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Looking Behind the Outer Shell

Any modern bow maker could easily be forgiven should s/he begin to show early signs of paranoia. Almost all the materials of their trade, except perhaps horsehair, have become increasingly difficult or even impossible to obtain. Some might suggest that the next entry on the CITES* register of endangered species could be the bow makers themselves.

This is all rather unfair to bow makers who are seldom wasteful in their use of natural resources. It is hard to imagine elephant poachers justifying their unpleasant and dangerous trade merely on the basis of supplying bow makers with tiny fillers of ivory for headfaces whose life expectancy, barring accidents, is about 80-100 years. However, although, the bow makers' shortages are mainly due to overexploitation by others, there is still every reason to promote good conservation practices in relation to whatever supply of materials remains. With mother-of-pearl this means conservation of the natural environment of the living molluscs, safe storage of the harvested shell material, and caring for the finished shell in bows in everyday use. Each environment poses particular threats and mechanisms of decay which must be considered in context for effective conservation.

Oyster and Abalone

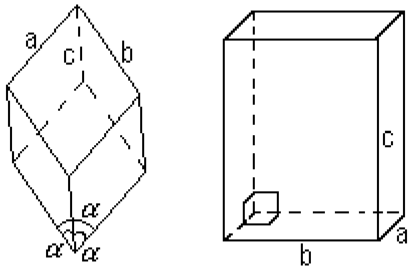
The mother-of-pearl normally encountered in bows is the lining or nacre of shells of the oyster (pinctada) or abalone (haliotis) families. Apart from the fact that the oyster is a bivalve (two shells) and the abalone a univalve (one shell), they differ in many other respects including their shell structure.

Calcium Carbonate ($CaC0_3$) is the second most abundant mineral found in the earth's crust, where it occurs as chalk, limestone and marble. It is responsible for such diverse wonders as the white cliffs of Dover, the Great Barrier Reef, and the sea shell. Calcium carbonate is the basic material of the lining of a molluscan shell, but it is not a simple covalent molecular compound. It crystallises into two quite different structures. The most common is calcite or calcspar which forms colourless rhombohedral or trigonal crystals. The other form is aragonite whose crystals are orthorhombic and are commonly redbrown or yellow in colour. Calcite is the main substance in oyster shells and aragonite in abalone, although many molluscs alternate layers of both.

The crystals form in a horizontal plane only and the shell lining consists of numerous very fine layers or lamellae of about 0,0002 mm thick, or c. 5.000 laminations per millimetre. As the crystals fit together so well on a molecular level the outer surface is smooth and polished.

Crystals

Many natural crystals have very well developed external faces whose regular arrangement reflects the regular arrangement of its atoms. Crystals form in seven possible systems which are defined by the angles between the crystal faces and the number of axes needed to define the principal features of their shapes. The terms rhombohedral and orthorhombic refer to two of these systems. Knowing the symmetry of the unit cell is useful when drawing conclusions about the properties of the solid such as optical activity, electrical resistance etc.



left: Rhombohedral, right: Orthorhombic.

Calcite is rhombohedral or trigonal. Such crystals have equivalent axes and interfacial angles such that a = b = c and α = β = γ < 120º. The unit cell is a rhombohedron, bounded by six equal rhombuses, or parallelograms with oblique angles and equal sides. The cell has a single triad or threefold axis of rotational symmetry. To visualise this, hold a football in your hand using only your thumb and first two fingers, spreading them as far apart as you can. The angles made by your fingers approximates to the axes of symmetry of the unit cell of the Calcite crystal. Other such crystals are Cinnabar and Arsenic.
Aragonite is orthorhombic. Such crystals have three inequivalent axes, such that a b c and α = β = γ = 90º. Or we could say that the conventional cell has three mutually perpendicular diads or twofold axes of rotational symmetry. A simple visual metaphor for such a crystal would be the shape of a cornflakes packet. Other such crystals are Topaz and Sulphur.

