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Pliocene and Early Pleistocene paleoenvironmental conditions in the Pannonian Basin (Hungary, Slovakia): Stable isotope analyses of fossil proboscidean and perissodactyl teeth

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ABSTRACT

Stable carbon and oxygen isotope values of structural carbonate ($\delta^{13}C$, $\delta^{18}O_{CO3}$) and phosphate ($\delta^{18}O_{PO4}$) in bioapatite were measured for fossil mammalian teeth from Slovakia and Hungary. Oxygen isotope compositions of enamel provide new quantitative records of the Pliocene and Early Pleistocene paleoclimate in the Pannonian Basin (PB). The $\delta^{18}O_{PO4}$ values were used to study the temporal variations in the oxygen isotope compositions of precipitation and the changes in temperature over the PB. The new O-isotope data suggest that surface air temperatures between 4.5 and 2.0 Ma were 1 to 4 °C warmer with about 700 mm/yr more precipitation compared to the present. C-isotope analyses of samples from proboscideans (*Anancus* sp., *Mammut* sp.) and perissodactyls (*Stephanorhinus* sp., *Tapirus* sp.) from the Pliocene (MN15–MN16) and Early Pleistocene (MN17) suggest that they were primarily C_3 browsers. The mean $\delta^{13}C$ value is high at 4.5 to 3.7 Ma (MN14–15) during the Pliocene Warm Period and decreases at about 3.5 to 3.0 Ma (MN16; mid-Pliocene Warm Period), with the onset of more humid conditions in Europe. The $\delta^{13}C$ values return to higher values from 2.5 Ma onwards (MN17), most likely reflecting more arid conditions as a consequence of the onset of the Northern Hemisphere glaciation.

1. Introduction

Investigating the changes in Earth's past climate provides a context to better understand current changes in climate and can help to predict future climatic and environmental conditions. The Pliocene–Pleistocene transition (about 2.6 Ma) is undoubtedly one of the most important episodes for the evolution of mankind (deMenocal, 2004; Trauth et al., 2010; Maslin et al., 2014, 2015). Investigations of the stable isotope compositions of biomineralized tissues have added greatly to our knowledge of changes in past climates and dietary behaviors of mammals (e.g., Sullivan and Krüger, 1983; Luz et al., 1984, 1990; Luz and Kolodny, 1985; Ayliffe et al., 1992, 1994; Coplen, 1994; Bryant and Froelich, 1995; Delgado Huertas et al., 1995; Bocherens et al., 1996; Iacumin et al., 1996; Fricke et al., 1998; Cerling and Harris, 1999; Kohn et al., 1999; Kohn and Cerling, 2002; Zazzo et al., 2004a, 2004b; Arppe and Karhu, 2006; Levin et al., 2006; Tütken et al., 2006; Martin et al., 2008; Kohn, 2010; Pushkina et al., 2014). Quantitative paleoclimatological and paleoecological records based on stable isotope analyses of mammal teeth from the time period prior to the Pliocene and Early Pleistocene are scarce and fragmentary, and particularly poor in the region of East Central Europe (e.g., Kovács et al., 2012).

Mammal teeth and bones are mineralized as bioapatite, a calcium phosphate mineral, with a simplified chemical formula of $Ca_5(PO_4, CO_3)_3(OH, CO_3)$ (Skinner, 2005). Carbonate ion (CO_3^{2-}) is substituted in two structural sites, replacing the phosphate (PO_4^{3-}) and hydroxyl (OH^-) ions, and for mammals it is a main constituent of the biomineral. The stable carbon isotope composition of this structural carbonate is known to record the diet of the mammals, hence can be linked to past vegetation (e.g. Sullivan and Krueger, 1983; Cerling and Harris, 1999; Passey et al., 2005). The stable oxygen isotope composition of both structural carbonate ($\delta^{18}O_{CO3}$) and phosphate ($\delta^{18}O_{PO4}$) can be linked to the body water of the animals, and its isotopic composition is related to climate and ecophysiological factors (e.g., Longinelli, 1984; Luz and Kolodny, 1985; Kohn et al., 1996). Because of the strong P—O bonds

