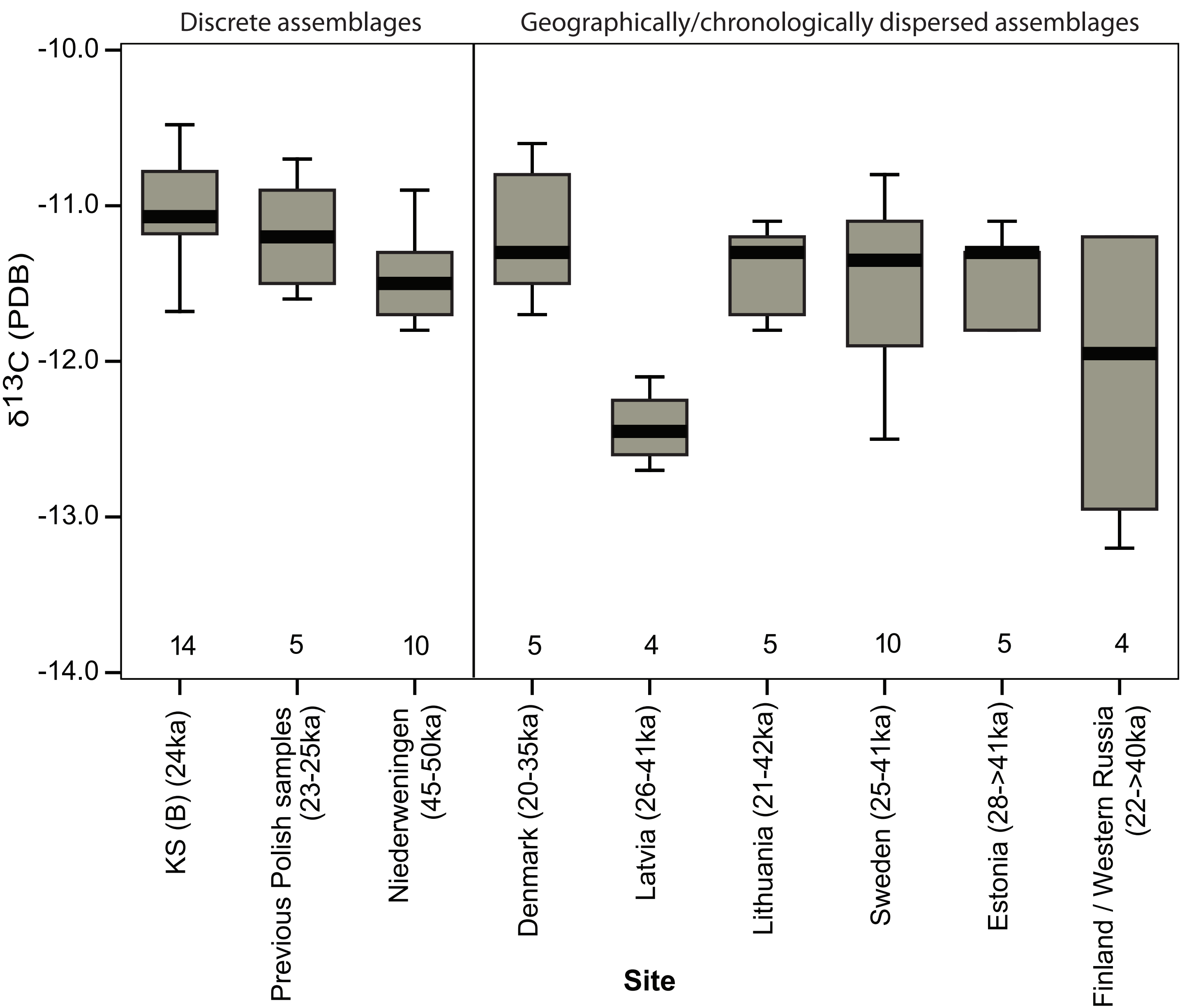


Figure 5 (colour for web)

