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To cite this article: Charles Hatchett Esq. F.R.S. (1800) VI. Experiments and observations on shell and bone , Philosophical Magazine Series 1, 6:21, 21-29, DOI: [10.1080/14786440008677181](https://doi.org/10.1080/14786440008677181)

To link to this article: <http://dx.doi.org/10.1080/14786440008677181>



Published online: 18 May 2009.



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VI. *Experiments and Observations on Shell and Bone.* By
CHARLES HATCHETT, Esq. F. R. S. *

SOME experiments which I lately made at the request of Mr. Home, and which he has done me the honour to mention in his ingenious paper on the teeth of granivorous quadrupeds, induced me to turn my attention more particularly to the chemical examination of shell and bone, especially as the former appeared to have been hitherto much neglected.

The time since these experiments were begun, has not been sufficient to enable me to enter into all the minutiae of the chemical analysis of these substances; but, as some remarkable facts were ascertained, I have now ventured to bring them forward, with the addition of some observations, although as yet the whole is little more than a very imperfect outline.

The first of these experiments were made on the shells of marine animals; and to avoid repetition and prolixity, I shall, in a great measure, once for all, describe the menstrua, the precipitants, and the mode of operation.

When shells were examined, they were immersed in acetous acid, or nitric acid, diluted, according to circumstances, with four, five, six, or more parts of distilled water; and the solution was always made without heat.

The carbonate of lime was precipitated by the carbonate of ammoniac, or of pot-ash; and phosphate of lime (if present) was previously precipitated by pure or caustic ammoniac.

If any other phosphate like that of soda was suspected, it was discovered by solution of acetite of lead.

Bones and teeth were also subjected to the action of the acetous, or diluted nitric and muriatic acids.

The dissolved portion was examined by the above-mentioned precipitants; and, in experiments where the quantity of the substance would permit, the phosphoric acid was also separated by nitric or fulphuric acid. The phosphoric acid thus obtained, was proved after concentration by experi-

* From the *Philosophical Transactions* for 1799.

ments, which being usually employed for such purposes, are too well known to require description.

It is necessary moreover to observe, that as the substances examined were very numerous, and my principal object was to discover the most prominent characters in them, I did not for the present attempt in general to ascertain minutely the proportions so much as the number and quality of their respective ingredients.

The greater part, if not all, of marine shells, appear to be of two descriptions in respect to the substance of which they are composed. Those which will be first noticed have a porcellaneous aspect with an enamelled surface, and when broken are often, in a slight degree, of a fibrous texture.

The shells of the other division have generally, if not always, a strong epidermis, under which is the shell, principally or entirely composed of the substance called *nacre*, or mother-of-pearl.

Of the porcellaneous shells, various species of *voluta*, *cypææ*, and others of a similar nature were examined.

Of the shells composed of *nacre*, or mother-of-pearl, I selected the oyster, the river muscle, the *baliotis iris*, and the *turbo olearius*.

Experiments on Porcellaneous Shells.

Shells of this description, when exposed to a red heat in a crucible during about a quarter of an hour, crackled and lost the colours of their enamelled surface; they did not emit any apparent smoke, nor any smell like that of burnt horn or cartilage. Their figure remained unchanged, excepting a few flaws; and they became of an opaque white, tinged partially with pale grey, but retained part of their original gloss.

The shells which had not been exposed to fire (whether entire or in powder) dissolved with great effervescence in the various acids; and the solution afterwards remained colourless and transparent. But the shells which had been burned, upon being dissolved, deposited a very small quantity of animal coal; and thereby the presence of some gluten was denoted, although the proportion was too small to be discovered in the solution of the shells which had not been burned.

The various solutions were filtrated, and were examined by pure ammoniac and acetite of lead; but I never obtained any trace of phosphate of lime, nor of any other combination of phosphoric acid.

