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Increasing accuracy for the radiocarbon dating of sites occupied by the first Americans

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ABSTRACT

Genetic analysis of Paleoamerican human remains suggests that people first entered the Americas sometime between ~14,000 and ~16,000 years ago. Evaluation of these data requires unequivocal archaeological evidence in a solid geological context that is well dated. Accurately determining the age of late Pleistocene sites is thus crucial in explaining when and how humans colonized the Americas. There are, however, significant challenges to dating reliability, especially when vertebrate fossils (i.e. bones, teeth and ivory) are often the only datable materials preserved at sites.

We re-dated vertebrate fossils associated with the North American butchering sites of Wally's Beach (Canada), La Prele [also known as Fetterman (Wyoming)], Lindsay (Montana), and Dent (Colorado). Our work illustrates the crucial importance of sample chemical preparation in completely removing contaminants derived from sediments or museum curation. Specifically, our work demonstrates that chromatographic methods, e.g. preparative High Performance Liquid Chromatography and column chromatography using XAD resins, are currently the only efficient methods for removing environmental and museum-derived contaminants. These advanced techniques yield demonstrably more accurate AMS ^{14}C measurements that refine the ages of these four sites and thereby contribute to advancing our understanding of human dispersals across North America during the late Pleistocene.

1. Introduction

The arrival time of the first humans into North America is an extremely debated topic within the scientific community (Goebel et al., 2008; Meltzer, 2009, 2015). For most of the 20th century, it was widely believed that near the end of the last Ice Age, when sea levels were lower, prehistoric hunters from eastern Siberia followed prey animals across the Beringia Land Bridge into modern-day Alaska. When the ice sheets receded and exposed a path southward, the colonizers moved across the vast unpopulated continent, established a permanent human presence and, while doing so, possibly caused the extinction of 30 + genera of large mammals (Grayson and Meltzer, 2003; Haynes, 2013; Martin, 1958, 1973). These presumed earliest settlers were termed “Clovis”, a name derived from the town of Clovis, New Mexico, where their distinctive tools, dating to ca. 13,000 Cal BP, were first recognized at the site of Blackwater Draw (Waters and Stafford, 2007). The ensuing discovery of Clovis stone and osseous tools across North America reinforced the idea that Clovis people were the first Americans (Meltzer, 2009; Waters and Stafford, 2007). The discovery of new archaeological sites and the re-evaluation of old collections, however, suggest that humans reached the Americas several millennia before 13,000 Cal BP—the earliest time range for the Clovis complex (Amick, 2017; Bourgeon et al., 2017; Halligan et al., 2016; Waters and Stafford, 2007, 2014). Radiocarbon dates on organic matter from the archaeological site of Monte Verde, Chile, for example, point to a human occupation aged at around 12,300 BP or 14,200 Cal BP (MV-II).

To build robust chronologies for the peopling of the Americas, accurate radiocarbon dating is required. For radiocarbon results to be accurate, however, samples must be free of contamination. In this paper, we focus on the dating of collagen from vertebrate fossils that

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are commonly contaminated with humates accumulated during burial and/or preservatives added by museum curation processes. Humates were identified as primary contaminants in the early 1950s (Münnich, 1957), while post-excavation conservation was addressed somewhat later (Bronk Ramsey, 2008). Inaccurate radiocarbon dates are rarely caused by problems associated with the measurement, but are predominately the result of inadequate sample pretreatment. Over the last 35 years, numerous methods have been used to chemically purify bone, teeth, and ivory for ^{14}C dating by accelerator mass spectrometry (AMS). At the Oxford Radiocarbon Accelerator Unit (ORAU), the most commonly used pre-treatment for bone samples is demineralization in HCl, followed by an alkali wash, and gelatinisation followed by ultrafiltration (Brock et al., 2010a; Higham et al., 2006). In some cases, this method is unable to completely isolate uncontaminated collagen because of cross-linking and degradation of the collagen molecule. This is particularly true when samples are heavily contaminated with humic substances, conservation materials, or both. To resolve this problem, a few laboratories have used an entirely different approach—chromatography—to isolate the compound of interest. Following the work of Abelson and Hoering, who used ion exchange chromatography to isolate individual amino acids for stable isotope analysis (Abelson and Hoering, 1961), Ho et al. used cation exchange chromatography to purify petroleum-contaminated bones (Ho et al., 1969). They were followed by groups isolating a specific amino acid, hydroxyproline (HYP), for direct radiocarbon dating (Benders, 2010; Gillespie et al., 1984; Marom et al., 2012, 2013; Stafford et al., 1982, 1991). Reverse phase chromatography is another chromatographic technique that separates humates from collagen hydrolyzates by using XAD resins (Stafford et al., 1987, 1988). There are different types of XAD resins that are commercially available and are described in (Stafford et al., 1988). They can be used to isolate weakly or non-ionized aliphatic and aromatic molecules from aqueous solutions. They are used, for example, to extract dilute organic chemicals from environmental and physiological fluids, to concentrate humates from fresh and marine waters, and in liquid chromatography, to separate weak polar compounds from aqueous solutions (Stafford et al., 1988). The first application of this approach for ^{14}C dating archaeological bones was by Stafford et al. in 1982 and 1988 (Stafford et al., 1982, 1988). They developed this procedure to remove humates from gelatin hydrolyzates for either subsequent isolation of hydroxyproline and proline or in the dating the XAD-purified hydrolyzate directly (Stafford et al., 1982, 1988). A flow chart showing the different fractions that can be isolated using this method is reported in Fig. 1. Subsequently, the method has been applied to numerous archaeological and paleontological dating projects, including samples from North and South America (Waters and Stafford, 2007; Waters et al., 2015).

