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ORIGINAL ARTICLES.

I.—ON THE ORIGIN AND MODE OF FORMATION OF THE CONCRETIONS
IN THE MAGNESIAN LIMESTONES OF DURHAM.

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(PLATES XII. AND XIII.)

IN 1826, 27, and 28, Prof. Sedgwick contributed to the Geological Society of London his classical papers on the Magnesian Limestone of the East of England,¹ in which he describes in detail the concretionary structures which occur in many of the beds of this formation in Durham.

Although he describes these concretions in minute detail, he says but little as to their probable origin, but it is clear that he regarded them as composed of carbonate of lime derived from the beds in which they occur, when he says—"The particles (of lime), after deposition, appear to have run into lumps and masses more or less crystalline, rejecting great portions of the earthy residuum."² Since Prof. Sedgwick's papers little seems to have been contributed to the subject of the mode of formation of these concretions.

Two opposite opinions are held with regard to the proximate source of the carbonate of lime:—One to the effect that the lime was introduced into the concretionary bed subsequent to its formation, in solution from without; the other that it was deposited contemporaneously and subsequently segregated out *in situ*.

The latter opinion is, we believe, that generally held,³ though there are some who advocate the former, which may be called "the Stalactitic"⁴ theory.

Looking at the Magnesian Limestone series as a whole, many of the concretionary structures appear as if they might have been formed in the stalactitic manner supposed; but when the individual beds containing the concretions are studied in detail, they are found to present many points which appear irreconcilable with the theory of their stalactitic origin.

The locality where these beds can be most satisfactorily examined

¹ Prof. Sedgwick, "On the Geological Relations and Internal Structure of the Magnesian Limestone," Trans. Geol. Soc. London, 2nd series, vol. iii. 1835.

² *Op. cit.* p. 89.

³ Prof. Green, Physical Geology, p. 279; Geikie, Textbook of Geology, 1835, p. 472.

⁴ R. Howse, "On the Stalactitic Origin of Conglobated Structures in the Magnesian Limestone," Tyneside Naturalists' Field-club, October, 1889.

is at Marsden quarries on the coast of Durham, between Sunderland and South Shields, where masses of stratified limestone are interbedded with marls containing concretions in every stage of development. Where fully developed, the concretions assume a spherical form, and are sometimes as much as 1 to 2 feet in diameter, the average size being from 3 to 6 inches. They are composed of fibrous crystals of calcite radiating symmetrically from the centre, which frequently consists of a valve of *Ascinus dubius* or *Myalina Hausmanni*. (See Plate XII. Fig. 1.) Very often, however, the centre is composed merely of a small cavity.

These concretions occur in irregular masses 20 to 30 feet thick, showing here and there rough stratification, and often passing laterally into well-bedded limestone. Many of the larger specimens show well-marked concentric bands developed at regular intervals.

The concretions are piled on one another with but scant matrix between; chemically they consist of 91 to 95 per cent. of carbonate of lime and 1.5 to 4 per cent. of magnesia.

It is difficult to see how such masses of limestone could have been formed by infiltration from beds above. Where are the beds into which the carbonate of lime dripped during the formation of the concretions? If we suppose these concretions to have been formed from carbonate of lime introduced in solution from an overlying bed subsequent to the consolidation of the deposit in which they occur, then the original bed, now replaced by concretions, must have disappeared. But this bed would originally contain 20 to 30 per cent. of magnesia, which must have been subsequently dissolved out; yet it is hardly likely that water which was saturated with carbonate of lime would dissolve out carbonate of magnesia the less soluble salt of the two,¹ and we cannot suppose that the magnesia bed was dissolved out first, leaving an enormous cavity into which the carbonate of lime afterwards dripped, forming around shells suspended in some mysterious manner; the symmetrical development of the concretions also, which is as perfect vertically upwards from the nucleus as it is laterally and vertically downwards, seems to preclude the possibility of their having been formed in a previously-solidified rock-mass.

Again, the shells forming the nucleus of the concretions are often in beautiful preservation, which is hardly likely to have been the case if they had lain in a porous bed exposed to the action of infiltrating waters, while in those cases where the centres are hollow it is impossible for the carbonate of lime trickling through the beds in solution to have crystallized out round a cavity, whereas we can easily imagine the centre to have originally consisted of an organic body in the sediment which, serving as the nucleus round which concretionary action was set up, afterwards decomposed.

But it is in the beds containing immature concretions in various stages of growth that the strongest arguments against the formation of the concretions by stalactitic action are supplied.

¹ Hardman, Carbonif. Dol. of Ireland, Proc. Roy. Irish Acad. vol. ii. ser. 2, 1877.