The carbonate of lime was afterwards precipitated by carbonate of ammoniac; and from many experiments it appeared, that porcellaneous shells consist of carbonate of lime, cemented by a very small portion of animal gluten.

Previous to the experiments on shells composed of nacre, or mother-of-pearl, I examined some patellæ from Madeira.

When these were exposed to a red heat in a crucible, there was a perceptible smell, like that of horn, hair, or feathers.

The proportion of carbonic matter deposited by the subsequent solution was more considerable than that of the shells above mentioned, and the proportion of carbonate of lime relative to their weight was less.

When the recent shells were immersed in very dilute nitric acid, the epidermis was separated, the whole of the carbonate of lime was dissolved, and a gelatinous substance, nearly liquid, remained, but without retaining the figure of the shell, and without any fibrous appearance.

These shells evidently, therefore, contain a larger portion of a more viscid gelatinous substance than those before mentioned; but the solution separated from the gelatinous substance afforded nothing but carbonate of lime.

Experiments on Shells composed of Nacre, or Mother-of-Pearl.

When the shell of the common oyster was exposed to a red heat, the effects were the same as those observed in the patellæ; and the solution of the unburned shell was similar, only the gelatinous part was of a greater consistency.

A species of the river muscle was next subjected to experiment. This, when burned in a crucible, emitted much smoke, with a strong smell of burned cartilage, or horn; the shell throughout became of a dark grey, and exfoliated. By solution in the acids a large quantity of carbonic matter was separated; and much less of carbonate of lime was obtained from a given weight of the shell than from those already mentioned.

Upon

Upon immersing an unburned shell in dilute nitric acid, a rapid solution and effervescence at first took place, but gradually became less, so that the disengagement of the carbonic acid gas was to be perceived only at intervals.

At the end of two days I found nearly the whole of the carbonate of lime dissolved, but a series of membranes retaining the figure of the shell remained, of which the epidermis constituted the first.

In the beginning the carbonate of lime was readily dissolved, because the acid menstruum had an easy access; but after this it had more difficulty to insinuate itself between the different membranes, and of course the solution of the carbonate of lime was slower.

During the solution the carbonic acid gas was entangled, and retained in many places between the membranes, so as to give to the whole a cellular appearance.

The *baliotis iris* and the *turbo olearius* resembled this muscle, excepting that their membranaceous parts were more compact and dense.

These shells, when deprived, by an acid menstruum, of their hardening substance, or carbonate of lime, appear to be formed of various membranes applied stratum super stratum.

Each membrane has a corresponding coat or crust of carbonate of lime; which is so situated that it is always between every two membranes, beginning with the epidermis, and ending with the last formed internal membrane.

The animals which inhabit these stratified shells, increase their habitation by the addition of a stratum of carbonate of lime, secured by a new membrane; and as every additional stratum exceeds in extent that which was previously formed, the shell becomes stronger in proportion as it is enlarged, and the growth and age of the animal becomes denoted by the number of the strata which concur to form the shell.

Although the *baliotis iris* and the *turbo olearius* are composed of the true mother-of-pearl, I was induced to repeat the foregoing experiments on some detached pieces of mother-of-pearl, such as are brought from China.

These experiments I need not describe, as the results were precisely the same.

I must,

I must, however, observe, that the membranaceous or cartilaginous parts of these shells, as of the pieces of mother-of-pearl, retained the exact figure of the shell or piece which had been immersed in the acid menstruum; and these membranaceous parts distinctly appeared to be composed of fibres placed in a parallel direction, corresponding to the configuration of the shell.

The same experiments were made on pearls; which proved to be similar in composition to the mother-of-pearl; and so far as their size would enable me to discern, they appeared to be formed by concentric coats of membrane and carbonate of lime: by this structure they much resemble the globular calcareous concretions found at Carlsbad, and other places, called *pisolithes*.

The wavy appearance and irradiancy of mother-of-pearl, and of pearl, are evidently the effect of their lamellated structure and semi-transparency; in which, in some degree, they are resembled by the lamellated stone, called *adularia*.

