

Implications for the Late Pleistocene climate in Finland and adjacent areas from the isotopic composition of mammoth skeletal remains

Laura M. Arppe*, Juha A. Karhu

Department of Geology, P.O. Box 64, FIN-00014 University of Helsinki, Finland

Received 22 February 2005; received in revised form 1 July 2005; accepted 26 August 2005

Abstract

Nine samples of subfossil bone and teeth remains from woolly mammoth (*Mammuthus primigenius*) discovered in Finland, Russian Karelia and Western Russia were analyzed for the oxygen isotope composition of the phosphate fraction and the carbon and oxygen isotope composition of the carbonate fraction in skeletal apatite. The samples have been radiocarbon dated in previous studies and are of late Middle Weichselian to Late Weichselian age. The preservation of the samples was tested analyzing the chemical composition and checking the isotopic equilibrium between the phosphate and carbonate components in skeletal apatite. According to these tests, five out of the nine samples were determined to have retained their original isotopic composition. These samples were used to estimate Late Pleistocene climatic conditions in Finland and neighboring areas. Based on the best-preserved enamel samples, the isotopic composition of oxygen in Late Pleistocene precipitation was 1–3‰ lower than that in the mean annual precipitation in southern and central Finland today. Using the relationship between the isotopic composition of precipitation and the ambient temperature, it can be estimated that the mean temperatures during the Middle Weichselian ice-free period were 2–6 °C lower compared to the present-day values.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Oxygen isotopes; Mammoth; Teeth; Enamel; Finland; Paleoclimatology

1. Introduction

The use of stable isotopes has proven to be one of the most effective methods in reconstructing paleoenvironmental conditions. On land, isotopic reconstruction of past climatic conditions is, however, complicated by the lack of suitable study material. The oxygen isotope composition of the mineral component of vertebrate skeletons, carbonate-hydroxyapatite $\text{Ca}_9[(\text{PO}_4)_{4.5}(\text{CO}_3)_{1.5}](\text{OH})_{1.5}$ (Driessens and Verbeeck, 1990) is a potential tool, which has been successfully used in paleoclimato-

logical reconstructions of continental climates (e.g. Ayliffe et al., 1992; Bryant et al., 1994, 1996b; Fricke et al., 1995; Genoni et al., 1998; Iacumin et al., 2004; Iacumin and Longinelli, 2002; Longinelli et al., 2003; Reinhard et al., 1996). Land mammals precipitate their skeletal parts at a constant temperature of ~37 °C. The oxygen isotope composition of the bioapatite is thus dependent only on the isotopic composition of the animal's body water (Longinelli, 1984; Luz et al., 1984). The $\delta^{18}\text{O}$ value of body water, in turn, is related to the isotopic composition of ingested environmental waters, which usually correspond to the mean $\delta^{18}\text{O}$ value in the regional precipitation. The isotopic composition of oxygen in meteoric waters correlates with the regional mean annual temperatures (Dansgaard, 1964). It follows that

* Corresponding author. Fax: +358 9 191 50826.

E-mail address: laura.arppe@helsinki.fi (L.M. Arppe).

the oxygen isotope composition of fossil skeletal material contains information of past atmospheric temperatures in terrestrial environments. Of all skeletal components, tooth enamel is generally considered to be most resistant to post-depositional alteration, and hence is the preferred material for isotopic investigations (e.g. Ayliffe et al., 1992, 1994; Bryant et al., 1994, 1996b; Koch et al., 1997; Lee-Thorp and Sponheimer, 2003; Zazzo et al., 2004).

According to a previously widely accepted glacial history of Scandinavia, it was thought that Finland was covered by the Scandinavian Ice Sheet throughout the Middle and Late Weichselian (e.g. Andersen and Mangerud, 1989). Recent interpretations based on new radiocarbon dating results revised this view (Ukkonen et al., 1999; Lunkka et al., 2001). Data from mammoth finds reported by Ukkonen et al. (1999) from different parts of Finland suggested that the southeastern parts of Fennoscandia remained ice-free for a period of at least 10 000 years between ca. 37 and 26 ka. Summarizing the findings of the extensive QUEEN program, Hubberten et al. (2004) concluded that the time from 30 ka to the Last Glacial Maximum at 20–15 ka was a period of progressive cooling in Scandinavia and elsewhere in the Eurasian Arctic. During this period, the growth rate of the Scandinavian Ice Sheet was very rapid. The ice front advanced from the Gulf of Bothnia to the Last Glacial Maximum position, some 1000 km southeast in

the northwestern Russian Plain, in only 7000 years (Lunkka et al., 2001).

Due to poor preservation of skeletal material in acid soil, only a few stray finds of terrestrial mammals have been made in Finland. A total of nine subfossil mammoth bones and teeth have been discovered, described in detail by Ukkonen et al. (2003). All finds have been radiocarbon dated in previous studies, and they range in age from >45 800 to 18 700 cal BP (>40 000 to 15 910 BP) (Table 1).

The aim of this study is to recover the climatic signal recorded in the oxygen isotope composition of skeletal remains discovered in Finland and adjacent areas. In order to evaluate the extent of diagenetic alteration, the concentrations of selected trace elements were measured. Oxygen isotope ratios were determined on carbonate and phosphate fractions in carbonate-hydroxyapatite. Comparison of the isotope records in these structural components offers an additional measure of the preservation of the isotope signal (Bryant et al., 1996a; Iacumin et al., 1996a).

