24. *On the Occurrence of PHOSPHATES in the CAMBRIAN ROCKS.*
By HENRY HICKS, Esq., F.G.S. *With an Appendix on the*
CHEMICAL ANALYSES of the Rocks, by W. H. HUDLESTON, Esq.,
M.A., F.G.S., F.C.S. (Read February 24, 1875.)

IN a paper by the late Dr. Daubeny, F.R.S., in the *Quart. Journ. Chemical Society*, vol. vii., entitled "On the produce obtained from Barley sown in rocks of various ages," he endeavoured to prove, by experiments made with rocks from different parts of the Cambrian strata of North Wales, that there was an almost entire absence of phosphoric acid in the rocks of that age. Having failed to extract any phosphoric acid from these by direct analysis, he adopted the plan of testing the relative capacity of rocks of various ages to yield this ingredient to the crops which grew in them; and by this process he calculated that the Cambrian rocks did not in any case contain more than about $\frac{1}{300,000}$ part, some containing only $\frac{1}{1,000,000}$. The rock-specimens examined were taken from the slate-quarries near Bangor, the quarries of Llanberis, and from near Dolgelly, probably Lingula-flags. In addition to these, he experimented also with Skiddaw slate from Cumberland, and with micaceous slate from near Glasgow, and from them obtained only much the same proportions. From these results he was led to infer that the seas in which these deposits had accumulated contained little or no animal life, and that we had here approached the borders at least of the lower limit of organic existence, especially as there seemed in addition to be an almost entire absence of lime in any form. In the last edition of 'Siluria,' these views are prominently brought forward to prove that very few organic remains could ever have existed in the Cambrian strata; and it is further mentioned that "in subsequent researches Dr. Daubeny could detect no traces of phosphoric acid in certain specimens from the Longmynd (which fundamental rock of the Silurian region is no more altered than the overlying Silurian strata), whilst the Ludlow rocks contained as much of it as any of the younger fossiliferous rocks on which he experimented"*.

I have already shown, in papers communicated to the Geological Society, that these views as to the probable absence of life in these early seas have not been supported by subsequent researches in the Cambrian rocks, and that we have evidence now, in the occurrence of zones of fossil remains to the very base of these rocks, that certain

* Until after this paper was written, I was unaware that Mr. D. Forbes, F.R.S., had published in the *Phil. Mag.* May 1857, analyses of Silurian and Cambrian Limestones, which showed results very different from those obtained by Dr. Daubeny. He does not give analyses of rocks of so early an age as those referred to by Dr. Daubeny and in the present paper; but there is one analysis of a limestone, probably of "Menevian" age, at Church Stretton, which gives as much as 0.56 per cent. of P_2O_5 and 63.10 of carbonate of lime. The other analyses include:—Llandeilo Limestone from Dinover Park, Llandeilo, P_2O_5 0.56; Bala Limestone, P_2O_5 0.16; Dudley Limestone, P_2O_5 0.46.

forms of animal life did exist, and in great abundance, in those early seas. It seemed questionable therefore whether Dr. Daubeny's results as to the absence of phosphoric acid from some of these rocks could be relied upon as in any way indicative of the general condition of the Cambrian rocks. To test this I recently made analyses of rocks from different portions of the Cambrian strata, selecting some beds which were known to contain certain forms only of organic remains, others in which different forms occurred together, and some which hitherto had proved to be unfossiliferous.

The results obtained tend to show that although some portions of the Cambrian rocks, like some series in comparatively recent formations, do not contain more than a mere trace of phosphoric acid, yet there are other portions of the strata, both underlying and interstratified with these beds, which give evidence of the presence of this ingredient in considerable quantity, it being equal in amount in some cases to that found in the very richest of the more recent deposits. It is evident, therefore, that the conclusions arrived at by Dr. Daubeny, and supported by so great an authority as Sir R. Murchison, are entirely fallacious when applied to the whole Cambrian epoch, and that they can now only be accepted for those special portions of the strata examined by him. The following analyses are sufficient to illustrate these facts, as they include rock-specimens from the very base of the Longmynd (or Harlech) group to the top of the Arenig group. Several of these analyses were made for me by my friends, Mr. Hudleston, F.C.S., and Mr. J. Hughes, F.C.S.

