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Thermogravimetric analysis of property changes and weight loss in incinerated bone☆

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ABSTRACT

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are thermal analyses techniques, which can give vital information about a material's properties and phase transitions when exposed to heating. This study utilised a combined TGA-DSC approach to determine how exposure to varying temperatures and different heating regimes affect the decomposition of skeletal hard tissue. It was found that an accelerated heating rate causes the onset of phase changes in the bone matrix to be delayed to higher temperatures. The progression of matrix changes within a certain phase is also highly dependent on the rate of heating. Longer exposure times or slower heating rates increase progression of decomposition within a certain phase, progression to a different material phase however will only occur after a key "activation temperature" is reached. These findings have important implications for the subsequent analytical investigations of burnt bone.

1. Introduction

Burnt bones are a frequent occurrence in forensic contexts, be it in the aftermath of a mass disaster, intentional immolation or to hide a homicide, as well as in archaeological contexts. Heat is an extremely destructive force, which changes not only the morphology and architecture but also the elemental and isotopic compositions of bone. The extracellular matrix of bone is composed of a mineral phase (65 wt.%), an organic phase (25 wt.%) and water (10 wt.%) (Chen et al., 2011). The mineral phase consists of a poorly crystalline, non-stoichiometric form of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), also known as dahllite, which incorporates several elemental substitutions, such as Mg and other ions, however the most abundant substitution is carbonate (3–8 wt.%) (Figueiredo et al., 2010). Depending on its crystal position, carbonate apatite is classified either as a "Type A" (OH^-) or "Type B" (PO_4^{3-}) substitution, with the latter being more commonly found in human bone. Despite the low percentage of lattice substitutions they play a vital role in the bone's metabolism, and it has been found that carbonate not only decreases bone's crystallinity, but also accelerates its biodegradation rate (Figueiredo et al., 2010). The main component of the organic matrix is type I collagen, secondary components are non-collagenous organic proteins including phosphoproteins, which may play a role in the regulation of crystal size, orientation and habit of the mineral matrix (Rho et al., 1998; Olszta et al., 2007). The composition and geometrical spatial arrangement of bone vary between different skeletal elements, or depending on factors such as age, pathology, disease or species (Aerssens et al., 1998; Quelch et al., 1983).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are techniques very well established in materials sciences and frequently applied to determine the properties of natural and synthetic hydroxyapatites (Stanczyk and Van Rietbergen, 2004; Raynaud et al., 2002; Figueiredo et al., 2010; Bertoni et al., 1998; Bahrololoom et al., 2009; Gelinsky et al., 2008) for tissue engineering. Both techniques measure the heat effects accompanying chemical reactions and phase transitions as a function of temperature.

Their potential for the advancement of knowledge in the archaeological sciences is yet to be fully utilised.

The literature is in congruence in finding the weight loss of heated bone to occur in three successive stages, the first below 200 °C, the second between 200 °C and 600 °C and a third step between 700 °C and 900 °C. At temperatures beyond 900 °C weight loss has been determined to not be of significance (Figueiredo et al., 2010; Mkukuma et al., 2004; Peters et al., 2000; Mayne Correia, 1997; Pramanik et al., 2013). The first weight loss phase corresponds to an evaporation of water bound to the bone matrix, the so-called "dehydration" phase (Thompson, 2004) whereas the second, the so-called "decomposition" phase is attributed to the combustion of the organic bone components, particularly collagen. The last weight loss phase is mainly due to the release of CO_2 produced though the decomposition of carbonate. This is accompanied by an appearance of hydroxide ions (Mkukuma et al., 2004) and a re-crystallisation of the mineral apatite in the "inversion" phase. The final phase of bone transition occurring at temperatures beyond 900 °C, the "fusion" phase, does not exhibit a large weight loss, but

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rather is characterised by the sintering and melting of the crystallites and the formation of an additional mineral phase, the β-tricalcium phosphate (Thompson, 2004; Ellingham et al., 2015).

In a study designed to determine the effects the proportions of organic content in bone have on the thermal decomposition of the mineral phase, Mkukuma et al. (Mkukuma et al., 2004) found that the two factors are indeed closely related. Whilst all bones lose carbon dioxide when heated between 200 °C and 600 °C, they found this loss to continue more predominantly in bones with a low organic content up to temperatures of 1500 °C, accompanying an adsorption of water. They also found bone of lower organic content to exhibit a greater carbonate content than ones with a higher percentage of organic material, which in turn have a larger content of HPO_4^{2-} ions in their mineral than the former.

Figueiredo et al. (Figueiredo et al., 2010) investigated the differential behaviour of bovine, porcine and human bone (sections from a femoral diaphysis) upon heating, thus drawing inferences on their property variations. Through thermogravimetric analysis (TGA) at a temperature increase of 10 °C/min, they discovered that whilst human and bovine bone exhibit similar water contents, the H_2O content of porcine bone was markedly higher. Collagen content differed no more than 4% between species, with porcine bone also showing the highest weight percentage. The carbonate content of all three tested species is also very similar, with the bovine bone showing slightly higher amounts than the other two.

