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Pliocene–Early Pleistocene climatic trends in the Italian Peninsula based on stable oxygen and carbon isotope compositions of rhinoceros and gomphothere tooth enamel

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A B S T R A C T

The Pliocene and Early Pleistocene (5.2–1 Ma) palaeoclimate for localities in Italy is evaluated using stable carbon and oxygen isotope compositions of tooth enamel of fossil specimens from Rhinocerotidae (*Stephanorhinus* sp.) and Gomphotheriidae (*Anancus* sp.) taxa. Carbon isotope composition was measured in the structural carbonate ($\delta^{13}C$), while oxygen isotope values were determined both in the structural carbonate ($\delta^{18}O_{CO3}$) and the phosphate ($\delta^{18}O_{PO4}$) of bioapatite.

The $\delta^{13}C_{CO3}$ values indicate that the taxa were grazers-browsers of a pure C_3 vegetation. Low $\delta^{13}C_{CO3}$ values for Central and North Italy indicate a humid climate with woodlands and forest cover in the Pliocene. For northern localities the $\delta^{13}C$ values increase between MN16a and MNQ16b biozones most likely linked to the Northern Hemisphere Glaciation at 2.7 Ma after the "Mid-Pliocene Warm Period". For Central Italy the values have a wide range with a long term increasing trend in the Early Pleistocene, indicating more arid climate and/or more open vegetation.

Overall, the $\delta^{18}O_{PO4}$ values in Central Italy change together with the $\delta^{13}C_{CO3}$ values and are taken to reflect the warmer/wetter interglacials and cooler/more arid glacial phases. The $\delta^{18}O_{PO4}$ values in North Italy are lower than those in Central Italy and show no clear temporal trend. One explanation for the low values especially in MN14-15 biozone is that these $\delta^{18}O_{PO4}$ values do not reflect entirely the isotopic composition of local precipitation but river waters from the Alps with ^{18}O-depleted isotopic compositions or a N-S directed rain-shadow effect on the precipitation. In general the new isotope data agree well with palaeoclimate reconstructions based on palynological and other proxies.

1. Introduction

There is an increasing interest in understanding Pliocene and Early Pleistocene terrestrial climates and environments because it can help to predict future climate changes more accurately. Reconstructions of terrestrial palaeoenvironments, palaeoecology, and palaeoclimates are commonly based on proxies like 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. (Sullivan and Krueger, 1981; Luz et al., 1984, 1990; Luz and Kolodny, 1985; Thorp and Van Der Merwe, 1987; Leethorp et al., 1989; Ayliffe et al., 1992, 1994; Bryant and Froelich, 1995; Bocherens et al., 1996; Fricke et al., 1998; Cerling and Harris, 1999; Kohn et al., 1999; Kohn and Cerling, 2002; Arppe and Karhu, 2006; Levin et al., 2006; Tütken et al., 2006;

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Martin et al., 2008; Kohn, 2010; Pellegrini et al., 2011; Kocsis et al., 2014; Pushkina et al., 2014; García-Alix, 2015; Kovács et al., 2015; Hartman et al., 2016; Metcalfe et al., 2016 and references therein).

In this study 51 Pliocene and Early Pleistocene tooth enamel samples of fossil rhinoceros ($n = 44$) and gomphothere ($n = 7$) were studied from Italy. Most of the samples are from Central and North Italy and a few samples from South Italy (Fig. 1). 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; 3) detect changes in vegetation based on the enamel carbon isotope analyses.

These climatic and ecological parameters derived from the isotope results are compared with palaeobotanical proxies, palaeontological and palaeoecological information (Fauquette et al., 1999; Pontini and Bertini, 2000; Bertini, 2001, 2010; Bredenkamp et al., 2002; Ji et al., 2002; Fauquette and Bertini, 2003; Klotz et al., 2006; Palombo, 2007; Magri et al., 2010; Rook and Martínez-Navarro, 2010; Petronio et al., 2011; Combourieu-Nebout et al., 2015; Loftus et al., 2015; Rivals et al., 2015).

