

# XLV.—*On the Colouring Matter of Blue Forest Marble.*

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THE existence of dark bands or zones in that member of the Great Oolite series known as the Forest Marble, has been frequently noticed by geological observers. My attention was directed to the subject by Professor John Morris, and at his suggestion, determinations of the total amount of sulphur in the dark and the light parts of a fragment of the banded forest marble were made in my laboratory by Mr. C. C. Jacobsen. He found that the dark band gave, after fusion with nitre and carbonate of sodium, just twice as much sulphate of barium as the lighter exterior of the stone.

The dark stone contained 50 per cent. of sulphur.

„ light „ „ 24 „ „

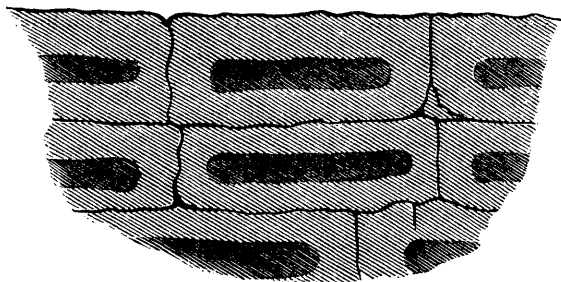
The result induced me to pursue the subject further, and with the able assistance of Mr. R. Warrington, junior, I have at last arrived at a satisfactory conclusion as to the true nature of the grey (or bluish grey) colouring matter of the forest marble. The investigation has proved tedious, and the results may not seem commensurate with the labour expended, yet it is probable that, upon minute and apparently insignificant peculiarities of composition, such as those I shall presently point out, may depend very important geological changes.

A few words of preface are requisite, in order to show the mode in which the dark band occurs.

On examining a section of the Forest Marble, it will be found that the dark bands invariably occupy the central portion of the various sized slabs into which the stone has naturally divided, that is to say, the dark band is not horizontally continuous, but is broken by each vertical fissure of the rock, as shown in the accompanying diagram.

Even when there is considerable dip in the stratum, the dark band still occupies its place in the centre of each slab of stone. The dark band frequently constitutes nine-tenths of the bulk of a thick slab, if it be of compact texture. Very thin slabs sometimes are without a dark band. The dark stone is more abundant, and

becomes of a deeper tint as we descend. The lowest layers rest upon a stratum of blue clay of exactly the same tint as the dark



stone, and owing its colour to the same substance. In one section which I have examined, where many of the slabs had a thickness of three inches, the light buff tint was seen to surround the dark grey band on all sides to the depth of about one inch. The exterior of the slab is stained russet-brown with ferric oxide.

The boundary between the dark and light (or grey and yellow) parts is perfectly well defined. There is no shading of one tint into the other. The colour of each part is also very uniform, not only in the same fragment, but in specimens from distant quarries. Occasionally, however, shells and small pieces of lignite occur irregularly scattered throughout the stone.

I may now proceed to describe as succinctly as possible the various experiments qualitative and quantitative which have been made with the view of comparing the dark and light stone. Firstly, as to the experiments with the

#### DARK STONE.

When the finely powdered dark stone is dissolved in hydrochloric acid, and the whole of the evolved gases passed through acetate of lead solution, no blackening occurs.

The existence of iron in the condition of a ferrous compound was proved by ferricyanide of potassium, the hydrochloric solution of the dark stone giving a blue precipitate with that reagent. Permanganate of potassium was also decolorised by it.

On ignition to full redness in a closed glass tube, no tarry matter distilled, and the dark grey colour of the stone remained unchanged. The small quantity of water condensed in the tube was found to have an acid reaction, and to contain sulphuric acid.

The dark stone heated to redness, with free access of air, assumed a pale reddish tint.

#### LIGHT STONE.

This variety of forest marble was found to contain iron in two conditions, and also sulphur, oxidized and unoxidized.

#### DARK STONE.

After these experiments, attention was more especially directed to the iron and sulphur present in the materials under investigation. The first step was to ascertain whether any of the sulphur known to be present (in some form or other of combination) in the dark stone could be removed by the action of water. For this purpose, the finely powdered dark stone was boiled for five hours with ten ounces of water, and the filtrate acidified and precipitated with BaCl.

- I. 150 grains *dark* stone gave .59 grains  $\text{Ba}_2\text{SO}_4 = .162 \text{ p. c. SO}_4$ .

#### LIGHT STONE.

The light stone was similarly treated, with the following result :

- II. 150 grains *light* stone gave .07 grain  $\text{Ba}_2\text{SO}_4 = .019 \text{ p. c. SO}_4$ .

The percentage of  $\text{SO}_4$  thus obtained from the light stone is but one-eighth of that which can be extracted by the same process from the dark stone. This result is explicable if we admit that the outside or light portion of the stone has been already submitted naturally to the action of water, which has not penetrated so as to affect the dark interior.