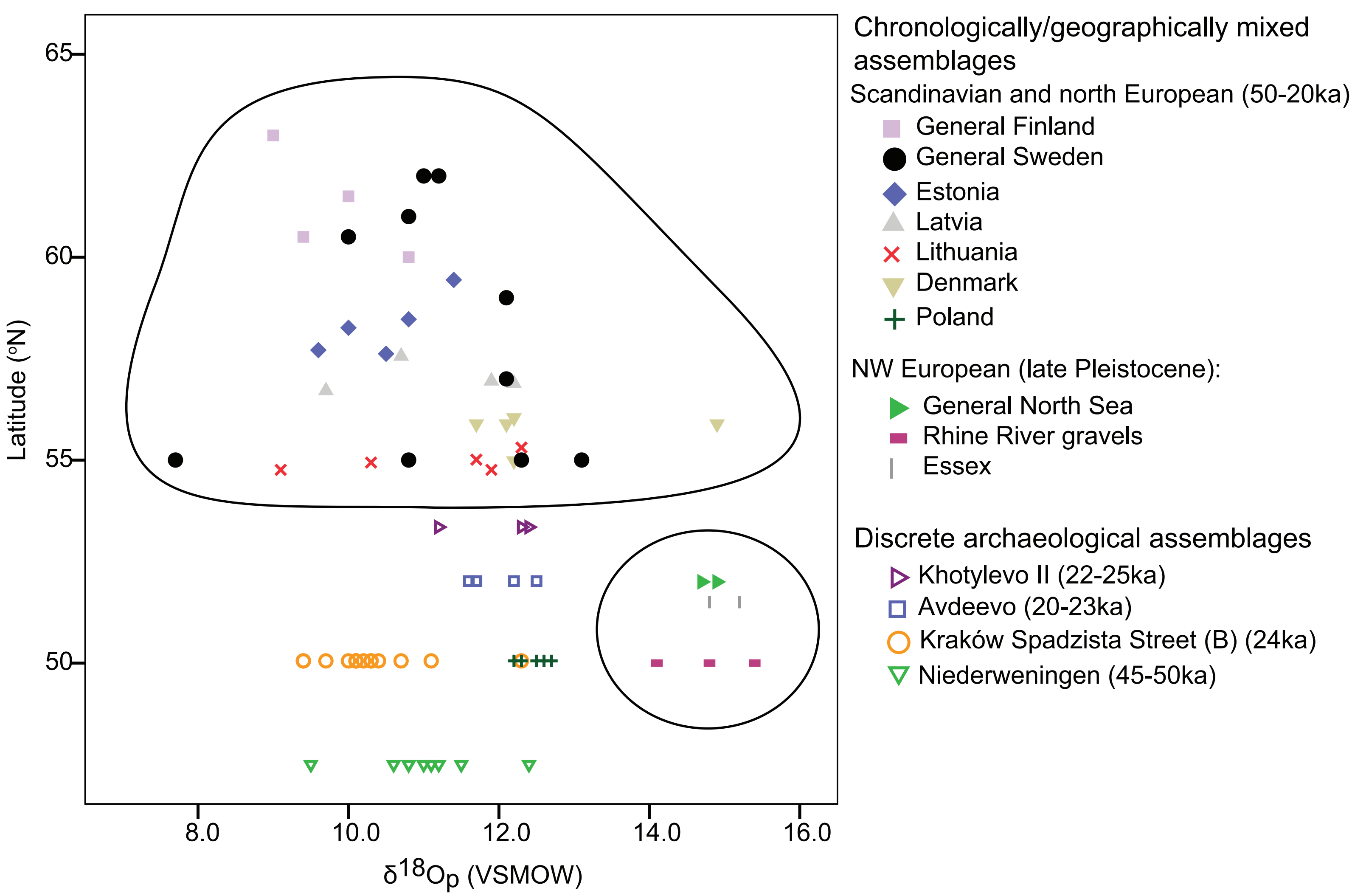


Figure 5 (greyscale for print)