These beds consist of friable yellow marl, in which are imbedded hard sphaeroidal concretions often much flattened. The concretions consist of 85–95 per cent. of carbonate of lime, and 6 to 12 per cent. of magnesia, while the matrix often contains as much as 50 parts of magnesia on 100 of carbonate of lime.

The beds are markedly stratified, the lines of bedding passing uninterruptedly through matrix and concretions alike. (See Pl. XIII.)

This fact was first noticed by Prof. Sedgwick, and it is perhaps the strongest argument in favour of what we may call the 'Segregation' theory. The advocates of the 'Stalactitic' theory refer these lines of stratification in the concretions to lines along which the carbonate of lime spread out when dripping from above in solution; but this does not account for the individual lines of bedding passing uninterruptedly from matrix to concretion, nor does it account (if the formation is still supposed to be taking place) for the fact that where the beds dip at a considerable angle, the lines in the concretions are still parallel to the general bedding of the rock, not parallel to the horizon, as would be the case if they were being formed up to the present day by infiltration.

These flattened concretions contain numerous small shells disseminated through them, notably *Pleuropterus costatus* and *Turbo helicius*, whereas these appear to be altogether absent from the matrix. This we should expect according to the 'Segregation' theory, the shells being the nucleus round which the carbonate of lime segregated, and any fossils remaining in the matrix, which is extremely porous, would, after the solidification of the bed, be readily dissolved out by subsequent infiltration, whilst those embedded in the concretions would be protected by their impervious covering of hard limestone.

These fossils are frequently found projecting from the sides of the concretion along lines of bedding, in the same way that one-half of a sponge spicule, or other organic body, is found embedded in a flint, while the other half projects into the surrounding chalk.

It is difficult to account for the presence of fossils in these flattened concretions if we assume their stalactitic origin, as we cannot suppose them to have been introduced in solution, and to have reformed as fossils on the solidification of the concretion.

Turning now to the chemical side of the question. It had been hoped that a detailed chemical investigation of these beds would have conclusively proved by which of the two processes under consideration these concretions had been formed. For supposing the average analysis of the beds containing concretions to have agreed with the analysis of beds containing no concretions, we should have been justified in concluding that the carbonate of lime, of which the concretions are mainly composed, had not been introduced from overlying beds in solution, but had been originally deposited as part of the bed in which they are now found; but the complicated nature and variable chemical composition of the different beds of the series cause the evidence so afforded to be less certain than had been hoped, although the results are by no means valueless in this connexion.

The great drawback to the evidence is the very variable composition of those beds in which no concretions are developed, and the difficulty of selecting a bed or beds representing the original composition of the deposit, as regards the relative quantities of carbonate of magnesia and carbonate of lime present. In the annexed table are given average analyses of concretionary, stratified, and compact magnesian beds:—

	I.		II.		III.		IV.		V.
	Matrix.		Concretions.		Average of I. and II.		Overlying Bed.		Roker Cliff. 100 feet.
Carb. Lime ...	46·07	100·00	86·14	100·00	59·43	100	85·78	100	59·81 100
Silicate	2·03		·26		1·50		·09		—
Carb. Magn....	30·68	66·74	9·5	11·0	23·62	40	6·5	7·5	26·06 43
Peroxide Iron	1·52		}	1·8	12·60		2·0		}
Alumina	16·58						3·15		
Insol. in HCl.	3·00			1·98	2·5		2·10		
	99·88		99·68		99·65		99·62		100·00

Column I. gives an average of 12 analyses of the matrix which are each tested from 15 samples, the composition shown being thus the average of 180 samples. In the same way Column II. shows the average composition of 180 samples of the concretions.

The bed selected for examination is that shown in the photograph, (Plate XIII.), which extends for some 12 to 15 feet in a downward direction. It will be seen that whereas the matrix contains 66, the concretions only contain 11 parts of magnesia to 100 parts of lime.

The overlying bed (No. IV. of the Table) is a well-bedded limestone, which forms the surface beds in this district, and if the concretions had been formed stalactitically, it is from this bed that the lime must have been derived; but the bed shows no honeycombed appearance, and is one of the most compact members of the series. This overlying bed, which is 20 to 30 feet thick, is itself thoroughly concretionary in its structure, although on a minute scale, on the type of the globular concretions which overlie and pass into it, and if the lime forming the concretions is to be regarded as derived from infiltration, the whole of this upper bed must then have been formed in like manner, for we cannot fix an arbitrary size of concretion and declare that all those larger than this size were formed by infiltration and all those smaller, although of exactly similar structure, represent the bed as originally deposited. Since then the beds immediately overlying our concretionary bed are also concretionary, we cannot consider them as representing (according to the stalactitic theory), the original deposit, and we cannot use them therefore for instituting a chemical comparison with the typical concretionary beds. If, however, we go to higher beds, omitting those which have concretionary limestone interbedded with them, we find at Roker a massive bed nearly 100 feet thick; its composition, as given by Messrs. Browell and Kirkby,¹ is shown in Column V. of our Table.

