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Early diagenesis of bone and tooth apatite in fluvial and marine settings: Constraints from combined oxygen isotope, nitrogen and REE analysis

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ABSTRACT

Fossil bones and teeth of Late Pleistocene terrestrial mammals from Rhine River gravels (RS) and the North Sea (NS), that have been exposed to chemically and isotopically distinct diagenetic fluids (fresh water *versus* seawater), were investigated to study the effects of early diagenesis on biogenic apatite. Changes in phosphate oxygen isotopic composition ($\delta^{18}O_{PO4}$), nitrogen content (wt.% N) and rare earth element (REE) concentrations were measured along profiles within bones that have not been completely fossilized, and in skeletal tissues (bone, dentine, enamel) with different susceptibilities to diagenetic alteration.

Early diagenetic changes of elemental and isotopic compositions of apatite in fossil bone are related to the loss of the stabilizing collagen matrix. The REE concentration is negatively correlated with the nitrogen content, and therefore the amount of collagen provides a sensitive proxy for early diagenetic alteration. REE patterns of RS and NS bones indicate initial fossilization in a fresh water fluid with similar REE compositions. Bones from both settings have nearly collagen-free, REE-, U-, F- and Sr-enriched altered outer rims, while the collagen-bearing bone compacta in the central part often display early diagenetic pyrite void-fillings. However, NS bones exposed to Holocene seawater have outer rim $\delta^{18}O_{PO4}$ values that are 1.1 to 2.6‰ higher compared to the central part of the same bones ($\delta^{18}O_{PO4}$ = 18.2 ± 0.9‰, n = 19). Surprisingly, even the collagen-rich bone compacta with low REE contents and apatite crystallinity seems altered, as NS tooth enamel ($\delta^{18}O_{PO4}$ = 15.0 ± 0.3‰, n = 4) has about 3‰ lower $\delta^{18}O_{PO4}$ values, values that are also similar to those of enamel from RS teeth. Therefore, REE concentration, N content and apatite crystallinity are in this case only poor proxies for the alteration of $\delta^{18}O_{PO4}$ values.

Seawater exposure of a few years up to 8 kyr can change the $\delta^{18}O_{PO4}$ values of the bone apatite by >3‰. Therefore, bones fossilized in marine settings must be treated with caution for palaeoclimatic reconstructions. However, enamel seems to preserve pristine $\delta^{18}O_{PO4}$ values on this time scale. Using species-specific calibrations for modern mammals, a mean $\delta^{18}O_{H2O}$ value can be reconstructed for Late Pleistocene mammalian drinking water of around −9.2 ± 0.5‰, which is similar to that of Late Pleistocene groundwater from central Europe.

1. Introduction

Geochemical investigations of fossil bones and teeth have become an important tool in anthropology, archaeology, palaeoecology and palaeontology to constrain the habitat and diet of individual animals and human beings during their lifetime (e.g. DeNiro, 1987; Koch et al., 1994; Thewissen et al., 1996; Koch, 1998; Kohn and Cerling, 2002; Palmqvist et al., 2003; MacFadden et al., 2004; Kohn et al., 2005, Tütken et al., 2006, 2008). In addition, biogenic skeletal apatite and its elemental and isotopic composition is a valuable chemical archive for the reconstruction of past climatic and environmental conditions (e.g. Longinelli, 1984; Ayliffe et al., 1992; Fricke and O'Neil, 1996; Cerling et al., 1997; Sharp and Cerling, 1998; Tütken et al., 2006), thermophysiology (e.g. Barrick and Showers, 1994; Fricke and Rogers, 2000; Amiot et al., 2006), and migration (e.g. Sillen et al., 1998; Hoppe et al., 1999; Müller et al., 2003). For most studies the preservation of primary, *in vivo*-incorporated chemical compositions in fossil bones and teeth is fundamental. However, the trace elements and isotopes, that are incorporated during diagenesis and recrystallisation of the nanocrystalline biogenic apatite, are a valuable source of information to reconstruct the diagenetic environment (e.g. Sillen, 1989; Trueman et al., 2006; Kohn and Law, 2006). The REE concentrations and

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