2. Materials and methods

Five of the nine subfossil mammoth specimens were available for isotopic analysis. In addition, four other mammoth samples from the Russian Karelia and western Russia were investigated. The find localities are

Table 1
Sample description and isotopic results

Sample	Type	Find locality	¹⁴ C age (years BP ¹)	Calibrated age (years BP ²)	δ ¹⁸ O _P (‰)	δ ¹⁸ O _C (‰)	δ ¹³ C _C (‰)	δ ¹³ C _{collagen} (‰) ³	δ ¹⁸ O _W (‰) ⁴
<i>Enamel</i>									
M-01	Molar	Nilsia, Syväri	22 420 ± 315 ^a	26 400 ± 360	9.0	17.9	−12.7	−21.4	−15.3
M-02	Molar	Salmi, Ladoga	>40 000 ^b	>45 800	10.0	18.9	−11.2	−20.5	−14.2
M-03	Premolar	Helsinki, Töölö	23 340 ± 350 ^a	27 500 ± 400	9.9	18.3	−13.2	−20.7	−14.2
M-07	Molar	Kirillov	27 915 ± 575 ^c	32 600 ± 640	9.6	19.7	−11.2		−14.6
<i>Bone</i>									
M-04	Humerus	Helsinki, Herttoniemi	15 910 ± 150 ^a	18 700 ± 180	14.3	22.1	−11.0	−21.3	−9.6
M-05	Femur	Lohtaja	24 450 ± 385 ^a	28 700 ± 440	10.5	16.1	−13.4	−21.6	
<i>Dentine</i>									
M-06	Tusk	Haapajärvi	28 740 ± 670 ^a	33 600 ± 750	11.9	21.0	−10.0	−29.1	
M-08	Tusk	Kostamuksha	25 990 ± 470 ^d	30 500 ± 530	12.2	16.9	−11.0		
M-09	Tusk	Kolodozero	>40 000 ^e	>45 800	12.1	18.2	−9.1		

Isotope values are given relative to VPDB (δ¹³C_C, δ¹³C_{collagen}) and VSMOW (δ¹⁸O_P, δ¹⁸O_C, δ¹⁸O_W).

¹ ¹⁴C ages: (a) Ukkonen et al. (1999), (b) Lõugas et al. (2002); (c) Saarnisto and Lunkka, unpublished; (d) M. Saarnisto, personal communication, 2003; (e) I. Demidov, personal communication, 2003.

² ¹⁴C ages were calibrated according to Bard (1998).

³ The carbon isotope composition of collagen (δ¹³C_{collagen}) with permission of Eloni Sonninen, the Dating Laboratory of the Finnish Museum of Natural History, University of Helsinki.

⁴ The mean annual oxygen isotope composition of environmental water (δ¹⁸O_W) is only given for unaltered samples.

shown in Fig. 1. A short description of the samples and the radiocarbon ages are given in Table 1.

The samples were drilled using a 2-mm diamond drill and ground in an agate mortar. Before sampling, the uppermost surface of the bone or tooth was removed.

For the analysis of the isotopic composition of oxygen in phosphate, the silver phosphate method was applied. The chemical procedure followed that of O'Neil et al. (1994) and Stephan (2000) with some modifications. To remove organic contaminants, the samples were treated with 3% NaOCl+NaOH solution for 24 h and rinsed with deionized water. The procedure was repeated twice for bone and dentine samples. The resulting sample powder was dissolved in 1 M HNO₃. Calcium and other interfering ions were removed using cation exchange chromatography. The phosphate ion was precipitated as Ag₃PO₄. The precipitate was reduced by graphite at 1340 °C and the resulting CO₂ was used for isotope determinations (O'Neil et al., 1994). For the

isotopic analysis of the carbonate fraction, the sample powders were pretreated following the method described by Bocherens et al. (1996a). The powders were soaked for 24 h in 3% NaOCl+NaOH solution to remove organic matter and rinsed with deionized water. In order to remove secondary carbonates, the powders were treated with a 1 M acetic acid–Ca acetate buffer solution for another 24 h. The powders were then reacted with anhydrous phosphoric acid at 100 °C with a reaction time of 1 h.

The isotope ratios of oxygen and carbon were measured at the Geological Survey of Finland, on a Finnigan MAT 251 mass spectrometer. The external precision based on multiple sample measurements was better than 0.1‰ for δ¹³C, 0.2‰ for δ¹⁸O_C and 0.2‰ for δ¹⁸O_P. Sixteen repeated analyses of the phosphate rock standard NBS-120b have yielded a δ¹⁸O_P value of 22.4 ± 0.3‰ (SMOW). The phosphoric acid fractionation factor of Swart et al. (1991) for calcite was used to