In order to compare the composition of this bed with that of our bed of concretions, we must obtain the average composition of the latter, and to do this we must determine the relative proportions of concretions and matrix present. Numerous estimates along the exposure give roughly 2 of matrix to 1 of concretions as the approximate proportions, and working this out (Column III. of the Table), it gives us 40 parts of magnesia to every 100 parts of carbonate of lime, which will be found to agree very closely with the analysis of the Roker bed, which gives 43 parts of magnesia to 100 of carbonate of lime.

This entirely confirms the theory that the lime composing the concretions was derived from the beds in which they occur, and was not introduced subsequent to their deposition. We must, however, frankly acknowledge that there are two uncertain factors in this comparison, namely, the difficulty of arriving at an exact estimate of the relative proportions of matrix and concretions, and the somewhat arbitrary selection of the bed with which they are compared; as, however, great importance has been attached to a detailed chemical investigation of these beds, we give the results of our work in this direction, which confirm, as far as they go, what we have before alluded to as the 'Segregation' theory.

There is, however, other evidence in this direction derived from a study of the chemical composition of the concretions, namely, the presence in them of magnesia and insoluble matter.

The amount of magnesia, which is sometimes as much as 12 per cent., varies considerably in different concretions in the same bed, analyses of two concretions lying a few feet apart yielding in one case 2.3, and in the other 6.3 per cent. If the concretions had been deposited from percolating water, it is difficult to see why the water should vary at the distance of a few feet in the amount of magnesia it contained, whereas on the segregation theory we should expect the amount of impurities imprisoned during the process to vary from point to point, and it is still more difficult to account for the presence of insoluble matter, which is usually about 2 per cent., and in one specimen amounts to as much as 8.5 per cent. of the concretion.

The last argument against the stalactitic origin of this deposit that we have to bring forward is the fact that large quantities of calcite occur in these beds which *have* undoubtedly been formed by stalactitic action. They consist of pure white fibrous calcite,² and contain no magnesia or insoluble matter, they line cavities and cracks, and fill in the interstices between the concretions, often coating their surfaces to the thickness of an inch, and roughly modelling themselves on their external shape. These deposits, which here and there attain a thickness of 5 to 6 inches, can be traced to joints in the overlying beds through which the carbonate of lime has undoubtedly obtained access in solution, the walls of the joints

¹ Browell and Kirkby, on "The Magnesian Limestone of Durham," Nat. Hist. Trans. of Northumberland and Durham, vol. i. pt. 2.

² Not aragonite, as often described locally.

being lined with a similar deposit. Figs. 3 and 4, on Plate XII., show concretions coated with it. In many cases (Fig. 4) the calcite has begun to replace the original concretion, or perhaps add to its original mass, but this replacement is limited to about a quarter of an inch on the surface, and it never penetrates far, except when it fills cracks in the concretion. It is obvious, then, that it is either replacing the concretion from without inwards, or is forming on the surface of previously existing concretions, and its secondary nature is quite unmistakable.

Summary.—We can then sum up the evidence against the stalactitic origin of these concretions under the following heads:—

I. *Stratigraphical.*—(a) The marked stratified condition of these beds as a whole, which would to a large extent have been obliterated by the copious infiltration necessary for the formation of the concretionary structures.

(b) The uninterrupted passage of the lines of bedding through matrix and concretions alike.

(c) The enormous thickness of some of the concretionary limestones.

(d) The fact that the concretions occur only in the Upper Magnesian Limestone, which is overlaid by the Triassic Marls and Sandstones, a deposit containing originally probably but little carbonate of lime.

(e) The fact that the concretions are confined to the Magnesian Limestone series.

II. *Evidence from fossils.*—(a) The occurrence of shells in the centre of the radial concretions.

(b) The occurrence of cavities at the centre, probably originally occupied by organic matter.

(c) The wonderful state of preservation of shells occurring in these concretions and the almost total absence of fossils from the earthy matrix.

III. *Chemical.*—(a) The great similarity in composition between the concretionary bed as a whole, and the massive beds higher in the series which contain no concretions, with reference to the relative amounts of carbonate of magnesia and carbonate of lime that they contain. Showing that it is unnecessary to assume the introduction of extra carbonate of lime from beds above.

(b) The variable amount of magnesia in contiguous concretions.

(c) The presence in the concretions of a considerable quantity of insoluble material.

(d) The presence of calcite in these beds which *has* undoubtedly been deposited by stalactitic action and which in appearance, composition, and behaviour is so dissimilar to these concretions.

Having shown that the carbonate of lime of the concretions has in all probability been derived from the beds in which the concretions occur, we should like to add a few words as to the manner in which they appear to have been produced.