	P ₂ O ₅ per cent.	
1. Lower red beds (Longmynd group) with <i>Lingulella primæva</i> .	0.30	H. Hicks.
2. Grey flaggy and purple sandstones, unfossiliferous (Longmynd group).	A trace only.	H. Hicks.
3. Grey flaggy beds (Longmynd group) with Trilobites (these beds contain a considerable amount of carbonate of lime).	1.50	H. Hicks.
4. Grey flags (junction of Longmynd group with Menevian group) containing fossils sparingly (carbonate of lime in considerable quantity).	0.50	H. Hicks.
5. Grey flags, very calcareous-looking (Menevian group), with abundance of Trilobites, but only a few other fossils (carbonate of lime as much as 50 per cent. in many parts).	From 2.00 to 4.00, in proportion to the amount of fossils present.	H. Hicks.
6. Dark grey and light blue flags (Menevian Group) with <i>Paradoxides Davidis</i> and other large Trilobites (carbonate of lime in some parts over 42 per cent.).	From 2.36 to 3.00.	J. Hughes.
7. The same bed, but from another part.	1.52	W. H. Hudleston.
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	P ₂ O ₅ per cent.	
8. The shell of <i>Paradoxides Davidis</i> , a fossil of large size, with as little matrix as possible.	20·00	H. Hicks.
9. The shell of <i>P. Davidis</i> with a little matrix attached.	17·05	W. H. Hudson.
10. <i>Lingula</i> -flags with <i>Lingulella Davidis</i> from Whitesand Bay, St. David's.	0·50	H. Hicks.
11. <i>Lingula</i> -flags with <i>Hymenocaris</i> from near Dolgelly, North Wales.	0·60	
12. Tremadoc rocks, with some Trilobites, but with a great abundance of Brachiopods and Lamelli-branches, from Ramsey Island, St. David's (carbonate of lime in considerable amount).	1·50	H. Hicks.
13. Lower Arenig rocks from Whitesand Bay, St. David's, with Graptolites, &c.	0·25	H. Hicks.
14. Middle Arenig rocks from Whitesand Bay, with Trilobites in considerable abundance.	From 0·50 to 1·50, in proportion to the amount of fossils present.	H. Hicks.
15. Upper Arenig rocks from near Abereiddy Bay, with a few Trilobites, Graptolites, &c.	0·35	H. Hicks.

The analyses show that, of these very early rocks, those which appear to contain no animal remains have, as might be expected, the least proportion of phosphoric acid, that the rocks in which the Brachiopoda or Graptolites occur alone do not contain any very large proportion of that ingredient*, and that the rocks which contain the remains of Crustacea have invariably the largest amount of phosphoric acid. The *Lingula*-flag beds which were examined contained only Brachiopoda; and the proportion of P₂O₅ in them was therefore small. The Tremadoc rocks, made up in great part of the shells of Brachiopoda, but with many Crustacea in addition, contained it in larger quantities; while the beds of the Menevian, containing little else than Crustacea (which occur there in great abundance), showed a marked increase in the amount present.

From these facts it is natural to infer that the Crustacea were the chief cause of the presence of so much phosphoric acid in these early deposits, and that the Mollusca were considerably inferior to the Crustacea in their power of producing this ingredient. For the purpose of testing this fact I made analyses of the fossil shells of several of the Mollusca; and, with the exception of the Brachiopods *Lingula*, *Discina*, and *Obolella*, which have more or less of a horny texture, but are of small size in these early deposits, I find that the

* The so-called horny shells of the Brachiopoda contain P₂O₅ in considerable quantity. Prof. Sterry Hunt found as much as 85·79 per cent. of phosphate of lime in the shell of *Lingula ovalis*; but in these early rocks the Brachiopoda are of small size, and do not occur in very great abundance; so the beds in which they occur alone are not usually rich in this ingredient.