Stability

Although both crystalline forms are found in mother-of-pearl, laid down within a matrix of the shell protein conchiolin, Calcite has been found to be the more stable form. This is highlighted by recent research investigating the use of nacre which possesses osteogenic properties, as a bio-material for bone implants. The research showed that at 300-400ºC Aragonite could be transformed into Calcite and that at 550-600ºC the Calcite was transformed into Calcium oxide (CaO) or Lime. The organic matrix of the nacre was also destroyed at this temperature.
The explanation for this behaviour concerns the relationship between the ionic radius of the Ca2+ ion and the strength of the charge upon it. Imagine the cation as a sphere to be packed closely with other spheres to form a crystal. Not only do the spheres have different radii but they also have different charges and therefore different co-ordination numbers. These indicate the number of atoms immediately surrounding any selected atom. For example, the co-ordination numbers for Calcite and Aragonite are 6 and 9 respectively. This would lead us to expect that the Calcite arrangement (less dense packing of spheres) would be preferred where the ionic radius is fairly small, and that the Aragonite arrangement (more densely packed spheres) would be preferred where the ionic radius is fairly large. Obviously, there would be a certain dimension of radius (0.98 Å) at which an ambivalent situation would exist. The cation radius of $CaC0_3$ is close to this value (0.99 Å) and hence both forms occur in mother of pearl.
The greater stability of the Calcite form relates to Kinetic theory which states that chemical reaction rate increases with temperature. As random motion becomes more energetic, greater mobility is imparted to individual components, and it becomes more difficult to maintain spatial relationships and structural arrangements, particularly in circumstances where the balance between the cation radius and electrostatic charge is already marginal. Under these conditions, Aragonite with its marginally higher co-ordination number 9 becomes less stable than the alternative Calcite with a co-ordination number of 6, and so the Aragonite converts to Calcite.

This has important implications for the conservator dealing with violin bows. In a recent article in the British Violin Making Association Newsletter, a violin maker suggested a method for the removal of a tight "bow slide". This is an ebony backed mortised rectangular strip of nacre which slides into the ebony frog, or adjusting block, near the hand of the

player. It is a decorative concealment of the point of hair attachment.
The suggestion was to "place the slide next to a candle to warm it up. When the dirt and sweat start oozing, repeat the operation with the rosined thumb." The description is not very precise and is all the more worrying for that. What degree of heat are we subjecting the pearl to? Obviously, if we reach temperatures which turn the pearl into lime it is destroyed, but even if we only alter the ratio of these two very different crystalline components of nacre, we may still be failing to fully conserve an important property of an original slide, its physical appearance, which may become altered if we adjust the balance of Calcite and Aragonite as each has a distinctive crystal morphology and optical activity, which only in their original state of balance will produce that precise iridescence which is original to that particular piece of shell.

Iridescence

The distinctive light diffracting ability of mother-of-pearl is the main quality ofthe shell requiring conservation. This results from the optica1 activity of the calcite crystal and the anisotropic nature of the shell. meaning, that because it is layered, it has different properties along the lavers and across the lavers. Crystal lattices because of the regular spacing of their atoms (at distances in the range of optical wavelengths) have an ability to diffract light beams of particular wavelengths. A nicol prism, which is an optical device incorporating a crystal of calcite, is commonly used to obtain plant polarised light. This is light which, in passing through the crystal, is forced to vibrate in a single plane only, as opposed to normal light which vibrates in every possible plane. If light polarised in this manner is passed through a second calcite prism, it will be rotated, that is, the plane of its polarisation will be rotated. It will continue to be further rotated as it passes through further calcite prisms. Since different wavelengths of light are rotated to different extents, normal light becomes broken down into separate colour components, which are themselves further rotated through the lavers, producing the effect of shimmering iridescence. Where the lamellae are more parallel, such as in the flatter shell of the pinctada, the effect is less pronounced, whereas in the highly curved and undulating layers of the haliotis shell the effect is quite dramatic. Reducing the number of lamellae will also reduce this effect.

In the Wild

Although the oyster and abalone are really vegetarian in diet, they are subject to predation by other, less vegetarian creatures. Those inhabiting the intertidal zone have to contend with large sea birds and rats, but those dwelling deeper have many additional predators. While crabs and other large life forms favour a physical approach to removing the mollusc from its shell, many smaller creatures affix themselves parasitically to abalone or even try to burrow through its shell. These include red boring sponges, boring bivalves, whelks and moon snails who bore a neat circular hole in the shell of their prey using a long rasping tongue, similar to the abalone's, called a radula. There is also a species of octopod who with the efficiency of an assassin, bores one precise hole just above the area of shell attachment, then injects its saliva which loosens the grip of the abalone to its shell and exposes it for consumption. Many of these predators owe their success to the shell's vulnerability to even the mildest acid.