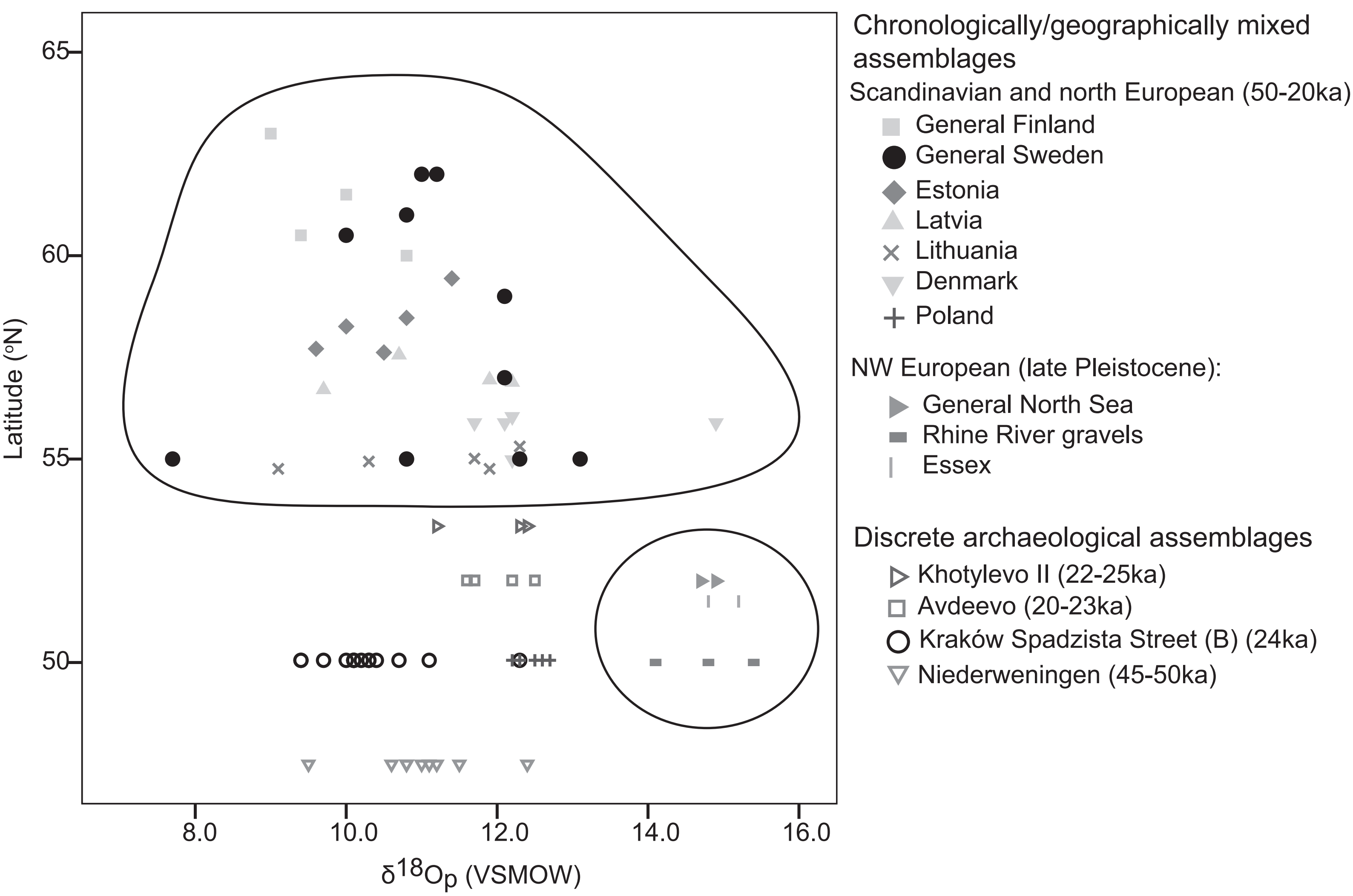


Table 1

Table 1 – Radiocarbon dates for sites in the Kraków Spadzista Street site complex and at Kraków Zwierzyniec. All samples are AMS dates unless otherwise stated. Calibrated using OxCal (Reimer et al. 2009).
Site code: KS = Kraków Spadzista Street sites B, C2, E and F; KZ = Kraków Zwierzyniec
†: 1 = Mammoth bone; 2 = Mammoth molar; 3 = Carbonised bone
*: Conventional radiocarbon date

