

# THE DESIGN OF MINERALISED HARD TISSUES FOR THEIR MECHANICAL FUNCTIONS

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## Summary

Most hard tissues have as their primary purpose to be stiff. Outside the arthropods, mineralisation of a soft organic matrix is the almost universal method of producing high stiffness. However, stiffening brings with it the undesirable mechanical result of brittleness (lack of toughness). The mineralisation of some tissues, such as bone and dentine, can be modified rather easily, in evolutionary terms, to produce the optimum mix of stiffness with bending strength (which, except at the highest mineralisations, go together) on one hand and toughness on the other hand. However, in most other tissues, such as mollusc shell, echinoderm skeleton, brachiopod shell, barnacle shell and enamel, mineralisation is almost all-or-none, and no subtle gradations seem possible. In such cases, other features, such as architecture, must be modified to produce a useful skeleton.

Not only the mechanical properties of the skeletal tissue, but its cost, mass and time taken for production will, biologists tend to assume, be balanced by natural selection to produce a satisfactory result. However, such complexity makes it difficult to be sure that we understand the extent to which mineralised skeletal materials are the best possible solution to the problems facing the animals and that we are not just telling 'Just-So' stories. Furthermore, there are some skeletal materials that do not seem to make much sense at the moment, although no doubt all will become clear eventually.

Key words: bone, mollusc shell, enamel, stereom, mechanical property, toughness.

## Introduction

Except in very active animals such as birds, the major mass of the musculoskeletal system is taken up with hard tissues. The word 'hard' in this context means 'stiff', although hardness can be measured in a way (using indentation) that seems to have little to do with stiffness. If we consider tissues to be 'stiff' if they have a modulus of greater than approximately 5 GPa, then there are essentially only two major types. These are heavily cross-linked arthropod cuticle and mineralised skeletal materials. Arthropod cuticle is marvellous stuff, but I shall not deal with it further. Instead, I shall discuss the way in which mineralised tissues are designed, at the material level, to perform their functions. We often have rather little idea of these precise functions. For instance, the echinoderm skeleton is a strange structure, and it is difficult to be clear about what it is intended to do. However, the vast majority of mineralised skeletal materials are clearly designed to be stiff.

It is natural to think that strength must be important, and in one sense it is. However, if the main function of mineralised tissues is to be stiff, then strength is really merely the ability to show the stiffness under high loads. That stiff materials need also to be tough (i.e. to be able to absorb energy without fracturing, and also to be insensitive to the presence of cracks and similar imperfections) is another complication. Strength is

usually measured in well-controlled situations, whereas toughness accords better with what goes on in the rough-and-tumble of real life.

The experience of materials scientists is that there are some pairs of mechanical properties that cannot both be increased indefinitely. Most obvious are stiffness and toughness. Whatever the detailed reason for this, in particular materials, it seems inherent in the nature of things that a very high initial stiffness is difficult to accommodate with a long post-yield region (Kelly and Macmillan, 1986). There are ways of marrying the two, but this involves making the material extremely anisotropic, so that it is stiff and tough in one direction, but weak or brittle in other directions. Much of the evolutionary pressure on heavily mineralised materials must have been to arrive at the correct balance between stiffness and toughness. In this paper, I shall deal first with bone, in which a variant of calcium phosphate, such as hydroxyapatite, crystallises in a matrix of collagen plus some other organic materials. There is usually a moderate amount of water present as well. I shall deal with it first because it is most clear in bone how the properties can be altered to produce different mixes of stiffness and toughness. At the end of this paper, I shall deal, much more shortly, with enamel and some invertebrate mineralised tissues.

**Bone**

*What determines the mechanical properties of bone?*

In bone, the main determinant of mechanical properties is the amount of mineral in the tissue. As more and more mineral displaces water, the bone becomes stiffer, but at the same time more brittle. Fig. 1 is a ternary diagram showing the relationship between the organic content, the water content and the mineral content of a number of different kinds of bone. The lower points on the diagram are probably almost the most extreme as regards the amount of organic material present – one does not find very mineral-poor bone. Nevertheless, it is possible to find bone that contains very little organic material or water.

Fig. 2 shows the relationship between the stiffness (Young's modulus) of bone and its bending strength. These values come from bone specimens from a wide variety of amniote species, each point representing the value for a single specimen. Apart from the specimens labelled 'A', there is clearly a very strong, almost linear, relationship between Young's modulus and strength, with the strength values being approximately 1/100 of the stiffness values. This near-linear relationship shows that the failure of bone in bending is determined by the strain to which it is subjected (Currey, 1999). This relationship seems to be true whether differences in modulus are determined by differences in mineralisation and/or by differences in porosity. That is to say, it is the strain in the outermost fibres of a specimen that will determine whether a specimen breaks when subjected to a particular bending moment, no matter what causes it to have these high strains.

The specimens labelled 'A' are from the tympanic bulla of the fin whale *Balaenoptera physalus*. This bone is extremely highly mineralised, and it seems that there is a level of mineralisation that changes the fracture behaviour of bone drastically, so that it become entirely brittle and can bear very little stress.