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the phosphate oxygen is considered more resistant to low temperature inorganic alteration processes compared to carbonate oxygen (e.g., Kohn et al., 1999; Vennemann et al., 2002), hence it is preferentially analyzed for climatic reconstruction. However, during microbiological reactions oxygen isotope exchange between PO_4^{3-} and water is possible due to enzymatic catalysis. In these cases the oxygen isotope composition of the phosphate can also be changed during diagenesis (e.g., Blake et al., 1997; Zazzo et al., 2004a, 2004b; Liang and Blake, 2007). For this reason, tooth enamel rather than bone or dentine is the preferred phase for analysis because it is more resistant to diagenesis (e.g., Lee-Thorp and van der Merwe, 1987; Quade et al., 1992; Ayliffe et al., 1994; Wang and Cerling, 1994; Koch et al., 1997), even in a microbially mediated environment (Zazzo et al., 2004a, 2004b). Compared to bone and dentine, enamel has a larger average crystal size and a lower porosity and lower organic matter content (Skinner, 2005). As a result, the recrystallization of bioapatite and the pore-space infilling by secondary minerals are more limited in enamel compared to bone and dentine in the same taphonomic context (Kohn et al., 1999).

To gain reliable information about the past dietary, paleoclimatic and paleoenvironmental changes, it is important for the samples to have preserved their primary compositions throughout diagenesis and/or low grade metamorphism. Comparing the oxygen isotopic compositions of the structural carbonate to that of the phosphate itself can often help constrain the impacts of diagenesis (e.g., Iacumin et al., 1996). Hence, an approach of using, where possible, enamel rather than dentine and analyzing the stable isotope compositions of carbonate and phosphate within bioapatite, has a good potential of constraining the past changes in terrestrial vegetation and climate, including rainfall and temperature (e.g., Kohn and Cerling, 2002; Kohn, 2010).

From the Pliocene to Early Quaternary period in Central Europe so far only very sporadic stable isotope data exist from mammals, and most of the analyses were done on proboscideans (Kovács et al., 2012; Virág et al., 2014). Rhinoceros have not been specifically investigated in this region, a gap that is to be filled by this study. The sampling localities (Fig. 1) are dated from the late-Early Pliocene to Early Pleistocene. Fossil teeth of large herbivores were selected according to their abundance in the deposits and their appearance of preservation. Altogether, twenty-nine Pliocene and Early Pleistocene samples of fossil proboscideans ($n = 9$), rhinoceroses ($n = 19$) and one of tapir from the Pannonian Basin (Slovakia and Hungary; Fig. 1) were studied. The carbon and oxygen isotope compositions of carbonate ($\delta^{13}C$, $\delta^{18}O_{CO3}$) and the oxygen isotope composition of phosphate ($\delta^{18}O_{PO4}$) in enamel were used to explore spatial patterns and temporal variations of $\delta^{18}O_w$ (oxygen isotope values of precipitation) in Central Europe prior to and after the Pliocene, during the MN15, MN16, and MN17 mammal biozones (about 4.5 to 2.0 Ma).

The goals of this paper are: (1) to reconstruct $\delta^{18}O_w$ and (2) surface air temperature on the basis of $\delta^{18}O_{PO4}$ values of fossil tooth enamel from two Slovakian and eight Hungarian localities, (3) to interpret the diet of the animals, and (4) their paleoenvironment based on tooth enamel carbon isotope compositions.

