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The effect of grain size on carbonate contaminant removal from tooth enamel: Towards an improved pretreatment for radiocarbon dating

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ABSTRACT

It is rarely possible to directly radiocarbon date skeletal remains from hot environments as collagen rapidly degrades. Although able to survive in the majority of burial environments for longer, unburnt biological apatites frequently produce inaccurate radiocarbon dates due to contamination from carbonate in the groundwater. The location of this contamination within the skeletal material is rarely investigated, hampering development of improved radiocarbon pretreatment methods. This paper focuses on tooth enamel and aims to test whether carbonate contaminants are sitting at the crystallite boundaries, and from this to test a pretreatment to produce more accurate radiocarbon age estimates. Although the porosity of enamel is low, trace elements are thought to diffuse between enamel prisms and crystallites. Gordon et al. (2015, *Science*, 347 (6223), 746-750) identified magnesium substituted amorphous calcium phosphate between the apatite crystallites. This phase contains the majority of magnesium within modern rodent enamel, providing an opportunity to monitor its removal, and thus test whether carbonate contaminants are located between or on the surface of the crystallites. Modern *Sus scrofa* and four ancient *Sus scrofa* teeth have been used to demonstrate that the more finely ground the enamel, the more magnesium can be removed with an acetic acid leach, and the more accurate the radiocarbon dates. After leaching in acetic acid, teeth dating to beyond the limit of the radiocarbon method (c.50 ka) produce ages of c.20 kBP when hand ground, and c.30 kBP when mechanically ground. This suggests that some contaminants are sitting at the crystallite boundaries. However, although mechanically grinding substantially increases the amount of carbonate contamination removed in an acid leach compared to hand grinding, not all contaminants could be removed from the samples examined in this study, and radiocarbon dates on tooth apatite should still be regarded as minimum ages.

1. Introduction

Bone, dentine and enamel are made of varying proportions of organic, primarily protein, mineral and water phases. The protein fraction is normally targeted when radiocarbon dating skeletal remains. A variety of cleaning protocols, or 'pretreatments', that effectively remove contaminants have been developed over several decades of intensive research (Brown et al., 1988; Longin, 1971; Marom et al., 2012; McCullagh et al., 2010; Ramsey et al., 2004; Stafford et al., 1988; Tisnérat-Laborde et al., 2003). However, in warm environments collagen rapidly degrades and, if water is present, leaches out of bone and dentine (Collins et al., 2002; Hedges, 2002). As a result, in these environments it is rarely

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possible obtain sufficient collagen to accurately radiocarbon date skeletal material beyond a few thousand years (Calo et al., 2015; Storm et al., 2013; Wood et al., 2013; Zazzo et al., 2014). Without the ability to directly date skeletal remains, it is exceptionally difficult to create high quality chronologies for e.g. cemetery sites or the domestication of fauna.

The mineral component of bone and enamel, bioapatite, outsurvives collagen in the majority of deposition environments. Although it can preserve stable isotopic signatures for more than 1 ma (Lee-Thorp, 2002), radiocarbon age estimates are normally found to be younger than expected. Within the Holocene, dates on bioapatite normally underestimate the expected age of a sample by a few hundred ^{14}C years, but in the Pleistocene this can increase to 10,000s ^{14}C years (Grün et al., 1997; Haynes, 1968; Hedges et al., 1995; Zazzo, 2014; Zazzo et al., 2013; Zazzo and Saliège, 2011).

Enamel has long been thought to provide a more reliable material for radiocarbon dating than bone apatite (Haynes, 1968) because it has lower porosity and a smaller surface area (Hedges et al., 1995; Millard and Hedges, 1996), larger crystallites (26.3 × 100–1000 nm vs. 5 × 100 nm (Bottero et al., 1992; Cui and Ge, 2007)), and is less soluble due to its lower carbonate content (3.5 wt% vs. 6 wt% (Elliott, 2002)). Despite these observations, relatively few studies have focused on radiocarbon dating enamel. When Zazzo (2014) reviewed the limited data and added several extra case studies he found that when bone and enamel apatite were pretreated in a similar manner, they underestimated the age of the samples to a similar extent, and he concluded that they are equally poor materials for radiocarbon dating.

However, enamel has a complex hierarchical structure which is quite different to that of bone. Does this mean that contamination could be more effectively removed from enamel if it were pretreated in a different way to bone? This paper aims to consider the effect of enamel structure on the potential diagenetic pathways which could add exogenous carbonate to tooth enamel, and investigate whether a better understanding of one of these pathways may enable more accurate radiocarbon dates to be produced.

1.1. The structure of tooth enamel

Tooth enamel consists of an inorganic mineral phase, the focus of this study, with a small proportion of organic material (<1% (Lee-Thorp, 2002)) and water. In mammals, the inorganic phase consists of crystallites of bioapatite (human: 26.3 × 68 x 100–1000 nm (Cui and Ge, 2007)) arranged into micrometer-sized prisms (also known as rods) which are woven into various structures through the enamel cross-section (known as the schmelzmuster). Between the prisms, crystallites are arranged into an interprismatic matrix (terminology follows Koenigswald and Sander (1997), Fig. 1).