proportion of phosphate of lime in each is exceedingly small. Recent shells of Mollusca also, as a rule, only contain it in very small quantity; while the recent Crustacea, such as the lobster, crab, and sea-crayfish, contain in their shell on an average from 6 to 7 per cent. of phosphate of lime. The animal matter of the latter is also known to contain a considerable amount of phosphoric acid. Mr. Hudleston's analysis of the flesh of the recent lobster gives 0.332, and of the lobster-shell 3.05 per cent of P_2O_5 . Doubtless also the animal matter of the Mollusca contains phosphoric acid in some quantity; for the matrix in which some of the fossil shells are imbedded, and the casts I find, frequently contain more than is to be found in the shell itself. The great Crustacean (*Paradoxides*) which occurs in such abundance in the Menevian rocks, contains in its fossil shell as much as from 17 to 20 per cent. of P_2O_5 , and hence a far greater amount than is found generally distributed throughout the rock in which it occurs. Doubtless this large Crustacean, in some cases over 20 inches in length, was also fully capable of producing all that is now present in these rocks; for we have no evidence of the existence of any other forms of animal life at this period which could produce it in any very considerable proportion. The Mollusca were very small and scantily distributed. The remains of sponges occur only as fine siliceous or pyritized spicules; and there is no evidence of much vegetable matter. We are therefore compelled to fall back on the Crustacea, which occurred in myriads in these seas, and which, having the power of casting off their shells frequently, must have added greatly to the deposits. Indeed most of the carbonate of lime, which is here also very abundant (being, according to Mr. Hughes's analyses, in the proportion of as much as 42.39 per cent. in some portions of the beds containing *P. Davidis*), was also in all probability deposited by them. In many of the little phosphatic nodules which are interspersed throughout these deposits, casts of bivalve Crustacea are frequently seen enclosed, thus making it probable that these nodules were produced chiefly through the decomposition of the soft tissues and shells of these animals.

It is evident that the shell of the Trilobite was thicker and contained a larger proportion of phosphate of lime than those of the other Crustacea which lived at this time; for in the rocks where the phyllopod Crustacea, for instance, alone occur (as the Lingula-flags with *Hymenocaris* and the Skiddaw slates with *Caryocaris**), the proportion of phosphate and also of carbonate of lime is much less than where Trilobites occur alone. I can only account for this by supposing that the shell of these phyllopod Crustacea must have been thinner and less rich in calcareous material; for where they occur they are as plentiful as are the Trilobites in some of their richest beds.

I have marked in the section (p. 372) the position of the beds in the "Menevian group" at Porth-y-rhaw which have already been examined for phosphoric acid. The degree in which it occurs

* Which I have been able to examine, through the kindness of Mr. Etheridge, F.R.S.

is found to be in exact proportion to the animal remains present—being in the proportion of less than $\frac{1}{2}$ per cent in those which contain but few remains, and as much as 4 per cent in the richest beds. This, however, is only found to be true in regard to the beds which have not undergone any metamorphic change by contact with or proximity to intrusive dykes; for the beds which in this section yield the largest proportion of phosphoric acid are so altered in another section, from contact with an intrusive mass, that scarcely a trace of this ingredient is left in them, though fossils are there in plenty as impressions, but with none of their structure left. In this section, also, a similar change has taken place in the character of the beds near to the trappean masses. For some distance below and above the trap, the beds show an altered character: instead of being grey, hard, flaggy, and calcareous-looking, as are the other beds in the section, they gradually become black and slaty in character, and have a distinct slaty cleavage near the dykes. About a foot from the trap there is a very rich line of fossils, in which the large *Paradoxides Davidis* occurs plentifully; but here none of the structure of its thick shell is left, and its arched character is gone, the impressions being flattened and distorted. An analysis of portions of this bed where the fossils are most plentiful shows an almost entire absence of phosphoric acid and of lime, whilst these ingredients ought, according to the evidence derived by the analyses of other beds in which this fossil occurs, to have been present in large proportions.