That some of the carbonate of lime disseminated through the deposit was abstracted from the general mass, and segregated round definite centres of attraction, is doubtless true, and, as Prof. Green remarks, we may give to this process a name of its own and call it

"Concretionary Action," but it does not enable us any better to realize the immediate cause of the process, or to understand the manner in which it was brought about. With regard to the first part of the problem, namely, the cause of the segregation, the following considerations may throw a little light on the subject.

The concretionary beds are usually crowded with fossils, and it is round these fossils that the carbonate of lime has segregated out; they, together with other foreign bodies (probably for the most part organic particles, and now represented by cavities), were the, so to speak, chemical magnets which attracted to themselves the available carbonate of lime.

The Roker beds, on the other hand, which are quite unfossiliferous but are, as shown above, approximately identical in composition, contain no concretions.

It might be urged against this that the Middle Limestone, which contains the most numerous assemblage of fossils in the whole system, has developed no concretions; but those beds contain a relatively large proportion of carbonate of magnesia to carbonate of lime, which, as we are about to point out, seems also to have influenced the decision as to whether a certain bed should or should not develop concretions.

The presence of carbonate of magnesia in the unconsolidated deposit appears up to a certain point to have assisted the segregation of carbonate of lime; but when the quantity of magnesia present reached over 30 per cent., it has prevented this segregation from taking place, except in small local patches. On the other hand, in those beds which are composed of almost pure carbonate of lime, the concretionary structure is only developed in a minute form throughout the mass.

It would appear, then, from this that where the deposit was fairly free from magnesia, the "concretionary action" started from so many centres, that no centre had time to aggregate more than a small quantity of lime to itself, before it came in contact with the growing peripheries of neighbouring concretions, and its further growth necessarily ceased. When, however, the deposit contained more magnesia, the particles of lime were consequently more widely separated, there was less inducement for individual effort on the part of would-be centres, and only the larger and stronger ones succeeded in attracting particles from the surrounding mass, and grew in size in proportion to their numerical scarcity; the distance from which they were able to draw particles increasing in proportion with the increase of their mass. When, however, the proportion of magnesia present exceeded a certain amount, the distance between the particles of lime became so great, and their mutual affinity was so weakened by this increased separation, that no foreign body was sufficiently powerful to start the migration of particles in its own direction, and the deposit solidified as an ordinary compact bed.

We have then in concretionary action a very analogous process to crystallization. When the solution of a salt is concentrated and

allowed to stand, it rapidly crystallizes, forming a mass of small crystals. If, however, the solution had been previously diluted, fewer and larger crystals would have been formed, and this dilution might have been carried to a point, after which further dilution would have prevented crystallization from taking place altogether.

That the presence of magnesia is the primary cause of the formation of the concretions is borne out by the fact that they are confined to this formation, although there are plenty of other limestones in the geological sequence in which they should otherwise have occurred. We may remark in passing that no argument in favour of the 'Stalactitic' theory can limit the application of that theory to these particular beds, for the character of the deposit into which the lime is supposed to have been introduced could have no influence whatever in causing that lime to be dissolved from the beds above.

The second part of the question, namely, the process by which the particles of lime were conveyed from their original positions in the deposit, and were aggregated round their respective nuclei, is a very difficult one to answer, and we do not appear to have advanced much towards the right understanding of this process since the days when Prof. Sedgwick wrote. Broadly, the process is comparable to the solution of sponge spicules in the chalk, and their redeposition round nuclei in the form of flints.¹ Carbonate of lime, and silica are, however, different material. What do we know about the pectous and colloid forms of carbonate of lime? It is true that the aragonite forming the shells of mollusca is an animal product, and may perhaps be analogous to the form of silica known as organic; and we know that it is frequently converted into calcite in fossil shells, showing that a rearrangement of the molecules of carbonate of lime does take place after the entombment of the shell. The carbonic acid and other gases given off from the decomposing organic matter in the deposit, and existing under considerable pressure, have probably played an important part in maintaining the particles of carbonate of lime in a state of molecular suspension, in which condition they were able to migrate to the nucleus which was irresistibly attracting them. Whether this state was one of true solution as usually understood, or whether it was one analogous to the colloid condition of silica, it is impossible to say. Recent experiments on the combination of solids under pressure, and the movement of the individual molecules of a dry mixture, show that more rearrangement probably takes place amongst the particles of an unconsolidated deposit than we are accustomed to imagine.

¹ W. J. Sollas, *Ann. and Mag. of Nat. Hist.* 5th series, vol. vi.

CONCRETIONS
FROM THE
MAGNESIAN LIMESTONE OF DURHAM.

MAGNESIAN LIMESTONE CONCRETIONS, SHOWING CONTINUITY OF BEDDING PLANES.