On the structure, chemistry and decay of bone, antler and ivory

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This paper was written in response to a request from the United Kingdom Institute for Conservation, and was delivered at a conference on the conservation of artefacts made from osseous and keratinaceous tissues organised by UKIC at London University in December 1984. The text given here does not constitute a publication and should not be quoted without reference to the author.

The aim of this paper is briefly to summarise the composition, structure and properties of calcified skeletal tissues which have been, and in some parts of the world still are, used in the manufacture of artefacts. The viewpoint is that of a bone specialist whose opinion is often sought on the raw material and possible origin of artefacts made from bone, antler or ivory. The information given is that which it is thought will be of most relevance to conservators, and this has led to the deliberate omission of details which would be of interest to biologists but which have no implications for the conservation of these materials. For most of this paper, the term 'bone' will be used to cover all calcified tissues other than tooth enamel, as details of composition and, to some extent, structure are common to many outwardly different tissues. Distinctions will be drawn between antler, dentine and bones sensu stricto only where explicit differences are to be described. Horn is a keratinaceous tissue which, although it forms over a bone core, has no place in this paper.

Composition

Fresh bone has three main components, namely a complex protein scaffolding, a mineral which stiffens this scaffold, and a 'ground substance' of other organic compounds, these three ingredients being present in different proportions in different hard tissues.

The mineral element is mainly hydroxyapatite, which may be loosely described by the formula Ca10(PO4)6.(OH)2 (Currey 1970, 26). Chemically, this is a fairly stable compound, although the calcium ions may be substituted by strontium, radium or lead, the phosphate ion by a carbonate radical, and the hydroxyl ions by fluoride. In addition, a variety of ions, particularly of metals, can be attached to the surfaces of hydroxyapatite crystals by adsorption rather than substitution. The chemical behaviour of hydroxyapatite appears to be much the same whether the mineral is within a living organism or not. Thus these substitutions and adsorption can be observed in the mineral component of buried bone. The chemistry of bone mineral is discussed in more detail by Fourman and Royer (1968, 11-23).

The structural element in fresh bone is a highly complex protein called collagen. This protein is unusual in containing high proportions of the amino acids glycine and hydroxyproline (Currey 1970, 17), the latter being a particularly characteristic breakdown product of collagen. The important point about the constituents of collagen is the lack of large side-chains on the amino acid groups. This allows the collagen macromolecules to pack together very closely and to bind at regular intervals. The macromolecules are arranged in a left-handedly spiralling triple helix, which itself spirals to the right about a central axis (Ramachandran 1963). To take useful analogy, the structure is not unlike a complex hawser-laid rope, and this gives collagen its characteristics of being strong under tension whilst remaining flexible.

The third element, the ground substance, makes up only a very small proportion of fresh bone, serving as packing and probably also to regulate hydration. It is composed of a variable mixture of mucoprotein and aminopolysaccharides, and for the present purposes is of little importance.

Although the proportions of these three elements vary from tissue to tissue, and even from time to time within one living bone, roughly half of the weight of fresh bone is mineral: the remainder is organic material and water. Of the organic fraction, about 95% is collagen (Fourman and Royer 1968, 5-6).

Structure

Mineralised bone is developed by the secretion of hydroxyapatite by specialised mesenchymal cells called osteoblasts which are arranged upon and within a framework of interwoven collagen fibrils. Although by no means parallel, the collagen fibrils will be roughly aligned to a common axis, which will be defined by the mechanical constraints placed upon the developing bone. It is this axial alignment which gives bone its markedly anisotropic properties, that is its physical characteristics vary according to the plane in which the specimens are tested. Depending upon the species, the part of the skeleton, and the age of the individual, the internal structure of the bone may take on a variety of forms. The compact bone which makes up limb-bone shafts and the outer layers of antlers is the tissue most widely used in artefact manufacture. At its simplest, compact bone takes the form of lamellae deposited more or less concentrically about the longitudinal axis of the bone or antler, and permeated by large and small channels. The cells which are responsible for the secretion and subsequent remodelling of the bone (osteocytes) remain encapsulated in voids (lacunae) within the bone, which are interconnected by an anastomosing network of fine channels (canaliculi). This system is connected at intervals to blood vessels, which thus link the living cells within the bone to the transport network of the rest of the body. Despite its homogeneous and compact appearance, therefore, bone is remarkably porous, albeit on a very fine scale.