Pollution Threat

Despite a variety of scary natural predators, oyster and abalone would be superabundant today, were it not for the threat of man-made pollution, which currently renders all marine life endangered. Since the advent of plastics, themselves a major pollution source, molluscs have generally escaped overfishing for industrial use. Instead, countries with less plastics technology, such as some in the Far East, exploit their natural resources of shell, to provide us with cheap jewellery and even fertiliser.
Large numbers of shells and large quantities of limestone are burned to make lime, which, in turn, is used to make cement, in steel and glass making and in water softening.
Unfortunately, burning limestone in a lime kiln, produces carbon dioxide:

$$CaC0_3 \longrightarrow CaO + C0_2$$

or limestone + heat = lime + carbon dioxide.
This gas, which is a major pollutant, causes further damage when combined with rain or sea water:

$$CO_2 + H_20 \longrightarrow H_2CO_3$$

or carbon dioxide + water = carbonic acid.
This chemical, a major contributor to acid rain, also offers a specific threat to mother-of-pearl, which, as we have seen, is sensitive to even the mildest acid, and in making the sea more acidic, we make it a more hostile environment for shell producing molluscs.
As yet, no sea shell or mollusc has been included on the CITES register of endangered species, but the collection of many species is now having to be controlled because of reduced populations. Some species of abalone are now commercially farmed, but like farmed salmon, they differ from wild specimens, in this instance by their tendency to produce more meat and less shell.

Collecting Abalone

Abalone present particular problems in collecting, due to the firmness of their attachment to rocks. A method has been devised to overcome this, which would be unwise and unnecessary to describe, but it should be borne in mind that careless or unskilled harvesting may be fatal to the living abalone, since they are haemophiliac and can bleed to death if injured.
Collection of living specimens is usually restricted to certain months to avoid the spawning season, and to full sized specimens to allow the population to grow. On the west coast of America, protected areas have been established since the 1970's and very strict regulations have been in force in the Channel Islands to protect their native species, the haliotis tuberculata (L.1758). These are still to be found on the menus of the island's restaurants, but permits are required to sell what I presume are farmed abalone. Should two Channel Island divers be found in a boat containing a single live specimen, they are liable to a fine of £ 1.000 each, and confiscation of their equipment which could cost a great deal more.

In the Bow

It is obvious to those who work on old bows that certain types of shell outlast others. As previously mentioned, pinctada shells are not only constructed of the more stable calcite, but being flatter they produce slides whose lamellae are more continuous and parallel to its surface, whereas haliotis, especially from the muscle-scarred area, presents less continuity and more 'end grain', making it more open to chemical attack and erosion. Very broad undulations or 'figure' in the pearl would have a similar effect.
The deterioration of mother-of-pearl begins with contact with the perspiring bow hand of the player. As perspiration is saline, a solution of sodium, chloride, a strong electrolyte, is absorbed by the highly hygroscopic ebony of the frog. As the liquid evaporates, the salt is deposited as a contaminant on the frog and the shell.
Salt is a deliquescent material, which can attract moisture from the atmosphere to form a concentrated solution on these surfaces. At 24 °C there is a critical humidity of 75% below which the salt is stable, and above which it will absorb moisture. The level is reached in use.
In itself, this situation is not very different from the shell's natural environment.
Unfortunately, it is now also surrounded by air, which is far from pure, containing pollutants such as carbon dioxide and sulphur dioxide. Since mother-of-pearl is very sensitive to acidic corrosion, it is at particular risk from these pollutants, both of which give rise to acids as part of a mechanism of chemical change as shown below.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$H_2SO_4 + CaCO_3 \longrightarrow CaSO_4 + CO_2$

$CO_2 + H_2O \longrightarrow H_2CO_3$
$H_2CO_3 + CaCO_3 \longrightarrow Ca(HCO_3)_2$

In this reaction the atmospheric sulphur dioxide combines with the water to form sulphurous acid which attacks the pearl to produce calcium sulphate with carbon dioxide gas as a by-product. This carbon dioxide as well as atmospheric carbon dioxide combine with the moisture to form carbonic acid which acts on the pearl to produce calcium hydrogen carbonate, which is soluble in water. Erosion results. All perspiration is acidic at first and potentially corrosive in its own right. The formation of ammonium compounds allows the solution to become alkaline in time: however, new acidic input is soon added. This may also contain enzymes which could have a catalytic effect on the erosion of the shell. It is often observed in shared workshops that the perspiration of particular people may have a far more corrosive effect on the common tools than that of their colleagues. This is presumably a function of diet and metabolism.

