UNIVERSITY OF PÉCS

Doctoral School of Chemistry

Pliocene-Early Pleistocene climate reconstruction based on stable isotope compositions of large mammal tooth enamel (in Central and South Europe)

Ph.D. Thesis

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PÉCS, 2018

1. Introduction

There is an increasing interest in understanding Pliocene and Early Pleistocene climate and environments, because it can help to predict future climate changes more accurately. Reconstructions of palaeoenvironments, palaeoecology and palaeoclimates are commonly based on proxies like marine sediments, paleosols, fossil plants (including pollen), vertebrate occurrences, speleothems, travertines, tufas, as well as the geochemistry and isotope geochemistry of biogenic carbonates and phosphates such as mammal teeth and bones. Marine paleoclimatology has been spectacularly successful, while climate reconstruction on land is more difficult because land ecosystems and climates exhibit greater spatial and temporal heterogeneity. Because teeth and bones are well preserved in the fossil record, and the natural variations in stable isotope ratios of apatite depend on environmental variables, over the past decade stable isotopes in teeth have become indispensable tools in reconstructing terrestrial paleoclimate and environment.

In this study, Pliocene and Early Pleistocene tooth enamel samples mostly of fossil rhinoceros and gomphothere species were studied. The samples are from different regions of Central and South Europe, while the age of the fossils covers the Early Pliocene to late Early Pleistocene, from about 5.2 to 1 Ma. The carbon and oxygen isotope compositions of structural carbonate and the oxygen isotope composition of phosphate in enamel bioapatite were used to explore variations in past climate and the environment of the animals. The aims of this study are:

1) Reconstructing the isotope composition of environmental water ($\delta^{18}O_w$) and estimating the changes in mean annual surface air temperature (MAT) on the basis of $\delta^{18}O_{PO4}$ values of fossil tooth enamel.

2) Interpretation of the diet of the species and detecting changes in vegetation and/or in humidity based on the carbon isotope analyses of the enamel.

3) Comparing the climatic and environmental parameters derived from the isotope results with palaeobotanical proxies, palaeontological and palaeoecological information. The comparisons can help to reconstruct the climate and environment more accurately and also to evaluate the reliability of the stable isotope proxy in different conditions.

4) Investigate intra-tooth isotopic variation via sequential sampling to gain additional information about seasonality, dietary ecology or movement patterns of the animals.

3. Materials and methods

Enamel was sampled with a diamond-studded drill (Dremel®). Where it was possible, enamel was sampled along a vertical line over the whole enamel length from the crown to the root to get a representative mean sample of the period of enamel formation. Due to sample limitations in some cases, enamel from tooth fragments was collected, but the samples can still represent an average isotope record of a longer period. Where possible, several samples were collected from each site to get representative results. In the case of sequential sampling, enamel was embedded in polyester resin and cut to 1 mm slices using a precision diamond wire saw. Then enamel of each slice is ground in an agate mortar.

Sample powder was pre-cleaned according to the method given in Koch et al. (1997). NaOCl was used to remove soluble organic material and acetic acid-Ca-acetate buffer to remove exogenous carbonates (Koch et al., 1997; Kocsis, 2011). After pre-cleaning, about 2 mg of sample was used for the carbonate isotopic measurements, while for the $\delta^{18}O$ analyses in the phosphate fraction further preparation was required. According to methods adapted after Dettman et al. (2001) and Kocsis (2011), 4-5 mg subsamples were dissolved in HF, the solution and the resultant CaF_2 were separated and after neutralization $AgNO_3$ was added to the solution which allowed the rapid precipitation of Ag_3PO_4. After drying, the silver phosphate was weighted into silver capsules (500–700 µg, d: 3.3/15 mm, saentis).

The silver-phosphate was analysed via reduction with graphite in a high-temperature conversion elemental analyser (TC/EA) coupled to a Finnigan MAT Delta Plus XL mass spectrometer according to the values and method given in Vennemann et al. (2002). At 1450°C the reduction of Ag_3PO_4 produced CO, which were carried in the He-stream through a gas chromatograph (molecular sieve 5A) and admitted to a Delta Plus XL mass spectrometer via a ConFlo interface. The results were corrected to in-house Ag_3PO_4 phosphate standards (LK-2L: 12.1‰ and LK-3L: 17.9‰) that showed standard deviations (1σ) better than ± 0.3‰ during the measurements. These in-house standards were calibrated by TC/EA to TU-1 (21.11‰)

and TU-2 (5.45‰) standards using values defined by the conventional fluorination method and were also calibrated with laser fluorination measurements, giving identical values to that of the TC/EA calibration.