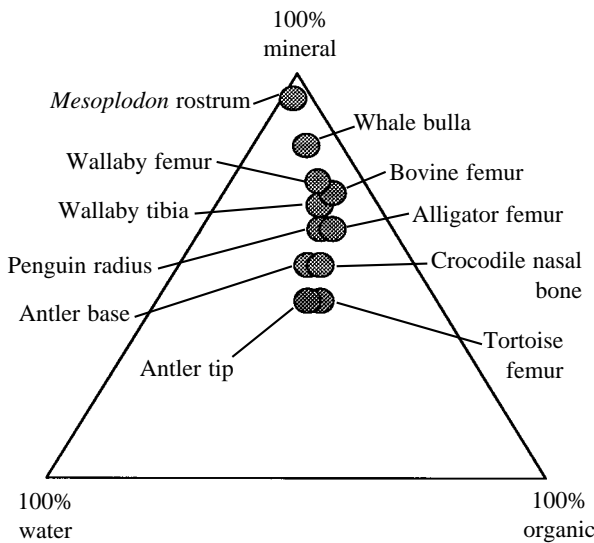


Fig. 1. Relationship between water content, organic content and mineral content of various bones on a per mass basis. The mineral content may become very high.

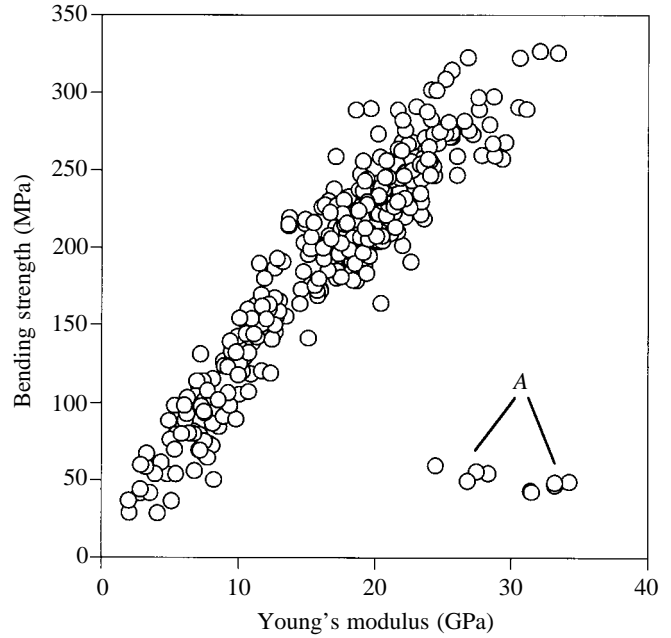


Fig. 2. Relationship between Young's modulus and bending strength for a large number of bone specimens from many species. The specimens shown as 'A' are from very highly mineralised bone of the tympanic bulla of the fin whale *Balaenoptera physalus*.

The situation is different, however, for toughness. Fig. 3 shows the relationship between Young's modulus, mineral content and ultimate strain to failure in tension (a convenient indicator of the toughness of the tissue) of a number of different types of bone. Increasing mineralisation is obviously associated with increasing Young's modulus, but with decreasing strain to failure.

Table 1 shows some representative values for three mechanical properties of various bones to give some idea of the range of values to be found.

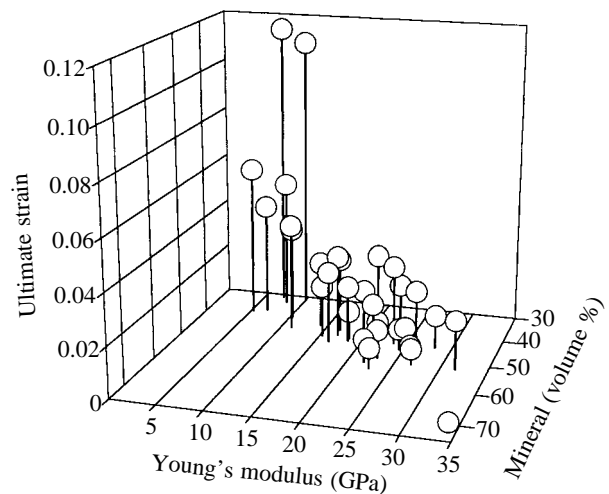


Fig. 3. Three-dimensional diagram of relationships between mineral content, Young's modulus of elasticity and strain to failure in tension of various types of bone.

Table 1. Three mechanical properties of various bones measured in tension (arranged in order of increasing Young's modulus) to give an idea of the range to be found

Species and tissue	<i>E</i> (GPa)	$\sigma_{ult}$ (MPa)	$\epsilon_{ult}$
Polar bear (3 months), femur	6.7	85	0.044
Red deer, mature antler	7.2	158	0.114
Red deer, immature antler	10.0	250	0.109
Narwhal, tusk dentine	10.3	120	0.037
Polar bear (9 months), femur	11.2	137	0.042
Donkey, radius	15.3	114	0.020
Polar bear (3 years), femur	16.5	142	0.028
Human (adult), femur	16.7	166	0.029
Sarus crane, ossified tendon	17.7	271	0.062
Roe deer, femur	18.4	150	0.011
Polar bear (3.5 years), femur	18.5	154	0.022
Cow, tibia	19.7	146	0.018
Wallaby, femur	21.8	183	0.009
Polar bear, femur	22.2	161	0.020
King penguin, humerus	22.8	175	0.008
King penguin, ulna	22.9	193	0.011
Sarus crane, tarsometatarsus	23.1	218	0.018
Sarus crane, tibiotarsus	23.5	254	0.031
Horse, femur	24.5	152	0.008
Wallaby, tibia	25.4	184	0.010
Fallow deer, radius	25.5	213	0.019
Cow, femur	26.1	148	0.004
Fallow deer, tibia	26.8	131	0.006
Flamingo, tibiotarsus	28.2	212	0.013
Axis deer, femur	31.6	221	0.019
Fin whale, ear bone	34.1	27	0.002

*E*, Young's modulus of elasticity;  $\sigma_{ult}$ , ultimate tensile stress;  $\epsilon_{ult}$ , ultimate tensile strain.

