Journal of Archaeological Science: Reports 17 (2018) 500–509

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

# Some thoughts on bone artefact discolouration at archaeological sites

Justin Bradfield

*Evolutionary Studies Institute, University of the Witwatersrand and School of Geography, Archaeology and Environmental Studies, University of the Witwatersrand, Private Bag 3, WITS 2060 Johannesburg, South Africa*

## ABSTRACT

This paper explores the role of plant enzymes associated with food processing in the discolouration of archaeological bone tools. I present the results of colorimetric analysis aimed at quantifying the range of discolourations produced on bone implements by various food produce (fruits, vegetables and cereals) and compare these data to discolourations produced through above-ground heating events. I show that certain plants, particularly ones with high polyphenol content, produce visible discolourations to the surface of experimental bone tools and, furthermore, that these discolourations are significantly different to the CIE colour values produced on bone surfaces exposed to heating events of longer than 2 min. Although some overlap exists, processing of certain plants produces elevated values primarily on the b* axis with concomitant low L* values relative to heated bone samples. These results are confirmed against FTIR and pXRF analysis. While further research is needed before these results can be applied meaningfully in an archaeological context, this paper highlights the potential of quantifying bone surface discolouration in investigating the probable function of archaeological tools, and that surface discolouration should never be dismissed as a taphonomic alteration.

## 1. Introduction

Bone artefacts recovered from archaeological sites frequently appear discoloured due either to taphonomic processes or cultural events (Emery, 2011). Patterning of bone discolouration may signal multiple taphonomic processes and is often used in forensic anthropology to interpret the sequence of events in body decomposition (Huculak and Rogers, 2009; Dupras and Schultz, 2014). Determining the origin of a stain may help in the interpretation of taphonomic events at a site. Bone surface discolouration may be linked to a variety of causal factors, including decomposition of the flesh, duration of exposure to sunlight, chemical composition of the soil, fungal activity, heating events, as well as cultural events, such as burial and ornamentation. The extended use-life of bone artefacts in many cultures around the world may also result in discolouration over time (Choyke and Daróczi-Szabó, 2010). Studies conducted by Huculak and Rogers (2009) and Dupras and Schultz (2014), among others (e.g., Bennett, 1999; Haglund and Sorg, 2001), have sought to describe and characterise bone discolouration linked to some of these events. In most instances, the Munsell Chart was used to describe the colours, despite more recent criticisms that this method of colour determination is subjective and woefully inadequate (e.g., Fredericks et al., 2015; Kars and van den Eijkel, 2016).

In this paper I explore a seldom-considered cause of bone discolouration: plant food processing. Plant processing was an important part of subsistence strategies in the past, and it stands to reason, given the high quantities of enzymes and tannins in some of these plants, that, over time, this would have an effect on the implements used to perform these processing activities; particularly implements made of bone. Although many of the foods are indigenous to the region in which I work, southern Africa, I have tried to present a representative sample of comestibles that could have been harvested and processed by bone tools in various regions and at various times in the past. My aim is to characterise the range of discolouration caused by plant processing activities by comparing the colorimetric values thus obtained against those obtained through heating events.

Following recent methodological advances in colorimetry (e.g., Fredericks et al., 2015; Rifkin et al., 2016) I present the CIE-L*a*b* and ΔE colour values of experimental bone implements used to process various types of fruit and cereals. CIE is an international standard convention for measuring colours produced using three spectra of light. These three spectra consist of white light or light intensity (the L* value) the colour spectrum from green to red (the a* value) and the yellow to blue spectrum (the b* value). When these three sources combine they form the ΔE value. In nature the perception of colour is dependent on, among other things, ambient light and the surface area of the object being viewed. Spectrophotometry ensures that colours can be compared to a reference standard independent of user, ambient light and surface area. Colorimetry has been used recently as a diagnostic tool to identify suitable bone for DNA studies by correlating colour changes of heated bone with changes in physical properties (Fredericks