When the experiments on the porcellaneous shells, and on those formed of mother-of-pearl, are compared, it appears that the porcellaneous shells are composed of carbonate of lime, cemented by a very small portion of gluten; and that mother-of-pearl, and pearl, do not differ from these, except by a smaller proportion of carbonate of lime; which, instead of being simply cemented by animal gluten, is intermixed with, and serves to harden a membranaceous or cartilaginous substance; and this substance, even when deprived of the carbonate of lime, still retains the figure of the shell.

But between these extremes there will probably be found many gradations; and these we have the greater reason to expect, from the example afforded by the patellæ, which have been lately mentioned.

Some few experiments were made on certain land-shells; and in the common garden-snail I thought that I discovered some traces of phosphate of lime; but as I did not find any in the *belix memoralis*, it may be doubted whether the presence of phosphate of lime should be considered as a chemical character of land-shells*.

Experi-

* Some experiments which I have lately made upon the cuttle-bone of
 Vol. VI. E the

Experiments on the covering Substance of Crustaceous Marine Animals.*

As I was not acquainted with any experiments by which the chemical nature of the substance which covers crustaceous marine animals had been determined, I was desirous to ascertain in what respect it was different from shell; and I began these experiments on three species of the echinus, with which I had been favoured by the Right Hon. President.

I was the more inclined to begin with the echini, because naturalists do not appear to be perfectly agreed whether to call them testaceous or crustaceous animals.

Klein, who has written a work upon echini, after having noticed the various opinions of Rondelet, Rumphius, and others, determines that they are to be regarded as testaceous animals. His words are: "Sic plurimas testas marinas, in statu naturali consideratas, cum echinodermatis potius quam cum crustis affacorum vel cancerorum conferre licebit. Itaque echinoderma cum Aristotele qui echinos inter testacea quibus facultas ingrediendi est reponit, nec non cum Beonio, Aldrovando, et excellentissimo Sloanio religiose testam appellamus, quam satis duram in nonnullis offendimus†."

But Linnæus was of the contrary opinion, as appears from his definition of the echinus: "Corpus subrotundum *crustacea* officia testum spinis mobilibus sæpius aspera‡."

Now, as the experiments above related had proved that the shells of marine animals were composed of carbonate of lime, without any phosphate, I thought it very possible that the covering of the crustaceous animals might, in some respect, be different; and if so, I should thus, by chemical

the shops have proved that the term *bone* is here misapplied, if the presence of phosphate of lime is to be regarded as the characteristic of bone; for this substance in composition is exactly similar to shell, and consists of various membranes hardened by carbonate of lime, without the smallest mixture of phosphate.

* Under this head I have included my experiments upon echini, starfish, crabs, lobsters, &c.

† Klein's *Naturalis Dispositio Echinodermatum*, &c. p. 10.

‡ *Systema Naturæ*, Edit. Gmelin. p. 168

characters,

characters, be enabled to ascertain the class to which the echinus was to be referred.

Of the three echini which were examined, one had small spines; the second had large obtuse spires; and the third was of a very flat form.

Portions of these echini were separately immersed in acetous, muriatic, and diluted nitric acid, by each of which they were completely dissolved with much effervescence; depositing at the same time a thin outer skin, or epidermis. The transparency of the solutions was also disturbed by a portion of gluten which remained suspended, and communicated a brownish colour to the liquors.

The solutions in acetous and diluted nitric acid were filtered; after which, from the acetous solution of each echinus, I obtained a precipitate of phosphate of lead by the addition of acetite of lead; and having thus proved the presence of phosphoric acid, I saturated the nitric solutions with pure ammoniac, by which a quantity of phosphate of lime was obtained, much inferior, however, in quantity to the carbonate of lime, which was afterwards precipitated by carbonate of ammoniac.