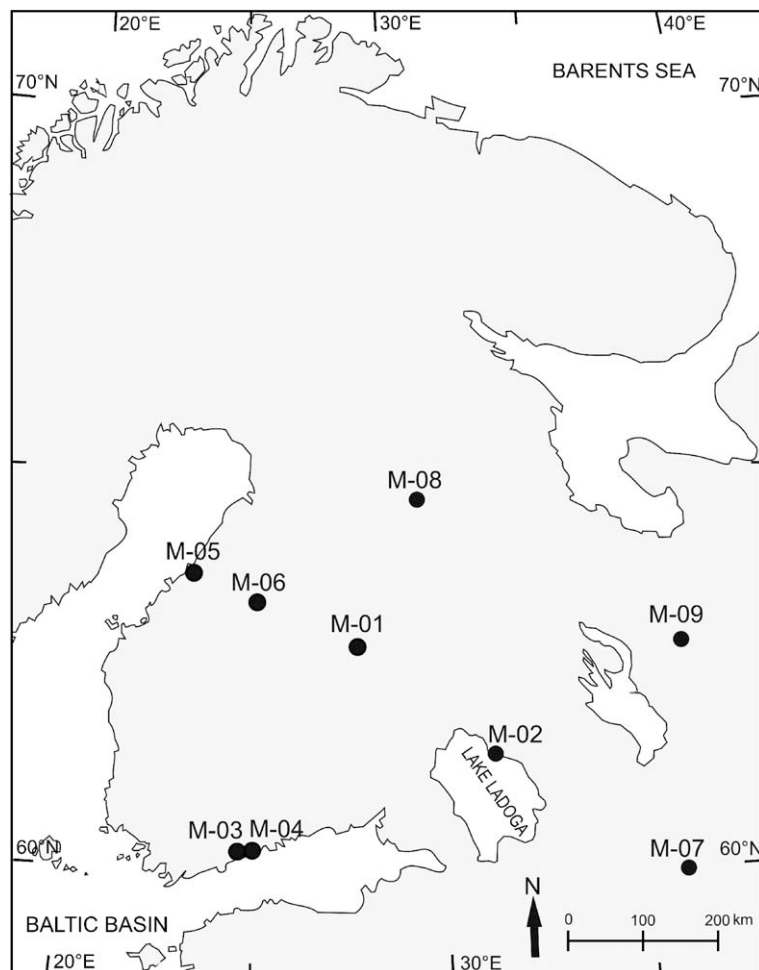


Fig. 1. Map of the mammoth find localities in Finland, Russian Karelia and Western Russia. Modified from Ukkonen et al. (1999).

correct for the effects of the acid reaction in the analysis of the carbonate fraction.

The contents Al, Ba, Cu, Fe, Mn, Si and Sr were determined using ICP-AES. For analysis, the sample powders were dissolved in 3 ml of concentrated HNO₃. The insoluble fractions were removed by centrifugation. After adding 2 ml of concentrated HNO₃, the solution was diluted to 50 ml.

The distribution of Fe and Mn in enamel samples was investigated using a scanning electron microprobe. Semiquantitative analyses were performed with a JEOL JXA-8600 instrument at the Department of Geology, University of Helsinki. Spot analyses were collected on carbon coated samples in EDS mode with an accelerating voltage of 15 keV. The beam current was 1 nA and the diameter 1 µm. The count time for one measurement was 100 effective seconds.

3. Results

The oxygen isotope composition of the phosphate fraction ($\delta^{18}\text{O}_\text{P}$) and the carbon and oxygen isotope compositions of the carbonate fraction ($\delta^{13}\text{C}_\text{C}$, $\delta^{18}\text{O}_\text{C}$) are given in Table 1. The $\delta^{18}\text{O}_\text{P}$ values range from 9.0‰ to 14.3‰. The total span of the values is very similar to that obtained from mammoth remains from Southern Siberia, Russia and Ukraine by Genoni et al. (1998). The enamel samples form a tight group with all $\delta^{18}\text{O}_\text{P}$ values falling between 9‰ and 10‰, whereas the bone and dentine samples yielded more positive values. Sample M-06, the humerus from Herttoniemi, Helsinki, yielded an unusually high $\delta^{18}\text{O}_\text{P}$ value of 14.3‰. The range of $\delta^{18}\text{O}_\text{C}$ is similar to that of $\delta^{18}\text{O}_\text{P}$, but shifted to higher values by 7–8‰.

Table 2
Analyses of mammoth skeletal remains (ppm)

	Al	Ba	Cu	Fe	Mn	Si	Sr
<i>Enamel</i>							
M-01	33	31	0.4	641	349	62	96
M-02	33	66	0.3	5089	120	77	98
M-03	450	113	34	4842	563	450	225
M-07	77	36	3	92	51	235	72
<i>Bone</i>							
M-04	2200	526	8.6	33,077	1345	1834	208
M-05	260	416	2	11,435	4314	1351	312
<i>Dentine</i>							
M-06	<110	495	25	22,400	3380	–	144
M-08	81	32	1.6	16	1.4	108	108
M-09	<53	106	<0.5	27	5.3	<53	69

The samples were analyzed by ICP-AES at the Department of Geology, University of Helsinki.

The $\delta^{13}\text{C}_\text{C}$ values vary from –13.4‰ to –9.1‰. These values are typical of C3-feeders and are in accordance with values measured from Siberian, Ukrainian and Russian mammoths by Iacumin et al. (2000). For comparison, the $\delta^{13}\text{C}_\text{collagen}$ values of the Finnish specimens are also reported in Table 1. These data were kindly provided by the Dating Laboratory of the Finnish Museum of Natural History, University of Helsinki. Excepting sample M-06, all specimens display values comparable to those obtained by Iacumin et al. (2000), reflecting C-3 plant based diets. The collagen fraction in sample M-06 is highly depleted in ¹³C, having a carbon isotope value of –29.1‰.

The contents Al, Ba, Cu, Fe, Mn, Si and Sr are given in Table 2.

4. Discussion

4.1. Diagenetic alteration

It has been suggested that increasing concentrations of rare earth elements, U, F and possibly Sr in fossil bones reflect diagenetic chemical alteration (Kohn et al., 1999). If this is observed, also isotopic signatures may be altered and, thus, the environmental signal from the isotopes could be biased.