*E-mail address:* justin.bradfield@wits.ac.za.

https://doi.org/10.1016/j.jasrep.2017.12.022
Received 7 September 2017; Received in revised form 27 November 2017; Accepted 8 December 2017
2352-409X/ 

et al., 2012, 2015). In this example, colorimetric analysis is used to identify bone that has been heated beyond the point that DNA typically survives. In food science colorimetry has been used specifically to quantify the browning effects of PPO in various fruits (Holderbaum et al., 2010; Zhang and Shao, 2015). In archaeology, colorimetry is now being used to measure the colours of ochres and other pigments, and, together with XRF and FTIR, is being used to help identify the sources of discolourations and to characterise ancient pigments (e.g., d'Errico et al., 2012; Rifkin et al., 2016).

### 1.1. Common causes of bone discolouration

Perhaps the most documented cause of archaeological bone discolouration is heating. Archaeological bone may be heated intentionally when cooking meat or as fuel for a fire, and unintentionally when a hearth is formed directly above or in close proximity to buried bone. When bone is heated beyond a certain point chemical processes take place including the oxidation of collagen, resulting in a darker appearance (Shipman et al., 1984; Fredericks et al., 2015). Colorimeric studies of burned bone have noted a direct correlation between the duration of the heating event and increases in a* and L* values (e.g., Abdel-Maksoud, 2010). Over time, as the collagen is eventually depleted, the bone starts to turn white in a process known as calcination. Bone that is continuously heated typically passes through a series of stages characterised by colour changes. In general, a yellowish-brown colour is succeeded by a darker brown, which eventually turns black, then ash-grey and finally chalk-white (Shipman et al., 1984; Shahack-Gross et al., 1997; Hanson and Cain, 2007; Imaizumi, 2015). The degree of bone discolouration is not just a factor of temperature, but of duration and soil matrix too (Bennett, 1999; Imaizumi, 2015). Calcination generally only occurs when bone is exposed directly to the fire and is seldom seen on bone heated while buried (Stiner et al., 1995), which will typically display a quasi-uniform surface discolouration (Bennett, 1999). It has been noted that the range of discolouration evident on archaeological bone is typically greater than that of experimentally-heated bone, although following the same trajectory of colour changes described above (Hanson and Cain, 2007). This is because archaeological bone may be exposed to many other factors that compound discolouration (Nicholson, 1993).

The role of mineral composition of soils on bone discolouration and staining has long been recognised (e.g., Oakley, 1954; Shahack-Gross et al., 1997). Soils with high humic content often result in richer brown hues developing on bone surfaces due to the high concentration of organic acids (Dupras and Schultz, 2014). Mineral precipitates, such as salts, present in the soil matrix may crystallise on the bone surface resulting in calcium carbonate encrustations, which may bleach the bone causing a white discolouration (Dupras and Schultz, 2014). The presence of tannins or iron oxides in the sediment typically result in bone turning a deep chocolate brown colour, while well-drained soils conducive to oxidising conditions can result in bright red to brown discolourations on bone. Similarly, the presence of reduced manganese will tend to produce darker brown to black stains (Schultz et al., 2003; Dupras and Schultz, 2014). The soil solution, unique chemistry and pH all contribute to diagenetic alterations of and effect colour changes in the outer layers of bone (Millard, 1996). Iron and manganese in the soil can infiltrate bone and other porous osseous materials causing dark stains to develop (Stermer et al., 1995; Brown et al., 2014). These stains may present pervasively over the bone surface or as patches of discolouration depending on the unique depositional conditions. Manganese is usually the most abundant metal present in soil and can occur in several varieties, each resulting in different colours to bone surfaces with which it has come in to close proximity (Emsley, 2001; Dupras and Schultz, 2014). For example, manganese dioxide causes black stains (Cukrowska et al., 2005), whereas manganese carbonate will result in pink to reddish-brown discolourations (Anthony et al., 2010) and permanganates in purple stains (House, 2008). Among the metallic elements, iron and copper occur most abundantly in archaeological deposits and are the most common metals to corrode and stain bone (Dupras and Schultz, 2014; Bradfield, 2016). Different copper alloys may also cause different blue-green hues similar to that produced by manganese (Dupras and Schultz, 2014). Moist, acidic conditions are conducive to corrosion (Janaway, 2008) and it is in these environments that we can expect a variety of bone discolourations.