#### DARK STONE.

The action of hydrochloric acid upon the dark stone was next studied,—the amount of sulphuric acid as well as of ferrosu<sup>m</sup>\* and ferricu<sup>m</sup> extracted by that reagent being determined.

- III. 66.3 grains gave .35 grains  $\text{Ba}_2\text{SO}_4 = .217 \text{ p. c. SO}_4$ .

- IV. 50.9 grains gave by permang. process (*ferrosu<sup>m</sup>*) = .313 p. c. Fe.

\* I here include under this expression, iron, whether existing in ferrous compounds proper, or in combination with sulphur, &c., as in pyrites.

- V. 50·06 grains gave by permang. process (*ferricum*) = ·043 p. c. Fe.  
 VI. 50·06 grains gave by permang. process (*total iron*) = ·356 p. c. Fe.  
 VII. 66·3 grains gave by permang. process (*total iron*) = ·336 p. c. Fe.

It is especially to be noted here that scarcely more than one-seventh of the iron extracted by hydrochloric acid from the dark stone exists as ferric compounds. This result is in striking contrast with the annexed experiments.

#### LIGHT STONE.

Similar analyses to those just given were made in the hydrochloric acid solution of the light stone.

- VIII. 76·05 grains gave ·21 grains  $\text{Ba}_2\text{SO}_4$  = ·122 p. c.  $\text{SO}_4$ .  
 IX. 51·94 grains gave by permang. process (*ferrosum*) = ·209 p. c. Fe.  
 X. 51·94 grains gave by permang. process (*ferricum*) = ·201 p. c. Fe.  
 XI. 51·94 grains gave by permang. process (*total iron*) = ·410 p. c. Fe.

#### DARK STONE.

After treatment of the powdered dark stone with tolerably strong hydrochloric acid, till no further action took place, boiling with water, and washing the residue till the filtrate was free from calcium-salts, the whole of the dark colouring matter appeared to remain unaltered. It was separated from the main bulk of the sand by careful decantation, and submitted to analysis in order to determine the sulphur and iron present in it.

- XII. 69·6 grains of dark stone gave 1·86 grains  $\text{Ba}_2\text{SO}_4$ .

When from this *total* amount converted into a per centage (2·672), the per centage of  $\text{Ba}_2\text{SO}_4$  (·527), yielded by the portion of the dark stone soluble in hydrochloric acid, is deducted (thus : 2·672—·527=2·145), we may arrive at the per centage of sulphur in the part of the dark stone insoluble in acid :

$$2·145 \text{ p. c. } \text{Ba}_2\text{SO}_4 = ·294 \text{ p. c. sulphur.}$$

- XIII. 66·3 grains gave, by permanganate process (in the insoluble part) ·231 p. c. iron.

## LIGHT STONE.

The action of hydrochloric acid upon the light stone, by removing the greater part of the iron existing in it as ferric oxide, caused its buff colour to disappear, a residue remaining which partook, to a modified extent, of the physical and chemical properties of the residue similarly prepared from the dark stone.

XIV. 68·92 grains (the insol. matter from) gave ·93 grm.  
 $\text{Ba}_2\text{SO}_4 = \cdot 133$  p.c. sulphur.

XV. 68·92 grains (as above), by permang. process, gave ·079 p. c. iron.

The bearings of the various experiments already recorded may be best seen by an examination of the results in a tabulated form :

Percentage of *Iron and Sulphur* in the *Dark and Light* bands  
of Forest Marble.

	Dark.	Light.
Soluble in Water ..... $\text{SO}_4$ .....	·162	·019
Soluble in hydrochloric acid ..... $\text{SO}_4$ .....	·181	·102
"    "    " ..... Ferrosium .....	·318	·209
"    "    " ..... Ferricum .....	·034	·201
"    "    " ..... Total Iron.....	·346	·410
Insoluble in hydrochloric acid..... Sulphur.....	·294	·133
"    "    " ..... Iron .....	·231	·079
Total Soluble and Insoluble..... Sulphur.....	·366	·171
"    "    "    " .. Iron .....	·583	·489

To sum up the chief conclusions at which we may arrive from the results of the experiments hitherto given :—

1. The sulphur in the soluble part of the dark stone most probably exists as sulphates, since it is extracted by water as well as by hydrochloric acid.

2. The sulphur in the insoluble part probably exists in the form of a sulphide, insoluble in acids, for it has to be oxidized before a precipitate is obtained with barium salts.

3. From the fact that in the dark stone by far the larger part of the iron exists in an unoxidised condition, and that much of this iron remains in that part of the dark stone which is insoluble in hydrochloric acid, it is probable that it is, in part at least, there combined with sulphur as the insoluble sulphide, pyrites,  $\text{Fe}_2\text{S}_2$ .