This description adequately summarises the main features of the laminar type of bone found commonly in most groups of vertebrates. There are exceptions, however, and for a detailed description of the full range of variations seen in bone structure, the reader is referred to Enlow and Brown (1956; 1957; 1958). For the purposes of this paper, the finer points of bone vascularisation and its evolutionary significance may be passed over. Some mammals, and a few birds and dinosaurs, show reorganisation of the lamellar bone to produce structure called secondary osteones. Essentially, an osteone is a cylindrical unit of heavily mineralised bone formed around a longitudinally-directed blood vessel (Amprino 1963). Compact bone which comprises a dense concentration of osteones flanked on the inner and outer surfaces by lamellar bone is termed 'dense Haversian bone', and a single osteone is sometimes referred to as an 'Haversian system'. Dense Haversian tissue is most commonly found in the bones of man and some large carnivores, less frequently in herbivores, and sporadically in other vertebrates.

Antler, being a fast growing and essentially temporary form of bone, does not normally develop osteones, but has a somewhat lamellated structure permeated by longitudinal, radial and circumferential blood vessels ('plexiform' structure: Enlow and Brown 1958, 206). Antler is also less well mineralised than other bone; that is, it contains a higher proportion of collagen by weight.

Ivory is composed of another form of bone called dentine. Despite having much the same chemistry as bone, dentine has a rather different structure. The cells which mineralise the dentine are not incorporated within the tissue, as in bone, but instead line up on the growing surface of the dentine, leaving only long processes extending into the mineralising tissue (Currey 1970, 28). This gives dentine, and thus ivory, an acellular, prismatic structure. Related to dentine, but unlikely to be found in artefacts, is a tissue called osteodentin. This much resembles dentine, but has the mineralised tissue organised into a structure of tightly-packed tubes. Osteodentin is found in the dermal denticles of skates and rays, and in the teeth of that excellent beast the aardvark (Halstead 1974, 80).

Tooth enamel may be encountered on artefacts, although most forms of ivory have little or no enamel covering. Enamel is almost purely hydroxyapatite. It contains no collagen, but has a small component of another protein. What this means in practice is that enamel may react quite differently from bone in the same burial conditions.

To consider structure at a coarser level, raw material for artefacts has, in the main, been derived from three parts of the skeleton: limb bones, antlers and 'tusks'.

At its simplest, a limb bone comprises a tube of compact bone capped at each end by an area made up of strap-like pieces (trabeculae) arranged in a stress-bearing and shock-absorbing pattern of arches and buttresses. This is termed cancellous, or, more descriptively, spongy bone. Cancellous bone is infrequently encountered in artefacts, although areas may persist near the extremities of objects largely composed of compact bone. In artefacts from British archaeological sites, cancellous bone is mainly encountered as hemispherical spindle

whorls cut from the head of the femur of a cow, or, more rarely, a horse. As compact bone comes, as it were, pre-formed as tubes, it is not surprising that bone is frequently used for cylindrical artefacts such as knife handles. In such cases, the original size and proportions of the bone may be evident, and if sufficient surface detail remains, an identification can often be made to skeletal part and species. However, with artefacts such as bone pins, which are cut from a strip of compact bone, it is seldom possible to say much beyond the fact that the specimen is of compact bone from a limb-bone of a large mammal. It may well be reasonable to speculate further, for example that the bone in question was an ox metatarsal, but such a judgement would hinge on an assessment of what material was likely to be available rather than on any intrinsic features of the specimen.