When I made my first analysis of this rock I felt much puzzled at the absence from it of P_2O_5 ; and on mentioning the result to one or two chemical friends I was assured by them that it must be there, and that it would be found in combination with some other base, if not with lime. On repeating my analysis, however, with every care, I could not find it in any quantity; and I then placed portions of the rock, with the impressions of the fossil upon them, in the hands of Mr. Hughes and Mr. Hudleston, telling them at the same time of the opinions expressed. The result obtained by Mr. Hughes from the altered rock was phosphoric acid 0.096, equivalent to tribasic phosphate of lime 0.209; whilst another piece of rock unaltered, with *Paradoxides Davidis*, the same fossil, upon it, gave phosphoric acid 3.00, = tribasic phosphate of lime 6.54, or thirty times as much as in the altered bed, showing an extraordinary difference, and one which can only be accounted for by supposing some chemical change to have taken place sufficient to have set free the P_2O_5 from this rock. Mr. Hudleston's analysis also gave very much the same result, being only in the proportion of 0.11 per cent of P_2O_5 in the rock near the trap. The carbonate of lime, which was also determined by Mr. Hughes to be present in the proportion of 42.39 per cent. in parts of the unaltered rock, has also disappeared almost entirely from the altered slate. There can be no doubt, I think, that the phosphoric acid occurs in the unaltered rock in the state of tribasic phosphate of lime; and as this is known not to undergo a change from any amount of heat applied to it by

ordinary processes, being fixed even in the fire, it seems probable that we must look for some other cause in addition to the heat, which would be capable of effecting this change. The extraordinary heat of so large a mass of melted matter, combined with the enormous pressure exerted at the same time upon the rock, may, however, have been capable alone of producing changes of which we have but little conception. Still I think it is probable that the change chiefly took place through the influence of watery vapour and gases generated at the time in the rock itself, or communicated to it from the intrusive vein.

The bedded rock, at the time this intrusion into it took place, was in the horizontal position, and doubtless in a plastic state and with many thousands of feet of other deposits superimposed upon it. These intrusive masses appear almost to follow the curves of the strata and to run in the direction of the line of the bedding along the coast; but they gradually get higher in the series in an easterly direction, and the direction of the flow seems evidently to have been from south-west to north-east.

Whenever the sedimentary beds come in contact with these trap dikes they always show an altered state; and as these masses can be traced for several miles, their effect on almost every bed of the Menevian group may be seen; for though the general direction is that of the line of bedding, yet in their course they gradually ascend and ultimately cross the series. The invariable effects produced are a deepening of the colour of the rocks, cleavage, loss of lime, of phosphoric acid, and of every evidence of such substances (as the horny texture of the shell of the Brachiopoda, the Crustacean shell, &c.), but with the fossil impressions left, in a compressed and distorted state. In addition to these changes, thin lines of iron pyrites are frequently seen running in the direction of the bedding in those beds which have undergone any considerable alteration in their character; and as, according to Mr. Hudleston's analysis, these altered beds are now deficient in pyrites, it seems evident that this must have been derived from them.

The analyses which I have made of portions taken from the intrusive dyke in the section at Porth-y-rhaw gave the following results:—(1) Under surface resting on black slate, P_2O_5 0.60 per cent, carbonate of lime 15 per cent; (2) Centre of mass, P_2O_5 0.40 per cent, carbonate of lime in small quantity only; (3) Upper surface of second mass, P_2O_5 0.50 per cent, carbonate of lime 8 per cent. Between the masses of trap there are, in black altered slate, veins of calcareous spar in a very pure state, and which when analyzed scarcely gave a trace of P_2O_5 . From these analyses it will be seen that phosphoric acid is distributed throughout the whole mass of the trap, but that it and the carbonate of lime occur in very great excess towards the surfaces.

If these dykes in forcing their way through the beds did not take up some of the ingredients which they were directly or indirectly the means of setting free from these beds, it is but natural to suppose that they must have frequently, indeed usually, have had their

composition changed and altered by the breaking-up of the rocks through which they were forced, and by the absorption of portions of these into their own substance. The phosphate and carbonate of lime in these masses may therefore have been obtained out of the rocks through which they were injected in the molten state; and these ingredients, in the condition in which they are found, may not have existed (or, at least, not in so large a proportion) in the intrusive mass prior to its meeting these sedimentary beds. This, of course, will not and is not intended to explain the origin of all the phosphoric acid in eruptive rocks; but it may nevertheless tend to explain the great preponderance present in some of the eruptive masses and the almost entire absence of it in others. In those passing through beds rich in organic materials we may naturally expect a preponderance; whilst in those dykes which, so far as we are able to judge, appear only to have met with barren strata, little should be expected; and I believe this is very much what is found to be the case.