All values are the mean of the values of several specimens.

### Adaptation

I have shown above that the mechanical properties of bone are strongly affected by their amount of mineralisation. However, I have not shown that the differences are adaptive. I give an example here of the way in which different bones have different trade-offs according to their functions. This is a very old example, but makes the point clearly. It compares deer's antler, the bovine femur and the tympanic bulla of the fin whale.

Ordinary limb bones (e.g. the bovine femur) can be taken as 'standard'. They must be fairly stiff and strong, but also quite good at resisting impact loads. Compared with them, antlers have rather different requirements. In the red deer *Cervus elaphus*, as in all deer except the caribou (or reindeer) *Rangifer tarandus*, antlers are found in the males only. They are grown in the spring and summer, used in the rut in the autumn and are shed in the late winter. During the rutting season, males compete to collect, maintain and impregnate harems. The ability to maintain a harem depends on many factors; important among these is the ability to outface an opponent male in a display. For this, antlers are to some extent important insofar

as they signal the age and physical state of the bearer. During the display, the antlers' mechanical properties are irrelevant – waterproof cardboard would be equally effective. However, if two opposing males appear to each other to be closely matched, they may fight. Fighting involves smashing the antlers together, fencing with them and attempting to make the opponent lose his footing. During the smashing together and fencing, the impact properties of the antler are very important.

Ear bones in mammals have markedly different functions from most other bones. By 'ear bones' I mean the auditory ossicles, the otic bone around the inner ear and the tympanic bulla. For various auditory reasons (Currey, 1979), it is important for all the ear bones to be very stiff.

The three types of bone: the antler of the red deer *Cervus elaphus*, the bovine femur and the tympanic bulla of the fin whale were tested for a variety of properties. These were work of fracture (the work needed to drive a crack through the material, which gives a good idea of impact resistance), bending strength, Young's modulus of elasticity, mineral content and density. The results are shown in Table 2.

The differences in mechanical properties are very large, and it is likely that they are produced mainly by differences in the amount of mineralisation, although there could be some effect of histology; in particular, the bulla material was less regularly arranged than the other two types of bone.

The high level of mineralization of the bulla is the cause of its high modulus. However, it is just this high level of mineralisation that makes the bulla brittle as well as stiff. The antler has a rather low level of mineralisation and a very high work of fracture. In fact, it is exceedingly difficult to break an antler specimen in impact if it is loaded across the grain; it usually deforms into a U-shape but does not fracture. The antler, therefore, has just the properties required of it. Compared with the 'standard' bone (the femur), the antler is rather compliant, but any slight disadvantage this may produce in the pushing match is more than made up for by the very high work of fracture and impact resistance. In contrast, the bulla, and presumably the other ear bones, has a much higher modulus even than standard bone. Its brittleness is not a difficulty, however, because it is hidden away inside the skull and not, except *in extremis*, subjected to large loads.

### What determines the mechanical properties of bone?

Bone at the microscopical and ultrastructural level is not a shapeless mass, but has a clear hierarchical structure. At the level of the hierarchy of a few micrometres, most bone has a lamellar structure. In this, the bone is divided into thin sheets,

Table 2. Some physical properties of three bone tissues

Property	Antler	Femur	Bulla
Work of fracture ( $J m^{-2}$ )	6190	2800	20
Bending strength (MPa)	179	247	33
Young's modulus (GPa)	7.4	13.5	31.3
Mineral content (% ash)	59	67	86
Density ( $kg m^{-3}$ )	$1.86 \times 10^3$	$2.06 \times 10^3$	$2.47 \times 10^3$

'lamellae', approximately 4  $\mu\text{m}$  thick. In any lamella, the collagen fibrils and their associated mineral crystals tend to have an orientation parallel to each other. The predominant orientation of the collagen may, and often does, vary considerably from one lamella to the next. Although as yet the mechanical properties of individual lamellae are unknown, it is obvious that they will be highly anisotropic. A great deal of effort is going on at the moment (a) to model the mechanical properties of individual lamellae, and (b) to model the bulk properties of bone made of lamellae with various different relative orientations (Rho et al., 1998, Weiner and Wagner, 1998). It is not possible to go into the complexities of this modelling here. The important feature of the lamellar arrangement of the bone tissue is that, in theory, it makes it possible for bone to be arranged in such a way as to be better at resisting loads in some directions than in others. I give one example here where the relationship is shown rather clearly, because the direction of loading of the bone is rather unvarying.

#### *Adaptation – structure*

The radius of the horse has a gentle anterior curvature and, as a result, although it is loaded primarily longitudinally, the curvature interacts with the longitudinal forces to produce bending, so that the anterior cortex is loaded in tension and the posterior cortex is loaded in compression (Rubin and Lanyon, 1982; Biewener et al., 1983).