Peters et al. (Peters et al., 2000) compared the different properties of human healthy spongy bone, callus bone and tumour bone, and found a substantially higher mineral content in tumour bone and the least mineralisation in spongy bone, with the values for callus bone lying in-between. Their study showed tumour bone to exhibit a carbonate content over twice as high as spongiosa, the amount of carbonate in callus bone ranging somewhere in-between. These studies give an insight into the various factors influencing bone composition.

Raynaud et al. (Raynaud et al., 2002) investigated the thermal properties of isolated hydroxyapatite powder. They found the first weight loss to occur at between 1000 °C and 1450 °C, caused by the dehydroxylation of the hydroxyapatite, which accompanies the formation of tricalcium phosphate and tetracalcium phosphate monoxide in a highly endothermic reaction.

Several studies have monitored the thermal behaviour of both, collagen and hydroxyapatite, separately (Lozano et al., 2003; Trębacz and Wójtowicz, 2005). A study comparing the thermal behaviour of intact bone samples and isolated collagen (Lozano et al., 2003) found extracted collagen to be more thermally stable than collagen in bone. They attribute the lack of stability of collagen in bone to the fact that hydroxyapatite crystals in the fibril intraspaces act as fracture centres, decreasing the number of collagenous cross linkage (Lozano et al., 2003; Miles et al., 2005). Trębacz and Wójtowicz (Trębacz and Wójtowicz, 2005) who compared the thermal behaviour of intact bone, demineralised bone and tendon collagen up to 300 °C found the first endothermic peak, which is associated with the loss of water, to occur at temperatures around 100 °C lower in collagen and demineralised bone than in intact bone.

It is the aim of this study to investigate the influence that different heating regimes and varying exposure times have on the rate of property changes of heated bone, and thus the exposure temperature ranges after which successful further analyses can be carried out.

2. Materials and methods

Fresh domestic sheep (*Ovis aries*) rib bones, acquired from a local butcher, containing both compact and cancellous bone, were cut into cross sections weighing approximately 20 mg and analysed on an Evisa® STA 1500 Simultaneous Thermal Analyzer (Bähr-Thermoanalyse GmbH, Hüllhorst, Germany). Samples were enclosed in aluminium oxide crucibles and heated from 20 °C to 1100 °C in a stream of air delivered from a cylinder. Samples were heated in triplicates at heating rates of 6 °C/min, 12 °C/min and 24 °C min. Additionally two sets of samples were heated at a rate of 12 °C/min up to a maximum of 300 °C and 400 °C, at which temperature they were held for 45 min. An empty crucible was heated simultaneously under the same conditions as the samples and the resulting thermogram was subtracted from that of the samples, enabling the correction of buoyancy effects.

3. Results

The thermograms of the samples subjected to the three different heating regimes exhibited comparable patterns showing three distinct stages of weight loss, however occurring at slightly different rates (Fig. 1).

Similarly, the DCS heat flow curves indicated an approximately 25 °C delay in the temperature onset of the matrix phase changes, with every doubling of the heating rate (Fig. 2).

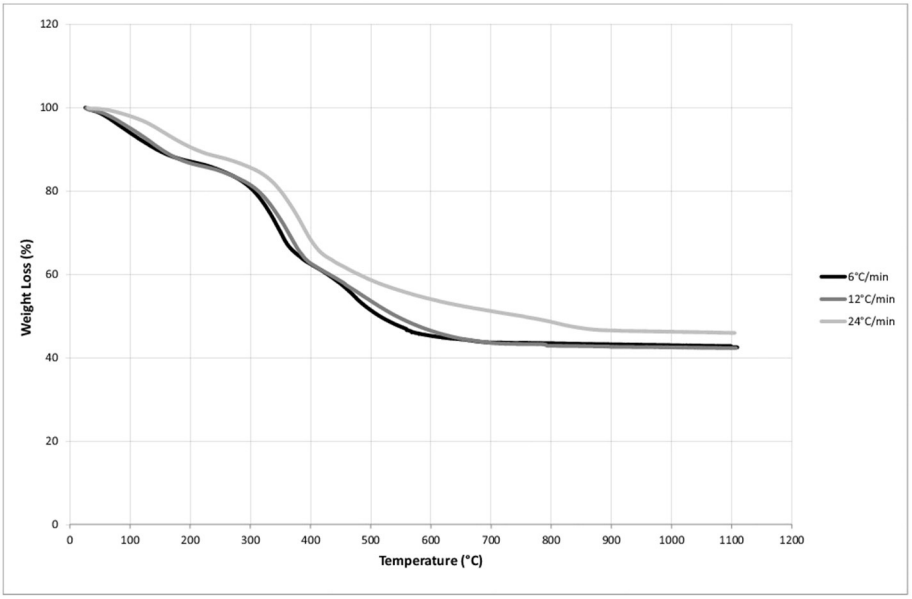

Fig. 1. Average TGA curves of bones subjected to differing heating regimes.