The carbon and oxygen isotopic compositions of structural carbonate were measured on a Finnigan MAT Delta Plus XL mass spectrometer equipped with a GASBENCH-II preparation unit. The samples were reacted with 99% orthophosphoric acid and the produced CO_2 was introduced to the mass spectrometer with He carrier gas following procedures similar to those described in Spötl and Vennemann (2003). Carrara Marble in-house standards ($\delta^{18}O$ = –1.70‰, VPDB; $\delta^{13}C$ = 2.05‰, VPDB) were run in the same sequence with the samples and used for correcting the data. The reproducibility of the in-house standard is better than 0.1‰ (1 σ) for both oxygen and carbon isotopic compositions.

4. Results

The stable isotope analyses of 120 enamel samples from many Central and South European localities from the Early Pliocene to the Early Pleistocene provide new information about the climate and environment of these regions and times. The main results are:

1) Based on $\delta^{18}O_{PO4}$ results many climatic changes were observed in the Pliocene and Early Pleistocene (**figures 1-4.**). Several different equations were used to calculate the possible range of $\delta^{18}O_W$ and MAT changes. In Central-Italy the $\delta^{18}O_{PO4}$ values support the warmest climate during the Early Pliocene followed by cooling with fluctuations toward the end of the Early Pleistocene. Based on the calculations the 1,4‰ decrease in $\delta^{18}O_{PO4}$ results between Early and Late Pliocene mean 1,5–1,8‰ decrease in $\delta^{18}O_w$ values and 2.2–3.1 °C decrease in MAT. The scale of the cooling is very similar in the Carpathian Basin (2–3.5 °C decrease). In North Italy, the $\delta^{18}O_{PO4}$ values are low compared to Central Italy and the calculations would result low MAT values especially during the Early Pliocene. In MN16 the values are higher, probably linked to the mid-Piacenzian warm period (MPWP) but no other trends can be observed. A possible explanation could be for the low values that the drinking water of the animals was influenced by an Alpine catchment with typically lower mean $\delta^{18}O_w$ values because of altitude and/or air mass origin differences for the northern parts of Italy.

No differences can be observed in South-East France and in the Carpathian Basin between the MN16 and MN17 biozones. This could indicate that the cooling linked to the Northern Hemisphere Glaciation (NHG) started at different times and varied in strength in the different regions.
The spatial distributions of the calculated $\delta^{18}O_w$ values in the examined three regions (South-East France, Central Italy and Carpathian basin) show similar $\delta^{18}O_w$ distributions in the MN14-15 and in MN16-MN17 biozones and it is also similar to present day distribution too.

2) All of the $\delta^{13}C$ values indicate that the investigated taxa lived in C_3 ecosystem which is compatible with earlier suggestions that C_4 grasses were absent in Europe during the Pliocene to Late Pleistocene. Because there are significant spatial and temporal differences in $\delta^{13}C$ values but the $\delta^{13}C$ values of the different species are similar, it supports the former data based on palaeontology that the investigated species had similar diets, these were browsers and mixed feeders. This could also imply that changes in measured $\delta^{13}C$ values are more likely the effect of vegetation or climatic changes than a change in food preference of the animals.

Based on the expected cut-off $\delta^{13}C$ values of modern equivalent diet ($\delta^{13}C_{diet, meq}$) for different habitats the results indicate woodland to mesic C_3 grassland as a major flora type, but the openness of the vegetation could change within this category **figures 1-4.**). The vegetation in Early Pliocene was more closed in North and Central Italy and was more open in the Carpathian Basin. In North Italy, the increase in $\delta^{13}C$ values between the MN16 and MN17 biozones could be linked to the increase in aridity at the beginning of the NHG but from other regions (South-East France, Carpathian Basin) no changes in $\delta^{13}C$ can be observed at that time. As in the case of $\delta^{18}O_w$ values, it could mean that the environmental changes linked to (NHG) started at different times and varied in strength in the different regions. Changes in $\delta^{13}C$ values can be observed from Central Italy from the different faunal units within the MN18 biozone. The results indicate more arid climate during the Olivola and Tasso and then during the Colle Curti Faunal Units, while the climate was more humid in the Farneta and Pirro Nord Faunal Units. The climate in the latter Faunal Units was similar to the climate in the Pliocene. The rapid significant changes in $\delta^{13}C$ values most likely represent the climates changes during glacial-interglacial cycles.