At the ORAU, attention has focused on dating the amino acid hydroxyproline, which is obtained after the hydrolysis of collagen and separation by preparative High Performance Liquid Chromatography (prep-HPLC) (Devièse et al., 2018; Gillespie et al., 1984, 1986; Marom et al., 2012; Nalawade-Chavan et al., 2014). A flow chart showing the different steps of the procedure is reported in Fig. 2. The efficiency of the method in removing contaminants from heavily contaminated samples and its ability to provide very accurate ^{14}C measurements has been demonstrated in several recent notable cases involving Paleolithic sites in France (Bourrillon et al., 2017), Croatia (Devièse et al., 2017), Russia (Marom et al., 2012; Nalawade-Chavan et al., 2014; Reynolds et al., 2017; Sikora et al., 2017) and the Americas (Becerra-Valdivia et al., 2018).

Accurate AMS ^{14}C dates on fossil bone are crucial to testing archaeological and paleontological hypotheses. In this paper, we evaluate the accuracy of two important chemical purification methods: isolating HYP by prep-HPLC, and using XAD resins to purify collagen hydrolysates. To do this, we chose four North American archaeological sites that had already been dated by XAD resin methods and we re-dated the same bone specimens by extracting hydroxyproline. We also compare the results against other ^{14}C determinations obtained using different pretreatment methods.

2. Materials

There are multiple Clovis-aged and older archaeological sites in North America where human presence is established by lithic assemblages, taphonomy, cut marks or combinations of these. For our experiment, seven vertebrate fossils associated with the North American butchering sites of Wally's Beach (Canada), La Prele [also known as Fetterman (Wyoming)], Lindsay (Montana) and Dent (Colorado) were selected (Table 1).

Three bone samples included in this study are from Wally's Beach (Table 1). This site is located at St. Mary's Reservoir, Alberta (Canada), and represents the only known late Pleistocene kill and butchery site at the southern margin of the ice-free corridor (Kooyman et al., 2006, 2012; Waters et al., 2015). The animal assemblage includes extinct megafauna (camel and horse), extinct muskox (*Bootherium bombifrons*), caribou and bison. The animal remains are being exposed by eolian deflation, but were originally buried by 1.5–2.0 m of eolian silt and sand that overlies Wisconsinan glacio-fluvial sediments. At the site, seven horses and one camel were killed and butchered by humans based on cut marks on bones and the partial scattering and dismemberment of the carcasses. Each of the carcasses was horizontally separated from one another by 25–100 m over a distance of 500 m and were found with non-diagnostic lithic artifacts (Waters et al., 2015).

Two samples are from Dent, Colorado (USA). This site was originally discovered in 1932 when flood runoff uncovered a mammoth bone near Milliken, Colorado (Brunswig, 2007). The initial excavation in 1932 revealed fluted Clovis projectile points among the bones (Brunswig, 2007). Subsequent excavations revealed the presence of 15 individual mammoths (Saunders, 1999) within a bone stratum 1.5 m thick. Brunswig considers the site to represent humans killing a mammoth herd based on the number and position of projectile points recovered among the bones. Both samples are from mammoth (*Mammuthus columbi*) elements and contain humic acid contamination. One of the two samples was also preserved with an unknown adhesive, possibly Gelva (Table 1).

Another mammoth sample selected for this study is from the La Prele site, Wyoming, USA (formerly called the Fetterman site). Excavations at the site in 1986 produced a single sub-adult mammoth (*Mammuthus columbi*), the fragmental remains of a bison (*Bison* sp.) and assorted lithic artifacts (Byers, 2002). The mammoth was found 27 cm below the surface of soil 4, which was colluvium and described as a “massive clayey sand” (Byers, 2002). Excavations during the last few years have also produced artifacts of the Clovis complex (Byers, 2002; Mackie et al., 2017). The bones were deemed physically unstable and were stabilized and reconstructed using adhesives, including Glyptol and Paraloid B-72. A neural spine unquestionably from the mammoth was selected for dating (Table 1).

The final specimen was from a mammoth (*Mammuthus columbi*) that was excavated in 1967 from late Pleistocene loess near Lindsay, Montana, USA (Davis and Wilson, 1985). At this site, loess began to accumulate at the end of the Pleistocene and was derived from a nearby glacial lake bed that was a few kilometers from the Wisconsin maximum ice margin (Davis and Wilson, 1985). The Lindsay mammoth was interpreted as a cultural site based on the taphonomic patterns of disarticulation and spiral fracturing (Davis and Wilson, 1985; Hill and Davis, 1998, 2014; Waters and Stafford, 2014). The absence of lithic artifacts was used to question the