The composition of the crust of the echinus is therefore different from that of marine shells; and by the relative proportions and nature of the ingredients, it approaches most nearly to the shells of the eggs of birds; which in like manner consist of carbonate, with a small proportion of phosphate of lime cemented by gluten.

It remained now to examine the composition of those substances which are decidedly called crustaceous; but previous to this, some experiments were made on the asterias or starfish, of which I took the species commonly found on our coasts, and known by the popular name of five fingers (*asterias rubens*.)

The asterias is thus described by Linnæus. "Corpus depressum, subtus sulcatum; crusta coriacea, tentaculis muricata *."

When the asterias was immersed in the acids, a considerable effervescence was produced, and a thin external stratum

* Systema Naturæ. Ed. Gmelin, p. 3160.

was dissolved; after which it remained in a perfectly coriaceous state, and complete in respect to the original figure.

The dissolved portion, being examined by the usual precipitants, proved to be carbonate of lime, without any mixture of phosphate; but in another species of the asterias, which had twelve rays (*asterias papposa*), I discovered a small quantity of phosphate of lime. I am therefore induced to suspect that, in the different species of the asterias, nature makes an imperfect attempt to form shell on some, and a crustaceous coating on others; and that a series of gradations is thus formed between the testaceous, the crustaceous, and the coriaceous marine animals.

It was now requisite to ascertain if phosphate of lime is a component part of the substance which covers the crustaceous marine or aquatic animals, such as the crab, lobster, prawn, and crayfish.

Pieces of this substance, taken from various parts of those animals, was at different times immersed in acetous and in diluted nitric acid; those which had been placed in the diluted nitric acid produced a moderate effervescence, and in a short time were found to be soft and elastic, of a yellowish-white colour, and like a cartilage, which retained the original figure.

The same effects were produced by acetous acid, but in a less degree; in the latter case, also, a colouring matter remained, and was soluble in alcohol.

All the solutions, both acetous and nitric, afforded carbonate and phosphate of lime, although the former was in the largest proportion.

There is reason to conclude, therefore, that phosphate of lime, mingled with the carbonate, is a chemical characteristic which distinguishes the crustaceous from the testaceous substances; and that the principal difference in the qualities of each, when complete, is caused by the proportion of the hardening substances relative to the gluten by which they are cemented, or by the abundance and consistency of the gelatinous, membranaceous, or cartilaginous substance, in and on which the carbonate of lime, or the mixture of carbonate and phosphate of lime, has been secreted and deposited,

Moreover,

Moreover, as the presence of phosphate of lime, mingled with carbonate, appears to be a chemical character of crustaceous marine animals, there is every reason to conclude that Linnæus did right not to place the echini among the testaceous ones.

The presence of phosphate of lime in the substance which covers the crustaceous marine animals appears to denote an approximation to the nature of bone, which, not only by the experiments of Mr. Gahn, but by the united testimony of all chemists, has been proved principally to consist (as far as the ossifying substance is concerned) of phosphate of lime.

This consideration, therefore, induced me to repeat the above experiments on the bones of various animals.

It is scarcely necessary for me to mention the usual effects of acids on bones steeped in them, as they are known to every physiologist and anatomist.

In every operation of this nature the ossifying substance, which is principally phosphate of lime, is dissolved, and a cartilage or membrane of the figure of the original bone remains; so that the first origin of bones appears to be by the formation of a membrane or cartilage of the requisite figure, which, when the subsequent secretion of the ossifying substance takes place, is penetrated by, and thus becomes more or less converted into the state of bone.

It is also known that the nature of the bone is more influenced by the greater or less predominance of the membranaceous or cartilaginous part than by any other cause. It is not, therefore, for me to add any thing to this part: and in respect to the substance which is the cause of ossification, little also requires to be mentioned; for this (as has been already observed) is known principally to consist of phosphate of lime. I shall only, therefore, briefly mention the result of certain experiments.

[To be continued.]