Contact with corrosive materials may be incidental, but in many cases it has a cultural cause and indeed bone discolouration can inform on certain socio-cultural practices or phenomena. Many societies bury their dead with jewellery and other personal paraphernalia. Copper jewellery, for instance, placed on or near the body imparts a green discolouration to the bone (Morris, 1981; Hopkinson et al., 2008), while corpses prepared with ochre impart a red or yellow colour to the bones when the body decays (Wreschner, 1980). Similarly, Argáez et al. (2011) found that amorphous black spots present on human bones from Mexico were caused by bitumen, a substance applied as a lubricant to a metal tool during corpse dismemberment prior to burial. Certain bone preparation agents, such as hydrochloric acid and sodium hydroxide may discolour bone brown and white respectively (Dupras and Schultz, 2014) and even certain medical conditions during life, such as diabetes or simply old age, may result in some anomalous bone discolourations, usually tending to a yellowish hue (Gruspier, 1999; Schafer, 2001). As noted in the introduction, many societies fashion tools and ornaments from bone, and these tend to have a long use-life. Bone that is in prolonged contact with skin, such as necklaces, pendants or awls, are exposed to oils secreted by the skin. Over time these oils impart a golden-brown colour to the bone (Choyke and Daróczi-Szabó, 2010).

In humic-rich sediments certain plant and fungal remains can also discolour bone (e.g., Turner et al., 2017). Purple stains on bones from medieval Britain were found to be caused by an enzyme of fungal origin, known as purple acid phosphatase (Cole and Waldron, 2016). Certain organic compounds present in plant tissue when it breaks down may impart specific colours to the surrounding soil matrix and to any bones in close proximity. For example, chlorophyll in algae and green leaves will impart a greenish stain, whereas xanthrophyll will cause a yellowish tinge to develop, and carotenoids typically produce orange discolourations (Davies, 2004). These stains may occur incidentally or when a bone tool is deliberately used to work or process plant material. Stokes (2016) describes the distinct brown staining produced on 17th century bone apple corers as a result of the chemical reaction of the enzyme polyphenol oxidase (PPO). Polyphenol oxidase is found in various concentrations in the chloroplasts of all plants, with the greatest concentrations occurring in the ripe fruit (Ortega-Garcia et al., 2008; Holderbaum et al., 2010). This enzyme is responsible for oxidising phenolic compounds in the plant and is the substance that turns a cut apple or potato brown (McLandsborough, 2007; Taranto et al., 2017). Given the abundance of this enzyme and the frequency with which archaeological tools would have contacted it, it is perhaps surprising that so little attention has been afforded its role in bone tool discolouration.

### 1.2. Plant properties and processing among hunter-gatherer societies

Humans obtain more than 90% of their diet from plant sources (Eaton and Konner, 1985). This statement is no less true of archaeological societies, be they hunter-gatherers or agri-pastoralists (e.g., Krige, 1937; Wehmeyer et al., 1969; Zarrilo and Kooyman, 2006). Many plant foods require processing to aid in their digestibility (Stahl, 2014). Plant food processing may range from fairly simple (e.g., husking, grinding, peeling, removing seeds) to comparatively complex (e.g., soaking, fermentation, baking), with most plant foods require heavy processing (Wollstonecroft, 2002; Torrence and Bartram, 2006). How a food is processed may result in nutritional gains or losses (Stahl, 2014). For example, a potato must be boiled or baked until soft for the human digestive system to derive any nutritional benefit from its consumption.