Kohn et al. (1999) reported Fe and Mn concentrations in modern enamel falling below 26 ppm and 19 ppm, respectively. The skeletal remains analyzed in this study are characterized by significant increases in the Fe and Mn contents in most samples (Table 2). Especially, two bone specimens (M-04 and M-05) and one dentine specimen (M-06) display dramatic increases in their Fe and Mn contents, which are as much as several orders of magnitude higher compared to the other samples. Also the concentrations of Si, Ba and Al in the bone samples (M-04, M-05) are distinctively higher than those observed in most dentine and enamel samples. These changes are likely due to precipitation of secondary Fe–Mn–Ba-bearing oxides and oxyhydroxides and the presence of clay minerals (Kohn et al., 1999; Elorza et al., 1999). Although no conclusion of isotopic alteration can be drawn from the high concentrations of these elements, they suggest, however, that some secondary precipitation of diagenetic minerals has occurred in all samples and the bone and dentine samples M-04, M-05 and M-06 are strongly affected.

The origin of the high concentrations of Fe and Mn in enamel and particularly in samples M-02 and M-03, was investigated further using a scanning electron microprobe (SEM). The outer surface of the lamellae are typically covered by a dark colored coating. In addition,

cracks filled by dark colored material do occur. Fig. 2a presents a cross section of an enamel lamella from sample M-02, and Fig. 2b shows a back-scattered electron (BSE) image of the same cross section. SEM-spot analyses collected from dark coatings showed a high Fe content of 28–62% and a Mn content of 0.2% to 0.7%. Analyses collected from the inner part of the lamellae showed no measurable Fe or Mn.

It can be concluded that the high concentrations of Fe and Mn do not represent pervasive alteration of enamel. The samples were probably exposed to diagenetic fluids after deposition, leading to precipitation of Fe–Mn coatings.

The strontium concentrations (Table 2) are below the values for modern herbivore enamel (Kohn et al., 1999) and are not indicative of chemical alteration of the apatite crystals.

The oxygen isotope fractionation between $\delta^{18}\text{O}_\text{P}$ and $\delta^{18}\text{O}_\text{C}$ of skeletal apatite has been used successfully to distinguish isotopically altered samples (Genoni et al., 1998; Iacumin et al., 1996a,b; Lécuyer et al., 1998). At a constant body temperature, the fractionation of oxygen isotopes between phosphate and carbonate components of skeletal apatite can be expected to be invariable. Fig. 3 displays the $\delta^{18}\text{O}_\text{P}$ – $\delta^{18}\text{O}_\text{C}$ equilibrium fractionation line ($\delta^{18}\text{O}_\text{P}=0.98 \cdot \delta^{18}\text{O}_\text{C} - 8.5$; Iacumin et al., 1996a) compared to the samples analyzed in this study. According to this relationship, $\Delta^{18}\text{O}_{\text{C-P}}$ ($\delta^{18}\text{O}_\text{C}-\delta^{18}\text{O}_\text{P}$) in well-preserved teeth and bones can be expected to remain close to 8.5‰. All enamel samples (M-01, M-02, M-03, M-07) lie close to the equilibrium fractionation line and their isotope systematics seem to be well preserved. In spite of the high Fe and Mn contents, the humerus sample from Herttoniemi (M-04) has $\delta^{18}\text{O}_\text{P}$ and $\delta^{18}\text{O}_\text{C}$ falling close to the equi-

librium fractionation (Fig. 3) with $\Delta^{18}\text{O}_{\text{C-P}}$ at 7.8‰. This suggests the possibility that the oxygen isotope system in this bone sample may have been preserved unchanged.

The bone and dentine samples M-05, M-06, M-08 and M-09 have $\Delta^{18}\text{O}_{\text{C-P}}$ ranging from 4.6‰ to 6.2‰. Judging from the large difference between these and the expected $\Delta^{18}\text{O}_{\text{C-P}}$, the samples are in isotopic disequilibrium. On the $\delta^{18}\text{O}_\text{C}$ – $\delta^{18}\text{O}_\text{P}$ graph (Fig. 3), the sample points lie left from the equilibrium fractionation line. This indicates that either the oxygen isotope composition of phosphate has shifted to more positive values or that of the carbonate component has decreased as a result of diagenetic alteration, or both components have changed.

Structural carbonate is considered to be less resistant to post-depositional alteration than phosphate (Iacumin et al., 1996a; Land et al., 1980; Nelson et al., 1986; Schoeninger and DeNiro, 1982) and therefore, it is possible that low $\Delta^{18}\text{O}_{\text{C-P}}$ in these samples could be caused by secondary changes in the isotope ratios of structural carbonate in apatite. The well preserved enamel samples, however, all exhibit lower $\delta^{18}\text{O}_\text{P}$ values compared to bone and dentine (Table 1), suggesting that the $\delta^{18}\text{O}_\text{P}$ values of bone and dentine may have increased as a result of diagenetic alteration. The situation is quite unusual, since diagenetic processes in natural environments usually tend to lower the $\delta^{18}\text{O}$ values of deposited material. At low temperatures, however, the fractionation of oxygen isotopes between phosphate and water is sufficiently high to increase the isotopic composition of reprecipitated phosphate, assuming isotopic equilibrium between phosphate and local groundwater. Using fractionation factors of Longinelli and Nuti (1973) and the isotopic composition of local groundwaters in southern Finland (–12‰), $\delta^{18}\text{O}_\text{P}$ values as high as 13.5‰ can be