The general conclusions which we seem to arrive at by these examinations and experiments are:—(1st) that animal life has been the chief means by which phosphate of lime has been produced from the very earliest time of which we are able to trace the record up to the present; that though all animal and vegetable life in the Cambrian and Lower Silurian seas contributed to its production, yet of the forms of life which are known to have lived during those epochs the Crustacea seem to have had by far the greatest share in its production, and of the Crustacea the Trilobites more particularly. Not only does it occur more abundantly wherever the Trilobites are present, but our analyses have proved that their shell, when preserved, contains an extraordinary amount of this ingredient, nearly one half being phosphate. The largest proportion known in recent Crustacea is that made out by Mr. Hudleston in the shell of the lobster—that is, 7·12 per cent of phosphate of lime; it is probable therefore that the Trilobites had a much larger amount in their shell than is to be found in recent Crustacea, where its place seems to be taken by carbonate of lime. We can hardly suppose, however, that the whole of the phosphate of lime which we now find to be present in the fossil occurred also in the natural shell; for during the process of decomposition of the animal matter, in which doubtless P_2O_5 occurred also in considerable quantity, the shell may have been made to undergo an important change, and a substitution have taken place. Still the great excess in the fossil compared with what is found in the matrix or generally throughout the rock leads one to suppose, especially when we take into consideration its comparative absence in the other fossil remains, that the natural shell did contain phosphate of lime in an unusual quantity. I am inclined to think that the shell of the Trilobite was of a more horny texture than that of the recent Crustacea, being somewhat of a character intermediate between the calcareous shell of these and the so-called horny shell of *Lingula*. Therefore, though it is useful to know the amount which by the analogy of recent Crustacea, the Trilobites may have been able to supply to the rocks, yet it would be most hazardous to rely on this test as in

any way sufficient. The large proportion of phosphate of lime present in the Bala rocks is probably due to their containing, like the "Menevian" rocks, so large a number of Trilobites—these two formations containing them in greater abundance than any others.

Secondly, though it is possible that some of the more recent deposits may have derived a part of the phosphate of lime contained in them from apatite dissolved out of eruptive rocks, as recently suggested before this Society, yet on the other hand it is even probable that eruptive rocks derived phosphate of lime from the earlier sedimentary rocks through which they passed, and where it had previously been deposited by animal and vegetable life. We know of no eruptive rocks in this country of so early a date as the time when these "Menevian" beds were deposited. The dykes, which in some cases appear to run almost in the line of the bedding of these older Cambrian rocks throughout Wales, always alter the beds on both sides; and I do not think that any of them are of older date than the Upper Arenig or Lower Llandeilo epoch, in which we for the first time in the succession meet with truly contemporaneous tuffs and ashes. In Canada, however, it is said there are eruptive rocks of Laurentian age; but whether these contain phosphate of lime I do not know. The source from which the P_2O_5 was first obtained must of course still remain a difficulty, and we can only expect at present to unravel the mystery so far as the facts laid open before us in nature enable us clearly to do so. We can hardly do more than inquire into the processes by which this ingredient, so indispensable now to animal and vegetable life, was first separated from the sea, in which from the very earliest period it seems to have existed in a state of solution, and the means by which it was afterwards deposited in such large proportions in some sedimentary rocks. In an agricultural point of view the presence of so much phosphate of lime in some of the series of beds, as "Menevian" and "Middle Arenig," must be a matter of considerable importance; and I find, on looking over the geological map of St. Davids, that where these series occur they underlie the very richest land in that neighbourhood. The Middle Arenig series particularly shows this; for it is of greater thickness and extends in a more continuous line than the "Menevian," and this line from time immemorial has had a fame for the goodness of its produce, whether in stock or cereals.

APPENDIX. *On the CHEMICAL ANALYSES of the Rocks.*
By W. H. HUDLESTON, Esq., M.A., F.G.S., F.C.S.

At the request of Mr. Hicks I made several analyses of Cambrian rocks, principally with the view of determining the amount of phosphoric acid in each; but incidentally, in one or two cases, an analysis, more or less complete, has been made of the specimen of rock itself.

No. I. is a darkish grey flaggy rock, with an impression of *Paradoxides Davidis* on one side. Portions of the slab immediately