Riggs et al. (1993a,b) showed that this difference in loading pattern is associated with differences in histology. The predominant orientation of the collagen and mineral in bone can be altered by secondary remodelling, producing secondary osteons, whose collagen orientation can be tailor-made for the loading situation in which the bone finds itself. The anterior and posterior cortices initially have a rather longitudinal orientation of the collagen and mineral. The anterior cortex remodels rather little, and such secondary osteons as are formed have a predominantly longitudinal orientation of their

constituents. The posterior cortex remodels considerably, and the secondary osteons so formed have a much more transverse orientation of their mineral and collagen (Riggs et al., 1993a). These histological differences in the two cortices are associated with differences in mechanical properties (Riggs et al., 1993b). The anterior cortex has a higher Young's modulus than the posterior cortex whether loaded in tension or in compression; the anterior cortex is stronger in tension than the posterior cortex; the posterior cortex is stronger in compression than the anterior cortex. In a case like this, probably quite rare, in which bone is loaded strongly in only one mode (tension or compression), it is possible to fine-tune the histological structure so as to maximise the appropriate mechanical property. Table 3 shows the properties of the anterior and posterior cortices of the equine radius as measured by various workers.

However, in general most bone must be more general-purpose in its mechanical properties than the horse's radius. Its properties must usually be a compromise between the requirements of the different loading modes to which it is subjected.

#### *A stiff tough tissue – ossified tendon*

Ossified tendon, which is not particularly outlandish (it is to be found in one's chicken dinner and, less approachably, in many dinosaurs) is a remarkable tissue. It starts off its development as standard tendon, but becomes progressively mineralised. It then usually undergoes secondary remodelling. It is extremely anisotropic in both its histology and its mechanical properties. It is almost impossible to break in a standard tension test, even if a transverse nick is made into the tendon. The transverse cracks that do develop almost immediately turn through 90° and travel along the specimen to the grips. For a material of such a high stiffness, it has a very high work under the load/deformation curve because it has both a high Young's modulus and a large ultimate strain. Probably uniquely among bony tissues, ossified tendon is stiff,

Table 3. *Mechanical properties of the bone material from the anterior and posterior cortices of the equine radius*

	Cortex	Tension (Riggs)	Compression (Riggs)	Bending		
				(Schryver)	(R & C)	(Batson)
<i>E</i> (GPa)	Ant (T)	22.1	18.6	20.1	21.1	17.9
	Post (C)	15.0	15.3	16.2	15.5	13.5
Strength (MPa)	Ant (T)	161	185	249	232	201
	Post (C)	105	217	217	203	154
Impact (kJ m <sup>-2</sup> )	Ant (T)	–	–	–	–	32.6
	Post (C)	–	–	–	–	17.5

As is frequently the case in bone, the bending strength is much greater than the tensile strength. 'Impact' refers to the impact loading in four-point bending of un-notched specimens and is a measure of the total energy absorbed in breaking a specimen in two.

Data from (Riggs) Riggs et al. (1993b), (Schryver) Schryver (1978), (R & C) Reilly and Currey (1999) and (Batson) Batson et al. (1999). Tension, Compression and Bending refer to the loading mode.

*E*, Young's modulus of elasticity; Ant (T), anterior cortex (loaded in tension *in vivo*); post (C), posterior cortex (loaded in compression *in vivo*).

strong and tough. However, it is not the wonder material that one might expect from this description, because it is also extremely anisotropic in strength. It is extremely weak in the transverse direction; despite its strength in the longitudinal direction, it can be easily peeled apart along its length with the fingers. Although we have no measurements of its stiffnesses in the transverse direction, it is probably rather compliant. Ossified tendon achieves its very high strength by being composed of what are essentially isolated fibres, each of which is thin but strong. The connections between the fibres are sufficiently weak for cracks not to be able to pass from one fibre to the next. Tendon is, of course, loaded only in one direction, and this extreme anisotropy is therefore not disadvantageous. Ossified tendon is an extreme example of a general phenomenon: if bone and other mineralised tissues perform well in one mode, this often comes at the expense of performance in another mode.

#### *Multiply-oriented tough plates – fish scales*

The range of structures seen in scales of different fish forms almost a complete spectrum from what is obviously ‘typical’ bone to what is obviously ‘typical’ enamel. This situation is often found in biology, of course, since nature is not concerned with categorisation, but with producing effective results.

Many fish scales frequently have a regular ‘plywood’ structure. Each ply is a sheet of ossified fibrils running in one direction and appears, at least in the herring, to be only one fibre thick ( $\approx 1 \mu\text{m}$ ). The change of fibre direction between plies can be a regular  $90^\circ$  or can be more subtle. Looking down through a scale, the fibres may be arranged in a helicoid. (In a helicoid, the preferred orientation changes layer by layer by a constant, usually rather small, angle.) Meunier (1987) characterised the orientation of successive bony layers in the scales of 25 fish, and showed that almost all kinds of arrangement exist, including strict orthogonality and helicoids, but also more complex arrangements. The precise mechanical significance of these different arrangements is not known, but clearly any plywood arrangement is going to make the scale more isotropic in mechanical behaviour and stronger. We have found some fish scales to be so tough that they are difficult to tear even after immersion in liquid nitrogen!