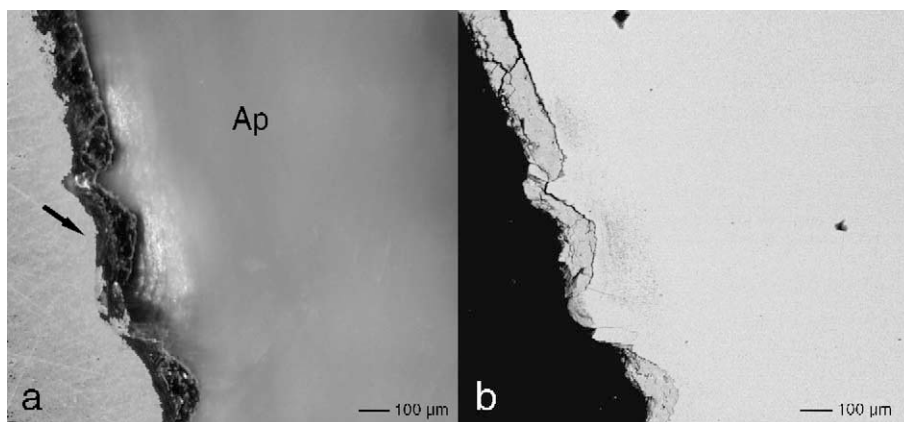


Fig. 2. (a) Cross section of an enamel lamella from sample M-02 seen by an optical microscope. Dark, Fe–Mn-rich coating is indicated by an arrow, Ap=apatite. (b) BSE image of the cross section. Fe–Mn coatings are visible as darker areas.

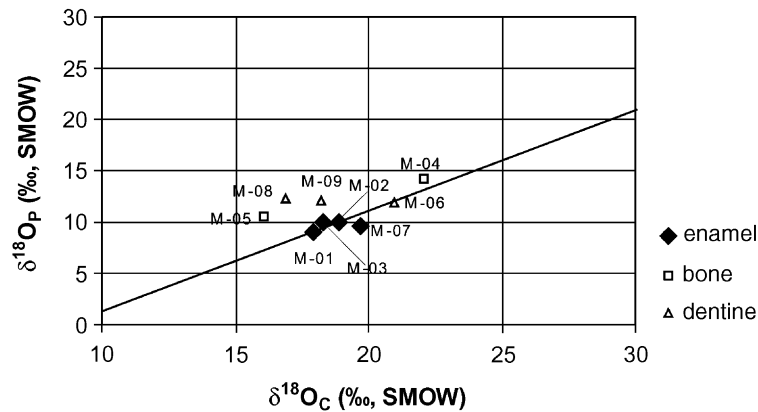


Fig. 3. Comparison of the oxygen isotope composition of skeletal carbonate with that of phosphate. The line ($\delta^{18}\text{O}_\text{P} = 0.98 \cdot \delta^{18}\text{O}_\text{C} - 8.5$) represents isotopic equilibrium between $\delta^{18}\text{O}_\text{C}$ and $\delta^{18}\text{O}_\text{P}$ according to Iacumin et al. (1996a).

expected to be observed in reprecipitated phosphates, equilibrated with environmental waters.

Zazzo et al. (2004) presented evidence for selective alteration of the carbonate and phosphate components pending on the mechanism of diagenetic reactions. During microbially mediated reactions, the exchange of oxygen isotopes between phosphate and water is at least 2 to 15 times faster than that between carbonate and water. According to their experiments, bone is particularly susceptible to microbially induced alteration, whereas enamel is affected in a lesser extent. Thus, the shift to more positive $\delta^{18}\text{O}_\text{P}$ values in the bone and dentine samples might be explained as a result of microbially mediated re-equilibration with groundwaters.

Also the dentine sample M-06 from Haapajärvi appears to be close to isotopic equilibrium. This may however be fortuitous, as there are reasons to believe that the sample is highly altered. The piece of tusk is in poor condition and severely degraded. It is fractured, brittle and has a yellow-greenish cover in parts of the bone. Fe and Mn contents in this sample are extremely high, 2.24% and 3380 ppm, respectively. In addition, the sample has an unusually low $\delta^{13}\text{C}_\text{collagen}$ value of -29.1‰ (Table 1). This value is strongly depleted in ^{13}C compared to all other collagen analyses given in this study and to those reported by Iacumin et al. (2000) and Bocherens et al. (1996b). The carbon isotope fractionation between collagen and the mineral component of skeletal apatite should be about 8‰ (Sul-Sullivan and Krueger, 1981) and for natural diets it may vary between 7‰ and 10‰ (e.g. Lee-Thorp et al., 1989). For sample M-06, the fractionation between collagen and structural carbonate is 19.1‰ , suggesting isotopic alteration.

Based on $\delta^{18}\text{O}_\text{C}$ and $\delta^{18}\text{O}_\text{P}$ fractionation patterns, the enamel samples are interpreted to have retained

their primary isotopic signal, and they are used to estimate Late Pleistocene climatic conditions in eastern Scandinavia and adjacent areas. In contrast, all bone and dentine samples, excepting M-04, show evidence of extensive diagenetic secondary crystallization and isotopic re-equilibration. The bone sample M-04 has $\Delta^{18}\text{O}_\text{C-P}$ falling close to the equilibrium value and the initial isotope ratios may have been preserved in this sample.

4.2. Environmental record in oxygen isotopes

Ayliffe et al. (1992) have shown that $\delta^{18}\text{O}_\text{P}$ of modern elephants is related to the isotopic composition of precipitation ($\delta^{18}\text{O}_\text{W}$) with a relationship $\delta^{18}\text{O}_\text{P} = 0.94 \cdot \delta^{18}\text{O}_\text{W} + 23.3$. It is known that among mammals, the parameters of the equation are dependent on the body mass of the animal (Bryant and Froelich, 1995). Elephants and extinct proboscideans such as mammoths are thought to have a similar body size and comparable feeding habits (Ayliffe et al., 1992; Ukraintseva, 1986), supporting the application of the same equation to all proboscideans.