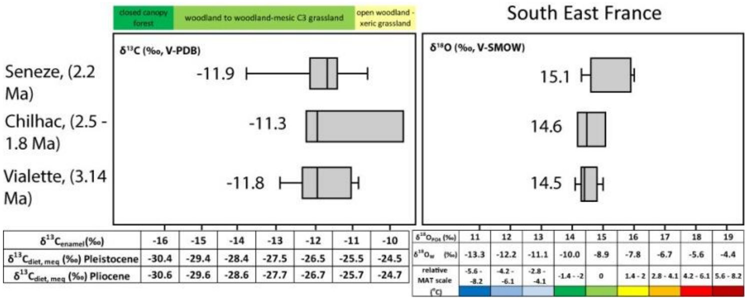

Figure 1. Average $\delta^{13}C$ and $\delta^{18}O_{PO4}$ results obtained from the teeth in South-East France with vegetation estimation, calculated environmental water values, and relative MAT scales

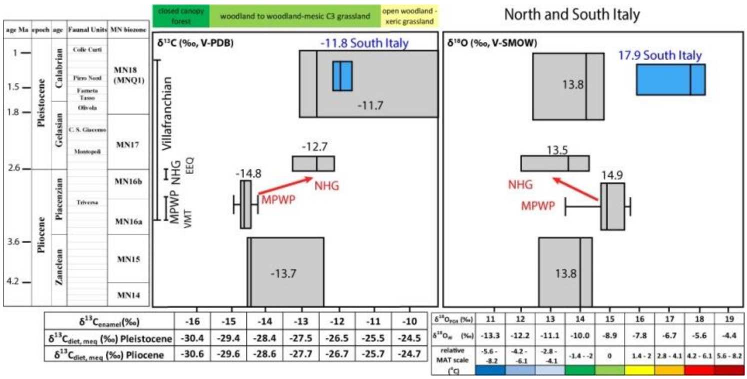

Figure 2. Average $\delta^{13}C$ and $\delta^{18}O_{PO4}$ results obtained from the teeth in North and South Italy with vegetation estimation, calculated environmental water values and relative MAT scales. NHG: Northern Hemisphere Glaciation, MPWP: Mid-Piacenzian Warm Period, VMT: Villafranchian mammal turnover, EEQ: Elephant-Equus event

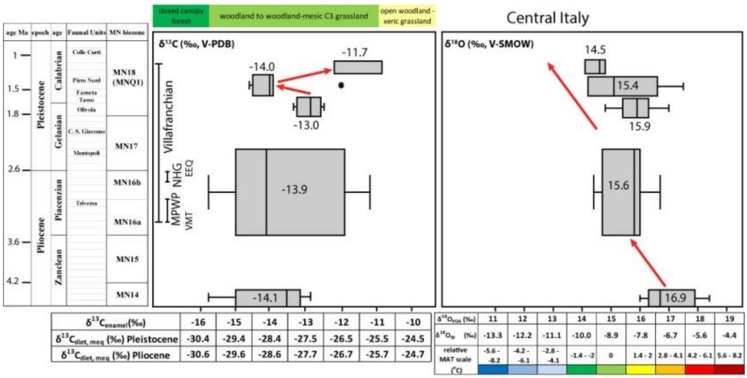

Figure 3. Average $\delta^{13}C$ and $\delta^{18}O_{PO4}$ results obtained from the teeth in Central-Italy with vegetation estimation, calculated environmental water values and relative MAT scales. NHG: Northern Hemisphere Glaciation, MPWP: Mid-Piacenzian Warm Period, VMT: Villafranchian mammal turnover, EEQ: Elephant-Equus event