#### *Whale rostrum – a puzzle*

It must be admitted that sometimes it does not seem possible to provide any simple adaptive explanation for the mechanical properties of a bone. We have studied the rostrum of the skull of the toothed whale *Mesoplodon densirostris* (Zioupos et al., 1997). This bone is extraordinarily dense, having the highest mineral content and some of the specimens having the highest Young’s modulus of any bone recorded (46 GPa). Not surprisingly, it is also extremely brittle. The histology of the bone is nearly normal in that it is full of blood channels and osteocytes with their interconnecting canaliculi, although there is a tendency for the blood channels eventually to have their lumen filled with mineral, thereby presumably leading to the death of the cells in the vicinity. The fine structure is peculiar;

amongst other things, it appears that there is not the intimate relationship between the collagen and the mineral found in ordinary bone, rather the extremely scanty collagen forms thin-walled tubes within which the mineral lies (Zylberberg et al., 1998). Furthermore, Rogers and Zioupos (1999) show by X-ray diffraction that the mineral is very well-oriented along the length of the rostrum.

It does not seem likely that the rostrum is used in fighting because, although it might make a rather efficient club, it is covered with soft tissues which would damp out the effect of any blows. It might perhaps act as ballast, enabling the animals to sink more rapidly than they might otherwise. It might possibly be used in some way in acoustic battles with other males. At the moment, its function, in this rarely found whale, is a mystery. It is very frustrating that this bone, which has a very extreme fine structure and which is mechanically the most extreme bone we have discovered, has an unknown function.

#### *Interactions between material properties and whole bone architecture*

The mechanical properties of any structure are determined by two quite separate things, the mechanical properties of the material, and the size and shape of the whole structure – its architecture. Here are two examples in which we have some idea of differences in the architecture and differences in material properties, and so can see whether how they are related to each other.

#### *Polar bears*

The femora of five wild polar bear (*Ursus maritimus*) of known age and mass were examined (Brear et al., 1990). The ages ranged from 3 months to 7 years (maturity occurs at approximately 2.5 years) and the mass from 9.5 kg to 407 kg. In the bones of the younger animals, the bone material was both weaker, having a lower yield and ultimate stress, and less stiff, having a lower Young’s modulus of elasticity, than the material from the bone of older animals. These differences correlated rather well with the lower degree of mineralisation of the younger bones. Does this mean that the bones themselves were less strong and stiff? Table 4 shows some of the characteristics of the bears and their bones. Making some assumptions about how the mass and size of the bear would affect the bending moments to which it would be subjected, we showed that there was a reasonable harmony between the shape of the bone and its material properties. We calculated the resistance to yielding and the shape change produced by the bending moments.

The masses of the bears vary by a factor of 43, and the lengths of the bones by a factor of 3.1, producing bending moments that vary by a factor of 130. Compared with this, the range of resistances to yielding, a factor of 2.4, and the stiffness of the whole bone (the inverse of the bending compliance in relation to its length), a factor of 3.1, is small. If the material in all the bones had had identical mechanical properties, but the shapes were as measured, then the resistance to yielding

Table 4. *Some properties of five polar bears and their femora*

Age	Mass (kg)	Length (mm)	$I$ (mm <sup>4</sup> )	Ca	Yield (MPa)	$E$ (GPa)	Bone strength	Bone stiffness
3 months	9.5	160	$3.4 \times 10^3$	235	63	6.7	1	1
9 months	58	240	$14.5 \times 10^3$	251	88	11.2	0.52	0.55
3 years	197	396	$29.1 \times 10^3$	259	107	18.5	0.39	0.37
3 years	251	435	$67.2 \times 10^3$	263	123	16.5	0.40	0.34
7 years	407	490	$101.0 \times 10^3$	269	129	22.2	0.41	0.32
Ratio	43	3.1	$30 \times 10^3$	1.14	2.0	3.3	0.41	0.32

Ratio is the value for the 7-year-old divided by the value for the 3-month-old.

Mass, mass of the bear; length, length of the femur;  $I$ , least second moment of area of the mid-section of the femur; Ca, calcium content of bone material (mg calcium g<sup>-1</sup> bone); Yield, yield stress in tension;  $E$ , Young's modulus of elasticity.

The last two columns are the strength of the whole bone and the stiffness of the whole bone, in arbitrary units, compared with the strength of the bone of the 3-month-old, when loaded by the mass of the bear. Calculation of these values requires information about the structure of the bone that is not given in the table.

Derived from Brear et al. (1990).

would have had a range of 5, rather than 2.4, and the shape change would have had a range of 10.3, rather than 3.1.

The implication of these calculations which, it must be remembered, are based on somewhat simplistic assumptions about loading, is that the architecture of the bones is rather precisely adapted both to the loads placed on them and to the mechanical properties of the bone material.

#### *Californian gulls*

A study of Californian gulls by Carrier and Leon (1990) shows similar features to the polar bears, but here it was possible to study the different behaviour of the leg bones (used almost from hatching) and the wing bones (which only increased much in diameter just before the juveniles started to fly). The bone tissue was initially weak in both the wings and legs. In the legs, this tissue weakness and compliance were compensated for by a relatively large cross section. When, towards the end of growth, the leg bones stopped increasing rapidly in cross-sectional area, the bone material became much stronger and stiffer, presumably through increased mineralisation. The wing bones grew in length quite steadily, although there was a spurt just before flight. However, the wing bones remained quite slender, and therefore very feeble and compliant, until just before flying started, when there was a very large growth spurt in diameter and an equally rapid increase in the strength and stiffness of the bone tissue. Bones of both limbs were functional, therefore, when they were needed, but the extra diameter needed to compensate for the feeble tissue was needed only in the legs, but not the wings.