The crystallites are formed of hydroxyapatite, also known as bioapatite, with the general formula $Ca_{10}(PO_4)_6OH_2$, into which various ions are substituted. Carbonates can be located in a number of environments within the apatite phase. Most carbonate is found in the B position, substituting for phosphate, with some found in the A position, substituting for hydroxyl ions, and the remaining in as yet poorly defined environments (Elliott, 1994). Several early studies proposed that non-apatite mineral phases may also be present in enamel (Driessens, 1982; Driessens and Verbeeck, 1982, 1985; Hallsworth et al., 1972), and in 2015 Gordon et al. demonstrated that magnesium is concentrated between crystallites in non-pigmented rodent enamel. They suggested this was contained in a magnesium substituted amorphous calcium phosphate (Mg-ACP). In rodent enamel, the Mg-ACP phase contains carbonate, and at crystallite junctions the concentration of carbonate is higher than in the apatite (Gordon and Joester, 2015). The chemical location of carbonate within this phase is not yet known.

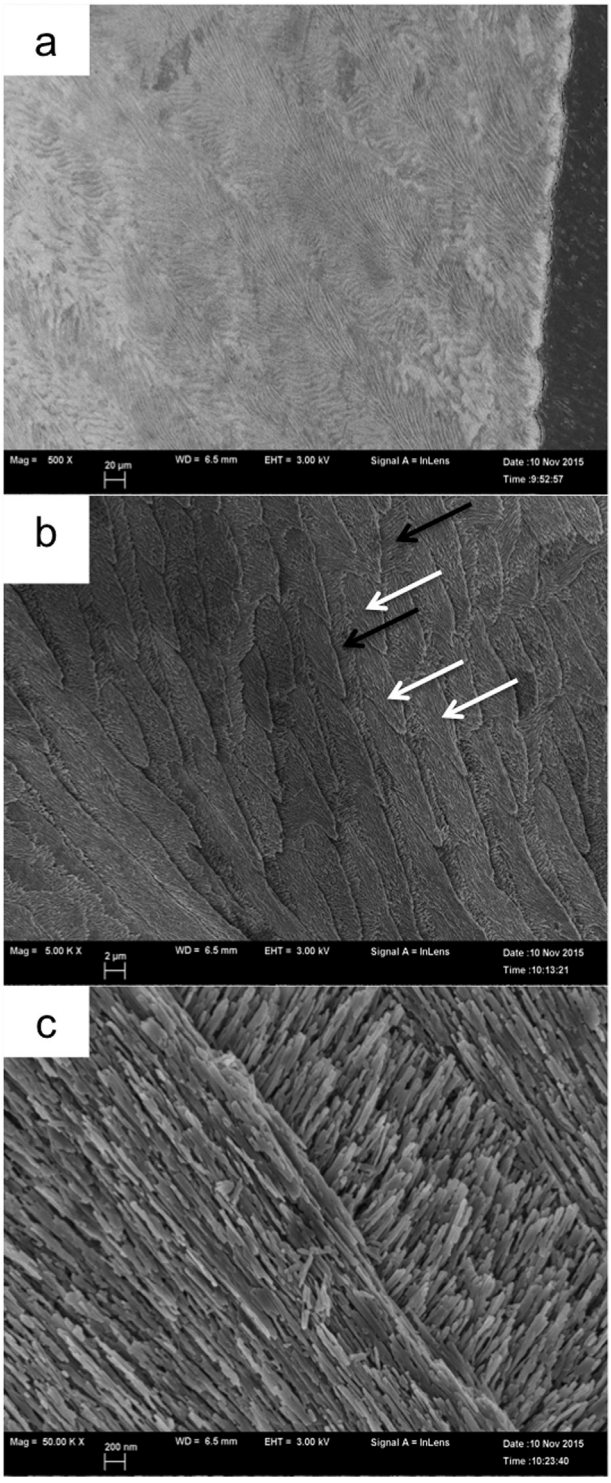

Fig. 1. Secondary electron FESEM images of a longitudinal section of a modern *Sus scrofa* M3 after etching in acid (2 M HCl, 30 s) and coating in Pt, demonstrating the microstructure of tooth enamel. a) Enamel is the pale material to the left and dentine the darker material to the right. Scale bar 20 µm b) Prisms (white arrows) and interprismatic matrix (black arrows). Scale bar 2 µm c) Crystallites in prismatic and interprismatic enamel. Scale bar 200 nm.

Although enamel porosity is low, pores are present and play an important role in the diffusion of water and solutes through the tooth (Shellis and Dibdin, 2000). Pores exist both between prisms and within prisms (Shellis and Dibdin, 2000). In agreement with