2. Background

2.1. Bioapatite and preservation of its isotopic compositions

Biogenic hydroxyapatite (i.e., bioapatite) is the main inorganic fraction of the skeletal tissues of mammals with up to 6 wt% of carbonate as structurally bound carbonate. The simplified formula is $Ca_5(PO_4, CO_3)_3(OH, CO_3)$ (e.g., Kohn et al., 1999). There are two types of carbonate forms in bioapatite, structural and labile carbonate. Structural carbonate substitutes for PO_4^{3-} and OH^-, while the labile CO_3^{2-} component's structural identity is ambiguous as it is often considered adsorbed onto the surface. Oxygen is present in three different ions in bioapatite: phosphate, hydroxyl and carbonate ions. Because of the strong P—O bonds phosphate oxygen is considered more resistant to low temperature inorganic alteration processes, than carbonate oxygen (Kohn et al., 1999; Kohn and Cerling, 2002). However, during microbiological reactions even the phosphate oxygen isotope composition can be changed due to enzymatic catalysis between PO_4^{3-} and water (e.g., Blake et al., 1997; Zazzo et al., 2004a,b; Liang and Blake, 2007). Nevertheless, it was shown experimentally that when enamel (i.e., well-crystalized bioapatite) is subjected to bacterially mediated conditions, the oxygen isotopic composition of the phosphate group was not affected (e.g., Zazzo et al., 2004a,b). Moreover, enamel is the preferred tissue for isotopic investigations because it contains the highest proportion of apatite (96%), and structurally compact with little pore space and large phosphate crystallites (up to 1 μm long), arranged in a decussate texture (Kohn et al., 1999). As a result enamel is more resistant to diagenesis than other tissues in the same taphonomic context (Thorp and Van Der Merwe, 1987; Quade et al., 1992; Ayliffe et al., 1994; Wang and Cerling, 1994; Koch et al., 1997).

There is a widely used method to monitor diagenetic effects. Oxygen from the body fluids is in isotopic equilibrium with both the carbonate and phosphate ions of the inorganic tissue. Several studies have found a constant offset between the $\delta^{18}O_{CO3}$ and $\delta^{18}O_{PO4}$ values for non-altered mammal tooth enamel and the $\delta^{18}O_{CO3} - \delta^{18}O_{PO4}$ slopes are similar for different species (Bryant et al., 1996; Iacumin et al., 1996; Arppe and Karhu, 2006, 2010; Tütken et al., 2007; Pellegrini et al., 2011; Domingo et al., 2013). Because it seems quite improbable to find isotopically altered

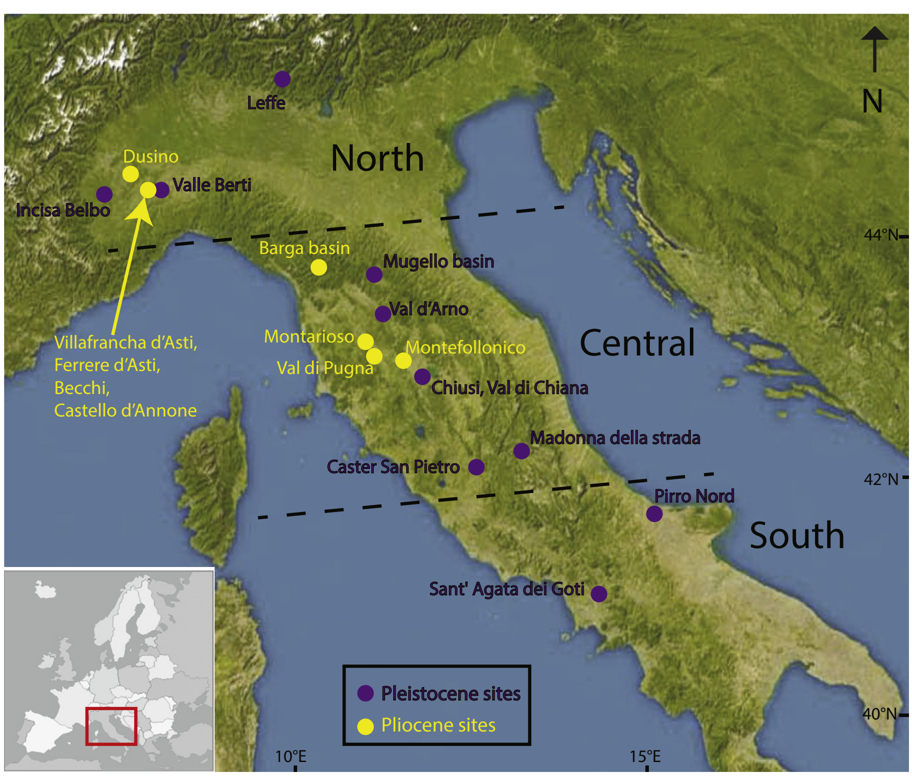

Fig. 1. Location of paleontological sites cited in Table A1 (the map shows the present day locations.).