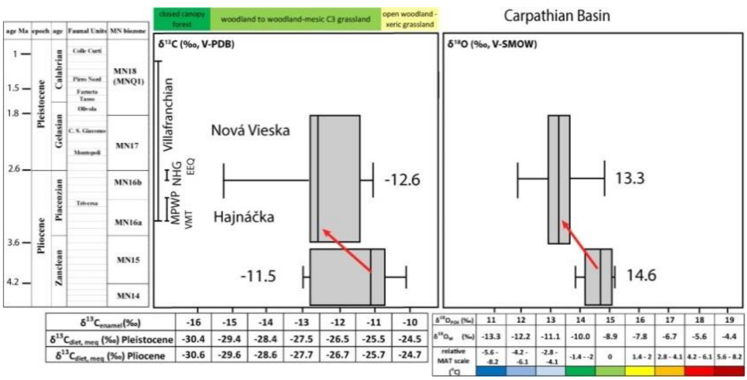

Figure 4. Average $\delta^{13}C$ and $\delta^{18}O_{PO4}$ results obtained from the teeth in the Carpathian Basin with vegetation estimation, calculated environmental water values and relative MAT scales. NHG: Northern Hemisphere Glaciation, MPWP: Mid-Piacenzian Warm Period, VMT: Villafranchian mammal turnover, EEQ: Elephant-Equus event

3) The vegetation and precipitation reconstructions based on $\delta^{13}C$ values were compared to independent proxy data from the literature. In most cases, the results are in agreement with reconstructions based on pollen data. For example, pollen sequences show similar temporal trends with similar amplitude in Central Italy within the MN18 biozone. During Olivola and Tasso then in the Colle Curti faunal unit, the percentages of grass pollen were higher indicating more open areas, while the vegetation was more closed in the Farneta and Pirro Nord faunal units. In most of the cases, reconstructions and trends based on paleontological data, for example, the occurrences of grazing species or hypsodonty indexes are also in good agreement with the results, however, there are exceptions. For example, a rapid increase of the large grazers can be observed in faunal assemblages in South-East France in MN17, while in $\delta^{13}C$ values there are no detectable changes between MN16 and MN17. The overall agreements of the reconstructions based on $\delta^{13}C$ values and on different independent proxies increase the reliability of the use of stable isotope measurements.

Besides the vegetation changes the reliability of the equation for the mean annual precipitation (MAP) (Kohn, 2010) was investigated. Based on theoretical considerations and the $\delta^{13}C$ results, the equation is not in agreement with the vegetation reconstruction in the case of very high and very low $\delta^{13}C$ values. However, in the case of $\delta^{13}C_{diet,\ meq}$ values between −30‰ and −25‰ the MAP results can be realistic and mostly are in agreement with values based on proxies like pollens, paleosol chemical compositions, and hypsodonty indexes.

4) The calculated MAT values were compared to independent proxy data from the literature. Proxy data for MAT are available only in a few regions and time periods, but there are regions from where different types of proxies are available. These based on chemical composition of paleosols, the isotopic composition of paleo groundwater, plant and animal fossils. Because all of these proxies have inherent errors and the different MAT estimations not always agree, only a few conclusions could be drawn from the comparisons. The trends and rates of MAT changes calculated from $\delta^{18}O$ values in overall fit well within the trends based on different proxies in Central Italy and in the Carpathian basin. The contradictions in North Italy can be explained by the low $\delta^{18}O$ values of drinking water from Alpine catchments. Compared to the present day $\delta^{18}O$ values of precipitation ($\delta^{18}O_{ppt}$) and MAT, the calculated $\delta^{18}O_{ppt}$ and MAT

would be too low in some regions and time periods and no explanation can be found for this. This confirms that reconstructing absolute $\delta^{18}O_{ppt}$ and MAT values can have greater uncertainty than reconstructing only the $\delta^{18}O$ and MAT changes.

5) Among the bulk samples, sequential samples were collected from two *Stephanorhinus sp.* teeth to gain more information about climate in Pula and Seneze sites. Semi-sinusoidal patterns in both of the teeth were found in $\delta^{18}O$ values. The fluctuation of the $\delta^{18}O$ values within the teeth could indicate the different built-in $\delta^{18}O_w$ values during summer and winter. Based on this, the formation and mineralization of each tooth could last for one and a half year. Although $\delta^{18}O$ values reflect changes in isotope compositions of environmental waters, estimating the seasonal MAT changes from these is not possible, because the environmental signals are dampened in the teeth. The variability of $\delta^{13}C$ values are higher in the case of the tooth from Pula site and the $\delta^{13}C$ values show the same temporal pattern that the $\delta^{18}O$ values. This could mean stronger seasonality and continentality at that site or possibly it could reflect the seasonal migration or microhabitat change of the animal.

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6. Publications directly connected to the thesis

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