Site code	Cat. No.	Uncalibrated		Calibrated		Sample type †	Notes/Bibliography
		^{14}C Date	1 S.D.	From	To		
KS (B)	GrN-6636*	23040	170	28464	26977	3	Wojtal and Sobczyk 2003
KS (B)	Poz-242	23020	180	28445	26960	1	Wojtal 2007
KS (B)	Poz-1248	23750	140	29050	28015	1	Wojtal 2007
KS (B)	Poz-1251	23770	160	29155	28046	1	Wojtal 2007
KS (B)	Poz-225	23980	280	29458	28190	1	Wojtal 2007
KS (B)	Poz-268	24000	300	29481	28176	1	Wojtal 2007
KS (B)	LuS 7417	23750	150	29085	28017	2	Arppe and Karhu 2010
KS (C2)	LuS-7418	23750	150	29085	28017	2	Arppe and Karhu 2010
KS (E)	LuS-7419	24700	180	30210	29173	2	Arppe and Karhu 2010
KS (F)	LuS-7420	24625	180	30180	28920	2	Arppe and Karhu 2010
KZ	LuS-7421	22800	150	28027	26899	2	Arppe and Karhu 2010

Table 2

Table 2 – $\delta^{18}O$ and $\delta^{13}C$ results from Kraków Spadzista Street (B).
†: Converted using equations 1 and 2.
‡: Converted using equation 3.
♦: Converted using equation 4.
*: Previously published sample for Kraków Spadzista Street (B) (Arppe and Karhu 2010)

Sample code	Element	Length enamel (mm)		$\delta^{18}O_c$ (PDB)	$\delta^{13}C$ (PDB)	$\delta^{18}O_p$ (VSMOW) †	$\delta^{18}O_{drinking\ water}$ ‡	Temperature (°C) ♦
KS-1	M6 Upper	106		-12.3	-11.2	9.4 (±0.3)	-14.8 (±1.1)	-1.0 (±2.0)
			Repeat	-11.8	-11.2			
			Difference	0.5	0.0			
KS-2	M6 Upper	51		-11.3	-10.7	10.4 (±0.3)	-13.8 (±1.0)	0.8 (±1.9)
KS-4	M5/M6 (upper left M6?)	117		-11.6	-11.2	10.1 (±0.3)	-14.0 (±1.0)	0.3 (±.9)
KS-5	M5/M6 Upper	71		-11.6	-11.1	10.1 (±0.3)	-14.1 (±1.0)	0.3 (±.9)
KS-6	M6 Upper	138		-11.5	-10.7	10.2 (±0.3)	-13.9 (±1.0)	0.5 (±1.9)
KS-7	M5/M6 Upper	80		-12.0	-11.1	9.7 (±0.3)	-14.5 (±1.1)	-0.4 (±2.0)
KS-8	M5 Upper right	63		-11.7	-11.0	10.0 (±0.3)	-14.2 (±1.0)	0.1 (±1.9)
KS-9	M5 Upper right	64		-11.4	-11.7	10.3 (±0.3)	-13.8 (±1.0)	0.7 (±1.9)
KS-10	M5 Upper left	57		-11.4	-11.1	10.3 (±0.3)	-13.9 (±1.0)	0.6 (±1.9)
KS-11	M6 Upper	89		-11.6	-10.9	10.1 (±0.3)	-14.1 (±1.0)	0.3 (±1.9)
KS-12	M6 Upper (right?)	78		-12.2	-11.5	9.4 (±0.3)	-14.7 (±1.1)	-0.8 (±2.0)
KS-13	M5/M6 Upper	65		-11.0	-10.5	10.7 (±0.3)	-13.4 (±1.0)	1.5 (±1.8)
			Repeat	-10.9	-10.6			
			Difference	0.1	-0.1			
KS-14	M5 Upper right	51		-10.6	-10.8	11.1 (±0.3)	-13.0 (±0.9)	2.1 (±1.8)
			Repeat	-10.7	-10.7			
			Difference	-0.1	0.1			
LuS 7417 *	?	15-20		--	-11.5	12.3 (±0.2)	-11.7 (±0.8)	4.3 (±1.7)

Table 3

Table 3 - Summary of woolly mammoth oxygen isotopic data available for Europe. Data based on carbonate results where possible, converted to phosphate values relative to VSMOW using Equations 1 and 2. Data based on phosphate results are indicated in the 'Pre-treatment' column. Raw data given in Appendix A.

†: Dates taken from cited publications unless otherwise stated

‡: Only samples of pre-LGM age were included from the cited references, falling within the age range given.