Excessive Erosion

In the case of highly-figured shell or muscle-scarred material, where it is possible for saline solutions actually to penetrate between the lamellae by means of the discontinuities or 'end-grain' corrosion becomes even more rapid due to the effect of the salt solution drying out and crystallising, thereby exerting pressure between the layers. With each subsequent encounter, the salt will become more and more deeply embedded.
The best solution for delicate shell material such as this is to cleanse it entirely of salt. This may prove quite difficult as ideally it should be removed from its backing, which may not be possible if the pearl is too delicate. It should be repeatedly washed in purified water until no salt is detected in the residue. If the material is very precious or from an important bow, intended for continued use, despite its delicacy, the pearl may be strengthened by the careful introduction of a very dilute solution of nitrocellulose adhesive. Otherwise, more general protection may be afforded to pearl in use by the application of renaissance microcrystalline wax, which forms a harmless and removable barrier to moisture, providing it is regularly renewed. A light varnish on a disassembled slide will also afford protection, although if not thoroughly cleansed of salt first, not only will the corrosion continue, but future cleaning will be more problematic, particularly on muscle-scarred areas. On relatively healthy pearl, a wipe after use with a clean tissue or cloth should will greatly help to preserve it.

In the Case

Having survived a hostile marine environment and the demanding conditions of frequent performance in a humid, polluted environment, one would hope that a mother-of-pearl slide might at least be safe when stored in a violin case. Unfortunately, this is not always so.
The materials of the case and its lining, particularly organic materials such as wood or felt, can inadvertently contribute to the decay of its contents. The potential for chemical change or decay of such materials is high, due to their more complex molecular structures, rich in available reactive sites by means of which they may react with each other or their environment. These reactions may be very slow but in the case of gaseous pollutants emitted by the materials of the case, the intensity of reaction can become accelerated if the concentration of gases is allowed to build up through lack of ventilation. Silver-mounted bows, for example, rarely tarnish in use. although they frequently do so in the case. If the case is felt-lined (wool), the proteins making up the natural fibre contain a group of sulphur-bearing amino acids which break down to release hydrogen sulphide gas. If the felt is dyed the situation worsens as certain dyes contain sulphur.

Tarnishing

It is the combination of the freed gases with the microscopic layer of moisture ubiquitous on most surfaces, including the surface of the silver, that leads to the black silver sulphide tarnishing often seen on stored silver bow fittings. Unfortunately even without the dyed felt, all cases contain, by virtue of the instrument itself, large amounts of protein-based animal glue and various timbers which may or not liberate gases, not to mention adhesives and coatings of unknown chemistry. Wood, even well-seasoned wood, continues to release gaseous pollutants long after seasoning. Even a piece of oak from 800 B.C. has been shown still to liberate sufficient acidic vapours to corrode lead.
The main pollutants released are known as carbonyl compounds due to the presence of a molecule containing one carbon atom double bonded to one oxygen atom. These are methanal, ethanal, methanoic and ethanoic acids (formaldehyde, acetaldehyde, formic and acetic acids). It is these last two acids to which mother-of-pearl is particularly sensitive.
The usual effect on the shell is marked by the appearance of white crystalline salts or efflorescence on the surface. The effect of this reaction is to deface and disintegrate the shell, lamella by lamella, until it eventually subsumes and destroys it. Hygroscopic salts such as those deposited by perspiration, have been found to favour the appearance of such efflorescence, as they increase the relative humidity in the vicinity of the shell surface.
Although this form of corrosion has been noted since the end of the 19th Century, its causes are only now beginning to become fully understood. Early studies by a researcher called Byne have now largely been revised and his unfortunate remarks of the time, that the efflorescence spread like a disease from shell to shell and drawer to drawer, have led to the now common but misleading term 'Byne's Disease' for such corrosion, and to the mistaken belief among some that the source is bacterial.

Hygiene Solution

Luckily, the solution is merely a matter of good hygiene. First the efflorescence must he removed. The usual calcium acetate and formate salt are easily dissolved in water. and a thorough series of rinses in purified water has the additional benefit of removing any previously deposited hygroscopic salts, which may have resulted from contact with either sea water or perspiration.
Work on the pearl of the slide is best done when it is free of the bow, as during rehairing. This is because of the obvious risk of introducing moisture to such moisture sensitive areas of the bow as the wedges, adjusting screw or underslide.
Once free of residue, the slide may be lightly coated with the renaissance wax mentioned earlier. This should be repeated occasionally and the whole frog wiped with a clean dry cloth or tissue after each performance or practice. With severely eroded examples it may be necessary to consolidate fragile shell material in the manner previously described. The provision of adequate ventilation to such polluting gases is also, yet another excellent reason for opening our cases more often.

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