The isotopic composition of oxygen and hydrogen in Finnish groundwaters has been recently studied by Kortelainen and Karhu (2004). They observed that the mean annual isotopic composition of oxygen in Finnish groundwaters varies from -15.5‰ in the North to -11.5‰ in the South. They also noticed that these isotope values directly follow those of the local mean annual precipitation and are correlated to mean annual temperatures by $\delta^{18}\text{O}_\text{W} = 0.53T - 14.42$ (T is temperature, $^{\circ}\text{C}$). This spatial relation between local temperatures and isotope values is used here to convert the $\delta^{18}\text{O}_\text{W}$ values derived from the oxygen isotope composition of phosphate to environmental temperatures.

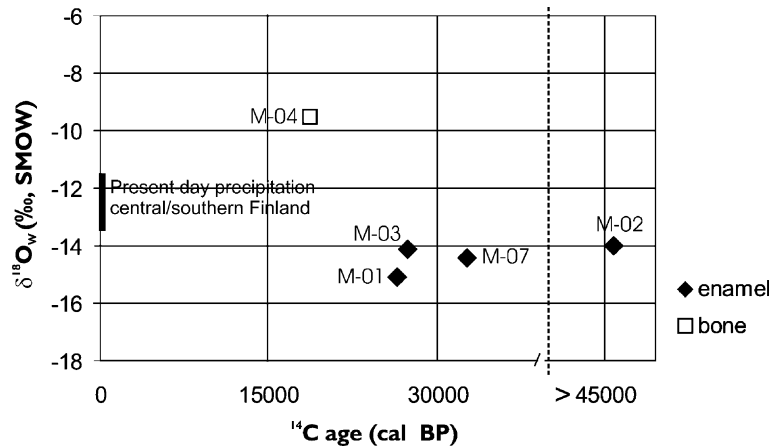


Fig. 4. Oxygen isotope composition of precipitation ($\delta^{18}\text{O}_W$) calculated from the well-preserved samples. The range of present-day oxygen isotope composition of precipitation in the areas of the mammoth find localities in central and southern Finland is indicated.

Based on $\delta^{18}\text{O}_P$ of the enamel samples, the oxygen isotope composition of the mean annual Late Pleistocene precipitation in eastern Scandinavia and neighboring areas varied from -15.3‰ to -14.2‰ , with an average value of -14.6‰ (Fig. 4). According to the relationship of Kortelainen and Karhu (2004), this would correspond to a mean annual temperature of -0.3 °C . The oxygen isotope composition of the present-day precipitation in the areas of the mammoth find localities in Southern and Central Finland ranges from -13.5‰ to -11.5‰ (Kortelainen and Karhu, 2004). The difference of 1–3‰ between Pleistocene and modern $\delta^{18}\text{O}_W$ values implies 2–6 °C lower mean annual temperatures for the Middle Weichselian ice-free period between 26 and 37 ka ago.

The humerus sample from Herttoniemi (M-04) has yielded an age of $18\,700 \pm 180$ cal BP ($15\,910 \pm 155$ BP; Ukkonen et al., 1999), which is problematic in relation to the current understanding of the glacial history of Scandinavia. The bone was discovered under a bog in littoral clay/sand. Ukkonen et al. (1999) suggested that it might have been transported to the site from elsewhere, possibly by icebergs. The contents of Fe and Mn in this sample showed evidence of extensive secondary crystallization, but at the same time, the $\Delta^{18}\text{O}_{C-P}$ value seems to have preserved the initial composition. The sample yielded a much higher $\delta^{18}\text{O}_P$ value compared to other well-preserved Pleistocene samples, being similar to those obtained from mammoth remains of glacial age in Britain (Ayliffe et al., 1992). The $\delta^{18}\text{O}_P$ -value corresponds to mean annual precipitation with $\delta^{18}\text{O}_W$ at -9.6‰ (Fig. 4). Warmer climatic conditions compared to those prevailing in Finland today are implied for the original natural environment of this specimen. The $\delta^{18}\text{O}_W$ value is close to that of modern

precipitation in Denmark or Latvia in the southern parts of the Baltic Sea.

5. Conclusions

This study was based on analysis of the isotopic composition of oxygen in nine subfossil mammoth skeletal samples from Finland and adjacent areas. For the assessment of diagenetic alteration, both the phosphate and carbonate fractions in skeletal apatite were analyzed separately and the contents of selected trace elements were determined. These tests indicated that all enamel samples were well preserved and likely had retained their original oxygen isotope compositions, whereas all bone and dentine samples, with one exception, show evidence of extensive diagenetic alteration. On the basis of these data, the following conclusions could be drawn:

- (1) Based on enamel samples, the isotopic composition of oxygen in Late Pleistocene precipitation was depleted in ^{18}O by 1–3‰, compared to the present-day mean annual precipitation in Southern and Central Finland.
- (2) Applying the $\delta^{18}\text{O}$ –temperature relationship in modern precipitation, the environmental temperatures during the Middle Weichselian ice-free period were 2–6 °C lower than the ambient temperatures today.
- (3) The humerus discovered in littoral clay/sand in Herttoniemi, Helsinki, dated at $18\,700 \pm 180$ cal BP, yielded an unusually high $\delta^{18}\text{O}_P$ value. This is consistent with earlier speculations that the bone might have been transported from warmer climatic zones in the southern part of the Baltic Sea.