#### **Calcified cartilage**

Cartilage can become mineralised, and the mechanical properties of mineralised (calcified) cartilage are of some interest, but are hardly known. Calcified cartilage appears in various places in vertebrates, including the ends of growing long bones, but of particular interest in the present context is its occurrence in the general skeleton of many sharks.

The chondrichthyes, the cartilaginous fish, have skeletons usually made of cartilage. Sometimes, however, the cartilage becomes calcified and therefore much stiffer. The calcified cartilage contains layers of prismatic calcium phosphate, probably apatite. The layers appear only on the outer surface of the cartilage, not in the interior. Dingerkus et al. (1991) showed that in large sharks, such as the great white shark *Carcharodon carcharias* and the tiger shark *Galeocerdo cuvieri*, smaller individuals had totally cartilaginous jaws, but that as the animals grew larger they developed one, and then many, layers of mineral. Presumably this is an adaptation to the need for stiff jaws in large animals that exert large forces. It is not merely an ageing change, because smaller species in the same genera never develop calcified cartilage, even when totally mature.

Sometimes the loads on the skeleton are very large, and in one case the chondrichthyes have developed an extraordinary convergence with what happens in trabecular bone. The cownose ray *Rhinoptera bonasus* crushes hard-shelled prey in mineralised tooth plates. Summers et al. (1998) show that not only do the tooth plates have many layers of mineral on the surface, but they have internal mineralised trabeculae that look remarkably like those found in the ends of long bones or in flat bones. The trabeculae are surrounded by the cartilage and seem to be well arranged to resist the loads imposed on them. One particularly interesting property of these trabeculae is that they are often hollow, i.e. they are hollow cylinders. This is an efficient way of arranging trabeculae, because it reduces the risk of buckling. Indeed, it is somewhat surprising that the trabeculae of cancellous bone seem never to be hollow.

#### **Enamel**

The function of enamel is to provide a hard surface for the slicing and trituration of food and, in some species, for wounding enemies. Enamel is approximately 97% mineral by mass (essentially apatite), 1% organic material (mostly protein that is not collagen) and 2% water (Waters, 1980). The enamel

crystals are much larger than the apatite crystals found in bone and dentine. The crystals are bound together in bundles called prisms. There is little protein within the prisms; what protein there is in enamel is concentrated at the inter-prism boundaries. These prisms are the characteristic feature of enamel, and how they are arranged has considerable effects on the enamel's mechanical properties.

Enamel, being 97 % or so mineral, is likely to be very brittle. In mammals, there is usually a thin superficial layer in which the enamel crystals lie normal to the surface. However, deep to this, things become more complicated. Here, the enamel is frequently arranged so that it is difficult for cracks to travel very far. The enamel prisms are arranged in a decussating, plywood-like structure. This is like the arrangement frequently seen in lamellar bone. However, in enamel, the arrangement is on a somewhat larger scale and is easier to visualise. There is usually an 'easy' direction for the cracks to travel, in which the cracks just separate layers of mineral prisms. There is also a 'difficult' direction in which the crack, as it advances, is continually having to break across the prisms if the crack front is to remain coherent. Sometimes the 'easy' direction is horizontal with respect to the long axis of the tooth, sometimes vertical, and sometimes it changes direction part-way through the thickness of the tooth.

Much work has been done on the way in which the predominant direction of decussation is related to the local state of stress. For instance, in many primitive herbivores, the tooth cusps are rather domed. Finite element analysis shows that such domes are likely to suffer tensile stresses acting normal to the crown-root axis (the vertical axis) and, therefore, that cracks are likely to run along vertical axis. In more derived herbivores, the teeth become taller and the maximum tensile stresses developed, as the crowns of the teeth shear past each other, are directed more vertically so that cracks will tend to run more horizontally. As the shape of the teeth changes, so the plane of decussation changes from being predominantly horizontal to being predominantly vertical, thereby ensuring that the cracks have to run in the 'difficult' direction (Rensberger, 1992; Rensberger and Pfretzschner, 1992). In the enamel of many rodents, this decussation is taken further: there are decussating prisms, but there are also fibres in the third direction, normal to the plane in which the decussating prisms lie. As a result, there is no 'easy' direction for the cracks to travel, and any crack will have to break across fibres or prisms.

Perhaps one of the clearest and best known examples of how mechanical properties and function combine is in the incisor teeth of rodents and lagomorphs. The teeth are ever-growing and form arcs of circles. The outer part of the circle is composed of enamel, is hard and is very wear-resistant. The inner part is composed of dentine, is softer and is less wear-resistant. As a result, the dentine wears much faster in use than the enamel, and a sharp chisel edge results.

Teeth are usually used for cutting or crushing, and the mechanical properties of the material of enamel and dentine would not seem to be suitable for function as bristles. However, the teeth of the pterosaur *Pterodaustro guinazui* became just