2. Background

2.1. Carbon isotopes and diet

The stable carbon isotopic values of teeth reflect the isotopic composition of plants at the base of the food chain in an ecosystem. C_4 plants (warm climate grasses) and C_3 plants (trees, shrubs and high-latitude grasses) are important in the case of paleodiet research. Because of different photosynthetic pathways, the C_3 and C_4 plants have different carbon isotope compositions (−27 and −13‰ for average C_3 and C_4 modern plants, respectively). CAM plants (largely succulents and few aquatic plants) have values intermediate between C_3 and C_4 plants (O'Leary, 1988; Farquhar et al., 1989; Martinelli et al., 1991). Bioapatite carbonate $\delta^{13}C$ values of large herbivores are offset from the plant isotope values by about 14‰ (e.g., Cerling and Harris, 1999). Thus, animals feeding on modern C_3 vegetation have bioapatite carbonate $\delta^{13}C$ values from −20 to −8‰, with mean values of around −13 to −12‰. Correspondingly, C_4 consumers usually have $\delta^{13}C$ values ranging from 0 to +5‰ for their enamel (e.g., Kohn and Cerling, 2002; Kohn, 2010; Arppe et al., 2011). Because these animal's $\delta^{13}C$ values are directly related to those of the diet and hence to their environment, the analysis of the carbon isotope ratios in bioapatite has been applied to address a variety of paleodietary, paleoecological, and paleoenvironmental problems (e.g., Lee-Thorp et al., 1989; Quade et al., 1992; Bocherens et al., 1996; Cerling and Harris, 1999; Iacumin et al., 2000; Feranec, 2004; Metcalfe et al., 2009; Arppe et al., 2011; Montanari et al., 2013; Kocsis

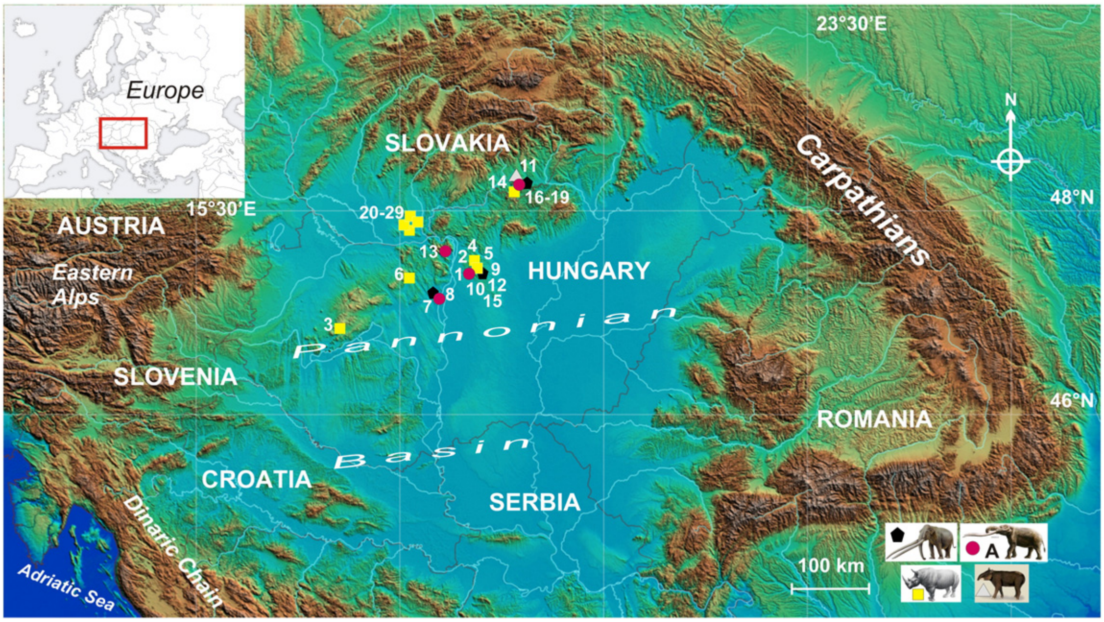

Fig. 1. Location of paleontological sites cited in Table 1.