Antlers are composed of an outer cortex of compact bone with an inner medulla of spongy tissue. The proportion of medulla varies from species to species, and may be of some value in species identification (Schmid 1972, 88-90), but also varies a great deal within one species according to the part of the antler concerned, the age of the individual and even the time of year (Penniman n.d., 35-38). For manufacturing purposes, antlers have two parts, namely the tapering, pointed tines, and the beam on which they are mounted. The compact cortex of the beam is most suitable for producing long, straight strips or flat plates of antler. The uses of tine antler are more constrained by the curved, cylindrical form of the tines. Because antler contains a high proportion of collagen, it is possible to alter the shape of a piece of compact antler by bending a piece which has been steamed or soaked in water. Thus the shape of a strip of antler may not necessarily reflect the form which it originally had before being worked. Identification of the species involved may be possible if any of the rugose outer surface or the spongy medulla is preserved.

The distinction of small pieces of compact bone from compact antler by non-destructive methods can be very difficult, as they are, after all, virtually the same material, and each varies considerably in structure. Under the binocular microscope, each will show a pattern of irregularities and small holes, even on a polished surface. As a very crude identification feature these irregularities are usually more regular and more uniformly oriented on bone, whilst on antler they appear to be more random. In addition, bone will usually take a much higher polish than antler. However, it is often necessary to consider the function of the artefact, bearing in mind that antler has in the past been selected for its greater elasticity and toughness and used for parts of objects which will be subjected to particular stresses (MacGregor and Currey 1983).

Mechanically, both bone and antler are markedly anisotropic. This is simply a consequence of the internal structure giving both substances a 'grain' analogous to that of wood. Tested across the grain, antler is the more flexible, by a factor of about 30%, and much tougher. The work required to break antler per unit cross-sectional area has been shown to be about 2.7 times that for bone (MacGregor and Currey op. cit.; Currey 1980).

Elephant ivory is obtained from tusks, which are massively over-developed upper incisors. The characteristic 'machine-turned' appearance seen in transverse sections of fresh ivory reflects the pattern of radial discontinuities left by the retreating cell processes as the dentine grows (Penniman n.d., 13-14). There are longitudinal discontinuities as well. The tusk grows by the deposition of layer upon layer of dentine around the insides of a conical pulp cavity, and this layering is what produces the 'cone-within-cone' structure into which degraded ivory tends to crack. It may also crack along the radial discontinuities, producing a heap of cubes and prisms.

Hippopotamus ivory is obtained both from the canines and from incisors. When fresh, it lacks the intersecting-arcs pattern of elephant ivory, and shows, in transverse section, a pattern of concentric light and dark lines, almost like tree-rings. Walrus ivory comes from the upper canines, and has a very distinctive structure. The outer layers of the tusk are formed of dense dentine, much like other forms of ivory, but as the tusk grows the inner pulp cavity fills with a very hard secondary dentine. This has a curiously porous structure, and, when polished, produces a very distinctive marbled effect.

Teeth of other diverse animals have occasionally been used in artefact manufacture, and each has its particular characteristics. For description of such structures as wart hog canines and sperm whale teeth, the inquisitive reader is referred to Penniman (n.d., 27-34).

Decay

The mineral and protein components of bone can be expected to react quite differently to burial environments. Summaries of the likely survival of bone and its (largely theoretical) degradation processes may be found in Chaplin (1971, 13-19), Garlick (1969, 503-5) and Ascenzi (1969). More recent work has tended to concentrate on the recovery of amino acid residues for relative dating or other biochemical procedures (for example Hedges and Wallace 1978). From the point of view of the conservation of an object, it is of importance to be able to judge whether the mineral or the protein component is likely to be the more degraded, and a few ground rules may be laid down.

Hydroxyapatite is chemically quite stable, being susceptible to degradation to soluble residues in acid conditions. Just how low the pH has to fall before this becomes a significant process is not clear: in British conditions bone will be rapidly demineralised in soils developing on peats or podsolised heathlands, so it can be said that demineralisation will occur at a pH of 5 or less. An appreciable throughput of groundwater (leaching) will be required to prevent the development of a phosphate-rich zone around the bone, with consequent common-ion effect inhibiting further solution of the hydroxyapatite. Comparisons of bone degradation with levels of ambient soil phosphate have shown that low soil phosphate levels will enhance the rate of dissolution (Rottlander 1976).