#### DARK STONE.

In order to verify, if possible, the above hypothesis, attempts were made to effect a further purification of the dark matter insoluble in hydrochloric acid. For this purpose the dark insoluble matter was separated mechanically from the accompanying grains of sand. This was effected by adding water, agitating and decanting the turbid liquid before the finely-divided dark particles had had time to subside. In this way the grey colouring material of the stone was obtained in a more concentrated form. It was further purified by a second treatment with hydrochloric acid and washing.

After drying at  $100^\circ$ , the prepared dark matter, when ignited with access of air, became bright red, evidently owing to the oxidation of the iron compound present.

Ignited in a small tube closed at one end, it gave off water and a considerable quantity of hydrosulphuric acid. A very distinct sublimate of sulphur was formed: the residue was now quite black, and when treated with hydrochloric acid gave off sulphuretted hydrogen abundantly, though the original dark substance had been prepared by treatment with hydrochloric acid. This behaviour quite accords with that of pyrites, which is unaffected by hydrochloric acid until it has been ignited, when the residual magnetic sulphide is easily decomposed by acids.

After fusion with pure nitre, the dark grey matter became bright red: the mass boiled in water gave a solution in which abundance of sulphate of potassium was found.

Boiled with strong hydrochloric acid, the dark matter suffers no change; the addition of a drop of nitric acid at once causes the grey colour to disappear.

The dark matter was found to be quite free from uncombined sulphur.

The insoluble matter from the dark stone contained a few particles of mica and some fragments of lignite.

Determinations of iron and sulphur in the prepared dark substance were made, with the following results:—

XVI. 4.89 grains dark substance, dried at  $100^\circ\text{C}$ , gave after

fusion with carbonate and nitrate of potassium 3·07 grns.  
 $\text{Ba}_2\text{SO}_4 = 8\cdot63$  p. c. sulphur.

XVII. 4·89 grns. dark substance, dried at  $100^\circ$ , gave after fusion with carbonate and nitrate of potassium by permang. process =  $8\cdot272$  p. c. iron.

If foreign matters be deducted, these numbers correspond to the following per centage proportions of sulphur and iron :—

	The prepared dark matter.	Sulphide of iron $\text{Fe}_2\text{S}_2$ .
Sulphur . . . . .	51·05	53·34
Iron . . . . .	48·95	46·66
	<hr/> 100·00	<hr/> 100·00

These results, taken in connection with the qualitative experiments, leave no doubt that the dark stone owes its colour to sulphide of iron—common pyrites.

#### LIGHT STONE.

The behaviour of the dark matter prepared from the light stone is similar to that of the dark stone, but from its containing but little pyrites that has escaped oxidation, its colour is much weaker ; and in the light stone itself, this grey colour is completely masked by the ferric oxide there present.

There is a slight difference in specific gravity between the dark and light varieties of the forest marble. Specimens were taken from three quarries, and the dark and light parts having been separated in each case, the following numbers were obtained :—

				Difference.
I.	{ Dark band	Specific gravity	2·627	} ·036
	{ Light „ „	„ „	2·591	
II.	{ Dark „ „	„ „	2·631	} ·031
	{ Light „ „	„ „	2·600	
III.	{ Dark „ „	„ „	2·585	} ·023
	{ Light „ „	„ „	2·562	

It will thus be seen that the dark part of any given specimen was of greater density than the light part. If we may assume that the stone was once wholly of the dark kind (and this assumption is supported by the occurrence throughout the stone of lignite rich in pyrites), this alteration of density becomes of some interest,

for to the expansion probably consequent upon this alteration some of the physical appearances of the beds of stone may be due. On the other hand, it is possible that the oxidation and consequent gain in weight of the oxidizable iron pyrites, &c., of the stones, may have been more than counterbalanced by the loss arising from the solvent action of water upon one of the products of this oxidation, namely, the sulphate of calcium, which, as one of my experiments shows, is contained in comparatively most minute proportion in the light stone.

I think, from the foregoing experiments, I am completely justified in concluding iron pyrites to be the colouring material of the dark bands of the forest marble; and that the paler yellow, brown, or buff tint of the outer parts of the slab of this stone is due to the ferric oxide resulting from the oxidation of the pyrites. Fine sand ground up with no more than one per cent. of pyrites present very much the appearance of the dark stone; while the separated dark substance, containing 16 p. c.  $\text{Fe}_2\text{S}_3$ , may be exactly imitated by a similar artificial mixture of sand and pyrites.

As will have been noticed (ante) the blue clay underlying the forest marble is, sometimes at all events, similarly coloured with pyrites; and it is probable that the same explanation of the phenomenon under discussion may be extended to other blue and grey-coloured clays, rocks, soils, &c.; in fact, iron pyrites appear to have been detected before in somewhat similar circumstances; and close to a stratum containing this mineral in abundance, Bischof found (at Röndorf) a chalybeate spring rich in ferrous carbonate, and also containing sulphates.

In an agronomic point of view, the facts I have related would appear of some importance, since we may now be able to trace the cause of the injurious influence which these blue and grey matters exert on vegetation.

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