*: δ13C data taken from Arppe 2009.

A - Abramova et al. 2001

1. This study - Sodium hypochlorite (24hrs), 0.1M acetic acid (4hrs)
2. Sodium hypochlorite (3%) + sodium hydroxide solution (1%) (24hrs), 1M acetic acid-calcium acetate buffer (pH 4.75) (24hrs)
3. Sodium hypochlorite (24hrs), 1M acetic acid-calcium acetate buffer (pH 4.75) (24hrs)
4. Sodium hypochlorite (20hrs), 1M acetic acid-calcium acetate buffer (pH 4.75) (20hrs)

P1. Phosphate prep (fluorination of Ag3PO4)

P2. Phosphate prep (modified silica tube graphite reduction)

P3. Phosphate prep (BiPO4 technique)

	Converted $\delta^{18}O_{phosphate}$ (VSMOW)				$\delta^{13}C$ (PDB)				Provenance and age †	Pre-treatment	Reference
	N	Mean	Std Deviation	Range	N	Mean	Std Deviation	Range			
KS (B)	13	10.1	0.5	1.7	13	-11.0	0.3	1.2	23-24ka	1	This study
KS (B) inc. previously published sample	14	10.3	0.7	2.9	14	-11.3	0.3	1.2	23-24ka	1 + 2	This study; Arppe and Karhu 2010*
Single results from Poland											
KS (B)	1	12.3			1	-11.5			Single sample, 24ka	2	Arppe and Karhu 2010*
KS (C2)	1	12.2			1	-10.9			Single sample, 24ka	2	Arppe and Karhu 2010*
KS (E)	1	12.5			1	-10.7			Single sample, 25ka	2	Arppe and Karhu 2010*
KS (F)	1	12.3			1	-11.3			Single sample, 25ka	2	Arppe and Karhu 2010*
KZ	1	12.6			1	-11.6			Single sample, no date	2	Arppe and Karhu 2010*
KZ	1	12.7			1	-11.1			Single sample, 23ka	2	Arppe and Karhu 2010*
Mean values	6	12.4	0.2	0.5	6	-11.2	0.3	0.9			
Discrete assemblages											
Niederweningen	10	11.0	0.7	2.9	10	-11.5	0.3	0.9	Short time interval, Interstadial 45-50ka	3	Tütken et al. 2007
Avdeevo	4	12.0	0.4	0.9					Short event between 20-23ka[A]	Phosphate (fluorination of Ag3PO4)	Genoni et al. 1998
Khotylevo II	3	12.0	0.7	1.2					Short event between 22-25ka[A]	Phosphate (fluorination of Ag3PO4)	Genoni et al. 1998
Geographically and/or temporally dispersed assemblages											
General Finland + western Russia	4	9.8	0.8	1.8					Geographically dispersed, 22->40ka ‡	2	Arppe and Karhu 2006
General Estonia	5	10.5	0.7	1.8	5	-11.5	0.3	0.7	Geographically dispersed, 28->41ka ‡	2	Arppe and Karhu 2010*
General Lithuania	5	11.1	1.3	3.2	5	-11.4	0.3	0.7	Geographically dispersed, 21-42ka ‡	2	Arppe and Karhu 2010*
General Sweden	10	11.1	1.5	5.4	10	-11.5	0.5	1.7	Geographically dispersed, 25-41ka ‡	4	Ukkonen et al. 2007
General Latvia	4	11.1	1.2	2.5	4	-12.4	0.3	0.6	Geographically dispersed, 26-41ka ‡	2	Arppe and Karhu 2010*
General Denmark	5	12.6	1.3	3.2	5	-11.2	0.5	1.1	Geographically dispersed, 20-35ka ‡	2	Arppe and Karhu 2010*
Rhine River, Germany	3	14.8	0.7	1.3					Mixed, Late Pleistocene	Phosphate (modified silica tube graphite reduction)	Tütken et al. 2008
General North Sea	2	14.8	0.1	0.2					Mixed, Late Pleistocene	Phosphate (modified silica tube graphite reduction)	Tütken et al. 2008
Lea Valley, England	2	15.0	0.3	0.4					Geographically dispersed, 28ka ‡	Phosphate (BiPO4 technique)	Ayliffe et al. 1992