Acknowledgements

This study is based on the MSc thesis of the corresponding author (LA) at the Department of Geology, University of Helsinki. The preparation of this paper was supported by a grant to LA from the Finnish Academy of Science and Letters, Vilho, Yrjö and Kalle Väisälä Foundation. The authors thank P. Ukkonen, M. Saarnisto, E. Sonninen and the Finnish Museum of Natural History for the samples, unpublished results, discussions and reviews of the manuscript. Two anonymous reviewers are thanked for useful comments that helped improve the manuscript and Ilona Romu for help with the microprobe analyses.

References

- Andersen, B.G., Mangerud, J., 1989. The last interglacial–glacial cycle in Fennoscandia. *Quaternary International* 3/4, 21–29.
- Ayliffe, L.K., Lister, A.M., Chivas, A.R., 1992. The preservation of glacial–interglacial climatic signatures in the oxygen isotopes of elephant skeletal phosphate. *Palaeogeography, Palaeoclimatology, Palaeoecology* 99, 179–191.
- Ayliffe, L.K., Chivas, A.R., Leakey, M.G., 1994. The retention of primary isotope compositions of fossil elephant phosphate. *Geochimica et Cosmochimica Acta* 58, 5291–5298.
- Bard, E., 1998. Geochemical and geophysical implications of the radiocarbon calibration. *Geochimica et Cosmochimica Acta* 62, 2025–2038.
- Bocherens, H., Koch, P.L., Mariotti, A., Geraads, D., Jaeger, J.-J., 1996a. Isotopic biochemistry (^{13}C , ^{18}O) of mammal enamel from African Pleistocene hominid sites: implications for the preservation of paleoclimatic isotopic signals. *Palaos* 11, 397–408.
- Bocherens, H., Picaud, G., Lazarev, P.A., Mariotti, A., 1996b. Stable isotope abundances (^{13}C , ^{15}N) in collagen and soft tissues from Pleistocene mammals from Yakutia: implications for the palaeobiology of the Mammoth Steppe. *Palaeogeography, Palaeoclimatology, Palaeoecology* 126, 31–44.
- Bryant, J.D., Froelich, P.N., 1995. A model of oxygen isotope fractionation in body water of large mammals. *Geochimica et Cosmochimica Acta* 59, 4523–4537.
- Bryant, J.D., Luz, B., Froelich, P.N., 1994. Oxygen isotope composition of fossil horse tooth phosphate as a record of continental paleoclimate. *Palaeogeography, Palaeoclimatology, Palaeoecology* 107, 303–316.
- Bryant, J.D., Koch, P.L., Froelich, P.N., Showers, W.J., Genna, B.J., 1996a. Oxygen isotope partitioning between phosphate and carbonate in mammalian apatite. *Geochimica et Cosmochimica Acta* 60, 5145–5148.
- Bryant, J.D., Froelich, P.N., Showers, W.J., Genna, B.J., 1996b. Biologic and climatic signals in the oxygen isotopic composition of Eocene–Oligocene equid enamel phosphate. *Palaeogeography, Palaeoclimatology, Palaeoecology* 126, 75–89.
- Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* 16, 436–468.
- Driessens, F.C.M., Verbeeck, R.M.H., 1990. *Biomaterials*. CRC Press, Boca Raton, FL, 440 pp.
- Elorza, J., Astibia, H., Murelaga, X., Pereda-Superbiola, X., 1999. Francelite as a diagenetic mineral in dinosaur and other Upper Cretaceous reptile bones (Laño, Iberian Peninsula): microstructural, petrological and geochemical features. *Cretaceous Research* 20, 169–187.
- Fricke, H.C., O'Neil, J.R., Lynnerup, N., 1995. Oxygen isotope composition of human tooth enamel from medieval Greenland: linking climate and society. *Geology* 23, 869–872.
- Genoni, L., Iacumin, P., Nikolaev, V., Gribchenko, Yu., 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, 587–592.
- Hubberten, H.W., Andreev, A., Astakhov, V.I., Demidov, I., Dowdeswell, J.A., Henriksen, M., Hjort, C., Houmark-Nielsen, M., Jakobsson, M., Kuzmina, S., Larsen, E., Lunkka, J.P., Lyså, A., Mangerud, J., Möller, P., Saarnisto, M., Schirmer, L., Sher, A.V., Siegert, C., Siegert, M.J., Svendsen, J.I., 2004. The periglacial climate and environment in northern Eurasia during the Last Glaciation. *Quaternary Science Reviews* 23, 1333–1357.
- Iacumin, P., Longinelli, A., 2002. Relationship between $\delta^{18}\text{O}$ for skeletal apatite from reindeer and foxes and yearly mean $\delta^{18}\text{O}$ values of environmental water. *Earth and Planetary Science Letters* 201, 213–219.
- Iacumin, P., Bocherens, H., Mariotti, A., Longinelli, A., 1996a. 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, 1–6.
- Iacumin, P., Bocherens, H., Mariotti, A., Longinelli, A., 1996b. An isotopic palaeoenvironmental study of human skeletal remains from the Nile Valley. *Palaeogeography, Palaeoclimatology, Palaeoecology* 126, 15–30.
- Iacumin, P., Nikolaev, V., Ramigni, M., 2000. C and N isotope measurements on Eurasian fossil mammals, 40000 to 10000 years BP: herbivore physiologies and palaeoenvironmental reconstruction. *Palaeogeography, Palaeoclimatology, Palaeoecology* 163, 33–47.
- Iacumin, P., Nikolaev, V., Ramigni, M., Longinelli, A., 2004. Oxygen isotope analyses of mammal bone remains from Holocene sites in European Russia: palaeoclimatic implications. *Global and Planetary Change* 40, 169–176.
- Koch, P., Tuross, N., Fogel, M., 1997. The effects of sample treatment and diagenesis on the isotopic integrity of carbonate in biogenic hydroxylapatite. *Journal of Archaeological Science* 24, 417–429.
- Kohn, M.J., Schoeninger, M.J., Barker, W.W., 1999. Altered states: effects of diagenesis on fossil tooth chemistry. *Geochimica et Cosmochimica Acta* 63, 2737–2747.
- Kortelainen, N.M., Karhu, J.A., 2004. Regional and seasonal trends in the oxygen and hydrogen isotope ratios of Finnish groundwaters: a key for mean annual precipitation. *Journal of Hydrology* 285, 143–157.
- Land, L.S., Lundelius Jr., E.L., Valastro, S., 1980. Isotopic ecology of deer bones. *Palaeogeography, Palaeoclimatology, Palaeoecology* 32, 143–151.
- Lécuyer, C., Grandjean, P., Barrat, J.-A., Nolvak, J., Emig, C., Florentin, P., Robardet, M., 1998. $\delta^{18}\text{O}$ and REE contents of phosphatic brachiopods: a comparison between modern and lower Paleozoic populations. *Geochimica et Cosmochimica Acta* 62, 2429–2436.
- Lee-Thorp, J., Sponheimer, M., 2003. Three case studies used to reassess the reliability of fossil bone and enamel isotope signals for paleodietary studies. *Journal of Anthropological Archaeology* 22, 208–216.