that. The long lower jaws bore many hundreds of filament-like teeth forming a comb, presumably to allow filter feeding, like the baleen of whales or the ridged roof of the mouth of flamingos. The teeth of *Pterodaustro guinazui* are true teeth, nevertheless, having a sheath of enamel surrounding a dentine core (Chiappe and Chinsamy, 1996). Enamel is rather brittle, and it might seem surprising that it could be a component of bristles, which must be flexible to function properly. However, there is an interesting feature of bending that is important here. It is possible to bend very slender sheets or rods into quite tight curves without their experiencing dangerous strains and stresses. Consider a straight rod of length  $X$ . It is bent into a circular curve of radius  $R$ . The neutral axis will remain of length  $X$ , and a fibre  $\Delta R$  away from the neutral axis will have a length  $X + \Delta X$ . Now,  $\Delta X = X\Delta R/R$ , and therefore  $\Delta X/X = \Delta R/R$ . Therefore, the strain in the specimen in the fibre at  $\Delta R$  is  $\Delta R/R$ . So, if  $\Delta R$  is very small, then it will be possible to make  $R$  small; i.e. it will be possible to produce a tight bend without the strain becoming unduly large. The teeth of *Pterodaustro guinazui* are very long in relation to the transverse dimensions (approximately 30 mm × 0.3 mm × 0.2 mm), and so they could have undergone reasonably large deflections without dangerous strains being imposed on the dentine or even the enamel. For instance, if we assume that the teeth were bent into a quarter circle, which is a very severe bend, about the shorter axis of the cross section, the radius of curvature would be 19 mm and so the strain would be  $0.1/19 = 0.0052$ . Even this is rather large for enamel in tension, but it does indicate how slenderness can lead to small strains at large deformations.

### Invertebrate skeletal materials

Invertebrate skeletal materials are far more varied in their chemical composition and structure than those of vertebrates. However, we know much less about them. In the remainder of this paper, I shall confine myself to discussing only three types of skeletal material: mollusc shell, echinoderm stereom and sea urchin teeth.

#### *Mollusc shell*

Mollusc shell is a remarkable material because it is more than 95 % by mass of mineral (calcium carbonate usually in the crystallographic form of calcite or aragonite), yet it can be quite tough. There are a number of different types of mollusc shell material. The 'crossed lamellar' structure consists of a plywood-like arrangement of aragonite needles. The plies are arranged so that a crack finds it rather easy to travel in one direction as it is separating the sheets, but difficult to travel in another, because it is always having to cut across the structure (Currey and Kohn, 1976). This is just the same type of arrangement as is found in enamel. Every so often, the whole structure is rotated through 90°, so that a crack that was finding it easy to travel finds itself in material with a different orientation, through which it is difficult to travel (Fig. 4). The structural arrangement by which crossed-lamellar structure achieves some degree of toughness is quite effective, but the

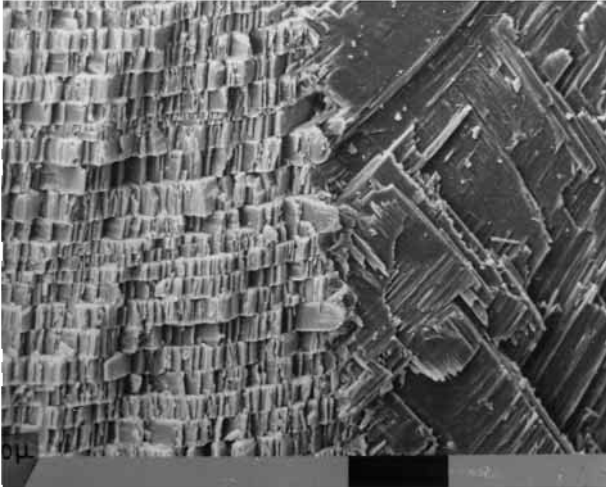


Fig. 4. Fracture surface of a specimen of shell of *Conus litteratus*, a snail. On the right, the crack is travelling between the lamellae. Note their plywood-like arrangement. Crack travel is easy, and the fracture surface smooth. On the left, the direction of the layers has changed though approximately 90°, making it more difficult for the crack to travel. The fracture surface is rough. Scale bar, 100 µm.

structure of mother of pearl is more sophisticated. Jackson et al. (1988, 1990) have shown that mother of pearl (nacre) is superior to most other artificial composite ceramics in stiffness, strength and toughness.

Nacre consists of flat sheets of aragonite or calcite, approximately 0.5 µm thick. Between each layer of mineral is a very thin layer of organic material, mainly protein, of complex constitution. The precise structure of the proteins seems to determine such things as which crystallographic species is laid down and, indeed, to determine the shapes of the crystals (Walters et al., 1997; Addadi and Weiner, 1997). Apart from its role in determining the structure of the nacre, the organic layer acts as a powerful toughening device. Jackson et al. (1988) showed that, as a crack travelled down through and round the various layers of crystals, the plates sprang apart and, in doing so, extended the organic sheets so that the plates had chewing-gum-like connections. Considerable work would be necessary to extend this organic material. Smith et al. (1999) have cloned and expressed one of the principal proteins, lustrin A. Using atomic force microscopy, they have shown that it has a very characteristic load/deformation curve. After the yield point, it has a saw-toothed shape, with the load increasing and then periodically dropping sharply as the strain increases. This mechanical periodicity is apparently caused by the sequential unwrapping of periodic regions in the protein. The result is that a large strain can be accommodated without very high loads being required, even though the original load/deformation curve is quite steep. This is an ideal property for such an energy-absorbing filler between the aragonite sheets. Furthermore, there is evidence that this unwrapping can self-heal if the strain is reduced. Lustrin lives to fight another day.