Of the organic components of bone, the mucoprotein and other constituents of the ground substance seem to be lost very quickly. This may in part be due to groundwater percolation, although microfaunal and -floral activity probably accounts for much of this speedy loss. Collagen, on the other hand, is made of sterner stuff, and tales of the identification of collagen fibrils in fossil materials of immense age (e.g. in Garlick 1969) might lead to the conclusion that it is almost indestructible. However, given appropriate soil conditions, collagen can be degraded quite rapidly, and since this protein constitutes the structural base of bone tissues, loss of collagen may lead to disintegration of the bone faster than loss of mineral.

In a recent study of poorly-preserved dentine from archaeological sites, Beeley and Lunt (1980) found that specimens of soft, crumbly dentine had lost most of their collagen content, leaving a friable mass of mineral. Loss of collagen was shown to be a function of burial conditions rather than the duration of burial. It was thought that bacterial collagenases may have been largely to blame, breaking down the collagen to peptides which were leached away by groundwater. Other writers have suggested the gas-gangrene bacterium Clostridium histolyticum to be an important agent in collagen degradation (Garlick 1969, 504; Rottlander 1976, 86). This microorganism functions most vigorously in pH around 7-8. Perhaps more to the point for conservation, C. histolyticum is inhibited by a very high or low pH (below 5 or above 9), or in the presence of ferrous iron or other metals (Garlick op. cit.). The propensity of hydroxyapatite for adsorbing metal ions has been mentioned above, and this may have an additional effect in inhibiting bacterial activity.

So far, then, we may expect bone to degrade by demineralisation in very acid conditions, or by destruction of collagen in conditions of pH around 6 to 8 unless the ground water is heavily loaded with ferrous or heavy metals ions. Waterlogging will tend to favour bone preservation, if only by providing a stable burial environment, as distinct from the dynamic environment associated with constantly moving groundwater. Chaplin (1971, 16) observes that bone from waterlogged cesspits is commonly well-preserved, and our experience in York is that bone from highly organic waterlogged deposits of the 9th to 13th centuries A.D. will be particularly well-preserved, albeit deeply discoloured by mineral deposition.

The porosity of bone leads to the deposition of minerals within the cavities left by the decomposition of its cellular component. The minerals involved will depend upon, and reflect, the ions available in the surrounding soil, but calcite, pyrite and vivianite seem to be particularly common (S. Hillson in litt., and author's observations). This deposition is of interest to the osteologist because the minerals may either accentuate histological detail or obscure it completely. As to conservation, the disruptive effect of such mineral deposition will depend upon the extent to which other factors have caused degradation of the bone. Bone which is already weakened by loss of collagen may be further damaged, but well-preserved bone will show little macroscopic effect beyond a change in colour.

Examination of undecalcified sections of ancient bone has brought to light the presence in some specimens of a network of fine channels superimposed upon the transport system of the tissue (Ascenzi 1969, 533). Although first described over a century ago, the origin of these so-called 'bohrkanale' remains a matter of debate, although it seems probable that they result from an invasion of the bone by a mycelium-forming fungus which is, as yet, unidentified. Whatever their origin, the channels increase the porosity of the bone and thus the volume available for mineral deposition.

To summarise, bone, antler and ivory artefacts may be expected to survive in a variety of burial conditions, and will have the advantage over food-debris that they are unlikely to have had their collagen component depleted by boiling or roasting before burial. Mineral deposition may have changed the original creamy-white colour to anything from yellow through shades of brown to black. Unless there has been substantial loss of collagen, the histological structure of the tissues may be faithfully preserved, and in some, though by no means all, cases the origin of the specimen may be determined.

Acknowledgements

I would like to express my thanks to Dr. Simon Hillson for sharing with me some of his considerable expertise on this subject, and various colleagues for their critical reading of an earlier draft of this paper.

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