- Lee-Thorp, J.A., Sealy, J.C., van der Merwe, N.J., 1989. Stable carbon isotope ratio differences between bone and collagen and bone apatite, and their relationship to diet. *Journal of Archaeological Science* 16, 585–599.
- Longinelli, A., 1984. Oxygen isotopes in mammal bone phosphate: a new tool for paleohydrological and paleolimnological research? *Geochimica et Cosmochimica Acta* 48, 385–390.
- Longinelli, A., Nuti, S., 1973. Revised phosphate–water isotopic temperature scale. *Earth and Planetary Science Letters* 19, 373–376.
- Longinelli, A., Iacumin, P., Davanzo, S., Nikolaev, V., 2003. Modern reindeer and mice: revised phosphate–water isotope equations. *Earth and Planetary Science Letters* 214, 491–498.
- Lõugas, L., Ukkonen, P., Jungner, H., 2002. Dating the extinction of European mammoths: new evidence from Estonia. *Quaternary Science Reviews* 21, 1347–1354.
- Lunkka, J.P., Saarnisto, M., Gey, V., Demidov, I., Kiselova, V., 2001. Extent and age of the Last Glacial Maximum in the southeastern sector of the Scandinavian Ice Sheet. *Global and Planetary Change* 31, 407–425.
- Luz, B., Kolodny, Y., Horowitz, M., 1984. Fractionation of oxygen isotopes between mammalian bone-phosphate and environmental water. *Geochimica et Cosmochimica Acta* 48, 1689–1693.
- Nelson, B.K., De Niro, M.J., Schoeninger, M.J., De Paolo, D.J., 1986. Effects of diagenesis on strontium, carbon, nitrogen and oxygen concentration and isotopic composition of bone. *Geochimica et Cosmochimica Acta* 50, 1941–1949.
- O'Neil, J.R., Roe, L.J., Reinhard, E., Blake, R.E., 1994. A rapid and precise method of oxygen isotope analysis of biogenic phosphate. *Israel Journal of Earth-Sciences* 43, 203–212.
- Reinhard, E., de Torres, T., O'Neil, J., 1996. $^{18}\text{O}/^{16}\text{O}$ ratios of cave bear tooth enamel: a record of climate variability during the Pleistocene. *Palaeogeography, Palaeoclimatology, Palaeoecology* 126, 45–99.
- Schoeninger, M.J., DeNiro, M.J., 1982. Carbon isotope ratios of apatite from fossil bone cannot be used to reconstruct diets of animals. *Nature* 297, 577–578.
- Stephan, E., 2000. Oxygen isotope analysis of animal bone phosphate: method refinement, influence of consolidants, and reconstruction of palaeotemperatures for Holocene sites. *Journal of Archaeological Science* 27, 523–535.
- Sullivan, C.H., Krueger, H.W., 1981. Carbon isotope analysis of separate chemical phases in modern and fossil bone. *Nature* 292, 333–335.
- Swart, P.K., Burns, S., Leder, J., 1991. Fractionation of the stable isotopes of oxygen and carbon in carbon dioxide during the reaction of calcite with phosphoric acid as a function of temperature and technique. *Chemical Geology* 86, 89–96.
- Ukkonen, P., Lunkka, J.P., Jungner, H., Donner, J., 1999. New radiocarbon dates from Finnish mammoths indicating large ice-free areas in Fennoscandia during the Middle Weichselian. *Journal of Quaternary Science* 14/7, 711–714.
- Ukkonen, P., Lunkka, J.P., Jungner, H., Donner, J., 2003. Finnish mammoths. In: Reumer, J.W.F., de Vos, J., Mol, D. (Eds.), *Advances in Mammoth Research Proceedings of the Second International Mammoth Conference, Rotterdam, 16–20 May 1999*. *Deinsea*, vol. 9. pp. 429–435.
- Ukraitseva, V.V., 1986. On the composition of the forage of large herbivorous mammals of the mammoth epoch: significance for palaeobiological and palaeogeographical reconstruction. *Quartärpaläontologie* 6, 231–23.
- Zazzo, A., Lécuyer, C., 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, 1–12.