#### *Is the real world 'soft' or 'hard'?*

Jackson et al. (1988) make an important point about toughness in the real world. Nacre is efficient at causing crack travel to be expensive in terms of work required. However, the predators (crabs in particular) that prey on molluscs are 'soft' machines, i.e. they store a great deal of strain energy in their own tissues, unlike our beloved 'hard' Instron machines. In a hard machine, once the crack has started to travel, the extra energy to drive it forward must come from the material itself. In this situation, conventional toughening mechanisms are valuable. However, if the crab has much strain energy stored in itself, it may be that the release of this energy will be sufficient to fracture the material, even if it conventionally tough. Jackson et al. (1988) suggest that structures such as crossed-lamellar, which may have a small conventional toughness but have good crack-arresting mechanisms, may in fact be better adapted to cope with 'soft' predators than structures such as nacre. This complicated issue is one that would repay further study.

#### *Echinoderm skeleton, another puzzle*

Libbie Hyman, in her monumental treatise on the invertebrates, dedicated the volume on the echinoderms (Hyman, 1955) thus: 'I also here salute the echinoderms as a noble group designed especially to puzzle the zoologist.' In few of its many baffling features is the form/function relationship more obscure than in the skeleton. This is deposited initially as amorphous calcium carbonate, but converts to calcite, with extremely little organic material present (Beniash et al., 1997). In any one skeletal element, which may be centimetres in length in some skeletons, the calcite behaves optically as a single crystal. If this were not sufficiently bizarre, the skeletal elements are full of interconnecting cavities (Fig. 5) forming a so-called stereom. It was originally thought that the purpose of this arrangement was to make it difficult for cracks to travel through, because any crack would be continually be interrupted by the voids (Nichols and Currey, 1968). This suggestion, much repeated, is wrong. As Gibson and Ashby (1988) demonstrated, it simply

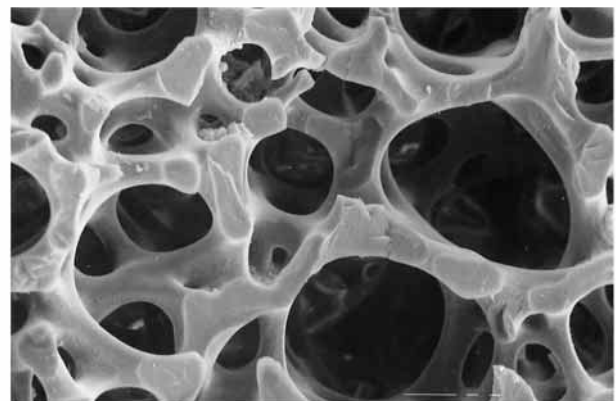


Fig. 5. Fractured stereom from the sea urchin *Heterocentrotus lividus*. Long scale bar, 10 µm.



will not work in a brittle material such as calcite. Fracture strength in compression and in tension, various fracture mechanics properties and resistance to fatigue all have a value proportional to at least  $(\rho^*)^{3/2}$ , where  $\rho^*$  is the density of the skeleton relative to the density of the solid material. From this, it is easy to show that a multiply-connected porous structure such as echinoderm skeleton or cancellous bone will, on its own, be heavier than a solid material with the same overall mechanical properties, be it stiffness, strength or toughness. Cancellous bone, which looks like echinoderm stereom, is a different case, because it is always part of a structure in which it is covered by compact bone, and the two tissues together are more efficient, on a per mass basis, than either on its own. However, echinoderm stereom usually does not have a continuous outer shell.

#### Sea urchin teeth

Unlike the stereom of most skeletal elements of echinoderms, the teeth of sea urchins have a structure/function relationship that is very obvious. They are remarkable, consisting of fibres of calcite in a matrix of high-magnesium calcite crystals. This was thought to be a classic composite of a ceramic in a ceramic, and that its toughness was due simply to the anatomical arrangement of the fibres and the matrix (Brear and Currey, 1976). However, there is a tenuous organic matrix, approximately 0.25% by mass, and recent work has shown that the presence of this matrix is crucial to the functioning of the tooth. The organic material wraps as a sheath round each fibre, and cracks are deflected by this sheath, which binds more tightly to the fibre than to the matrix. If the matrix is removed by treatment with NaOCl, the fracture surface becomes much smoother and the fracture toughness is reduced, but the hardness remains unaltered (Wang, 1998). Wang et al. (1997) have described many features of the mechanical properties of sea urchin tooth. One remarkable feature is the way in which the magnesium content of the 'calcite' increases towards the centre of the tooth. The hardness increases concomitantly and, as a result, the centre of the tooth is much more resistant to abrasion than the more peripheral parts, and the tooth self-sharpenes automatically. This arrangement is analogous to the arrangement found in rodent and lagomorph teeth. Wang et al. (1997) show that a whole host of anatomical features are brought into play to produce an extremely effective tooth that is built from calcite, an extremely unpromising raw material.

#### Final remarks

Biologists have the double problem of determining not only how the structure of a biological material fulfils its function, but also of determining what that function is. I have given two examples above, the rostrum of *Mesoplodon densirostris* and the echinoderm stereom, for which we can give a reasonable explanation of why they have the properties they do (although I did not explore this in the case of the stereom), but we have no real idea of their function. In the case of the stereom, this

is a lack of understanding that is little short of a scandal. One always has the feeling that the answer to the strange architecture of echinoderm skeleton is just round the corner. We never seem to be able to turn that corner.

However, it is probably not too hubristic to suppose that, for many vertebrate mineralised tissues, we are close to having a satisfactory understanding of the functional reasons for their particular designs.

Neill Alexander has a clarity of thought and a knack of tackling interesting yet soluble problems that is an example to us all. I have been greatly stimulated over the years by his work. Debra Balderson kindly commented on the manuscript.

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